Synthesis and stability of strongly acidic benzamide derivatives
Reactivity studies of strong organic acids based on the replacement of one or both of the oxygens in benzoic acids with the trifluoromethanesulfonamide group are reported. Novel derivatives of these types of acids were synthesized in good yields. The generated N-triflylbenzamides were further functionalized through cross-coupling and nucleophilic aromatic substitution reactions. All compounds were stable in dilute aqueous solutions. Studies of stability under acidic and basic conditions are also reported.
Vapor pressure and specific electrical conductivity in the solid and molten H$_2$O-CsH$_2$PO$_4$-CsPO$_3$ system—a novel electrolyte for water electrolysis at ~225–400 °C

Cesium dihydrogen phosphate, CsH$_2$PO$_4$ (CDP) was studied for water electrolysis at ~225–400 °C. In the presence of sufficient humidity, CDP is structurally disordered and super-protonic conducting with conductivities reaching 0.2–0.25 S cm$^{-1}$, when determined in suitable H-shaped sealed conductivity cells. Freshly prepared 99.7 ± 0.3% gravimetric pure CDP with correct X-ray diffraction and DSC diagram melted at ~345 °C. The vapor pressures, above CDP alone and mixed with 20–50 mol% CsPO$_3$ or 13 mol% H$_2$O, were determined in sealed ampoules up to 355 °C by means of Raman spectroscopy based on internal reference gases. Pressures up to ~49 bar were estimated, much higher than previously expected. Conductivities were given as polynomials and plotted in solid and liquid states. Water splitting electrolysis 2H$_2$O → 2H$_2$ + O$_2$ was demonstrated by Raman at ~355 °C under a water pressure of ~23 bar in a quartz cell with platinum electrodes, showing molten CDP to have significant potential for water electrolysis.

Development of Hybrid Vehicle for ground service handling operations

The objective of this work is to develop a hybrid power pack which both improves fuel efficiency and reduces the emission of ultra-fine particles at the same time. The power pack consists of a fuel cell and a battery and it operates on methanol-water mixture. The power pack represents a cost effective solution, while the hybrid vehicle has a number of advantages compared to an internal combustion engine (ICE) diesel powered vehicles: no particle emissions; possible indoor usage in hangars; fuel efficiency and fossil free transportation. Particle emissions from diesel ICE utility vehicles at the airport handling area (luggage, passenger in/out, fueling and service) represent serious health hazards. Especially the emission of ultra-fine particles represents a significant problem for the working environment at airports. The advantage of this concept is that the size of the individual components can be reduced (as compared to a non-hybrid system), while improving the overall energy efficiency by using the most efficient hybridization for a given power requirement (5 kW). The fuel cell technology is based on High Temperature PEM fuel cells (HTPEMFCs) from Danish Power Systems Company. The battery pack, battery management system (BMS) and on-board charger are being developed by Lithium Balance Company.
Influence of carbon monoxide on the cathode in high-temperature polymer electrolyte membrane fuel cells

This paper describes the results of adding small amounts of CO gas to the cathode side in a HT-PEM fuel cell with a polybenzimidazole (PBI) membrane running on either oxygen or air. Experimental conditions: Temperature ranges 120–160 °C, constant current either 200 mA/cm² or 800 mA/cm² and CO ranges 0.1–1.3%. In this case it was found that small amounts of CO under special conditions have a beneficial effect on the potential of the fuel cells, whereas larger amounts can bring the potential down to almost zero. An interesting phenomenon is that after the flow of CO is switched off a temporary improvement of the potential is seen before the situation goes back to normal. A good explanation for this is a competition between CO, O₂ and H₃PO₄ at the three phase boundaries, also that a steady state exist in which CO constantly is oxidized to CO₂.

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Source: Findit
Source-ID: 2352247193
Research output: Contribution to journal › Journal article – Annual report year: 2017 › Research › peer-review

Amino-Functional Polybenzimidazole Blends with Enhanced Phosphoric Acid Mediated Proton Conductivity as Fuel Cell Electrolytes

A new amino-functional polybenzimidazole copolymer is synthesized by homogeneous solution condensation polymerization from a novel monomer, N,N'-bis (2,4-diaminophenyl)-1,3-diaminopropane. The copolymer readily dissolves in organic solvents and shows good film forming characteristics. To balance the phosphoric acid uptake and to obtain mechanically robust membranes, the amino-functional polybenzimidazole derivative is blended with high molecular weight poly [2,2’-(m-phenylene)-5,5’-bisbenzimidazole] at different ratios. Due to the high acid uptake, the homogenous blend membranes show enhanced proton conductivity at temperatures well above 100 °C as also confirmed by the fuel cell polarization data.

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemical and Biochemical Engineering, The Danish Polymer Centre
Contributors: Aili, D., Javakhishvili, I., Han, J., Jankova Atanasova, K., Pan, C., Hvilsted, S., Jensen, J. O., Bjerrum, N. J., Li, Q.
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Volume: 217
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Determination of Water Vapor Pressure Over Corrosive Chemicals Versus Temperature Using Raman Spectroscopy as Exemplified with 85.5% Phosphoric Acid

A method to determine the water vapor pressure over a corrosive substance was developed and tested with 85.5±0.4% phosphoric acid. The water vapor pressure was obtained at a range of temperatures from ~25°C to ~200°C using Raman spectrometry. The acid was placed in an ampoule and sealed with a reference gas (either hydrogen or methane) at a known pressure (typically ~0.5 bar). By comparing the Raman signals from the water vapor and the references, the water pressure was determined as a function of temperature. A considerable amount of data on the vapor pressure of phosphoric acid are available in the literature, to which our results could successfully be compared. A record value of the vapor pressure, 3.40 bar, was determined at 210°C. The method required a determination of the precise Raman scattering ratios between the substance, water, and the used reference gas, hydrogen or methane. In our case the scattering ratios between water and reference ν1 Q-branches were found to be 1.20±0.03 and 0.40±0.02 for H2 and CH4, respectively.

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry, Aix-Marseille University
Contributors: Rodier, M., Li, Q., Berg, R. W., Bjerrum, N. J.
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Determination_of_Water_Vapor_Pressure_Over_Corrosive_Chemicals_Versus_Temperature_Using_Raman_Spectroscopy_as_Exemplified_with_85.5_Phosphoric_Acid.postprint.pdf. Embargo ended: 07/06/2017
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Research output: Contribution to journal › Journal article – Annual report year: 2016 › Research › peer-review

Electrochemical Studies of Corrosion in Liquid Electrolytes for Energy Conversion Applications at Elevated Temperatures

Stainless steels (AISI 316, 321 and 347), high-nickel alloys (Hastelloy®-C-276 and Inconel®625), tantalum, nickel, titanium, tungsten, molybdenum, niobium, platinum, and gold were tested for corrosion resistance in molten KH2PO4 (or KH2PO4-K2H2P2O7) as a promising electrolyte for the intermediate-temperature (200–400°C) water electrolysis. Pt, Ta, Nb, Ti, Inconel®625, and Ni demonstrated high corrosion resistance. Au and the rest of the tested materials were not corrosion
resistant. It means that Ni, Ti and Inconel®625 may be used as relatively cheap construction materials for the intermediate-temperature water electrolyzer.

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Kinetic Study of the Chemical Vapor Deposition of Tantalum in Long Narrow Channels
A kinetic study of the chemical vapor deposition of tantalum in long narrow channels is done to optimize the industrial process for the manufacture of tantalum coated plate heat exchangers. The developed model fits well at temperatures between 750 and 850 °C, and in the pressure range of 25–990 mbar. According to the model, the predominant tantalum growth species is TaCl3. The temperature is shown to have a pronounced effect on the morphology and rate of deposition of the tantalum and an apparent change in deposition mechanism occurs between 850–900 °C, resulting in the deposition rate at 900 °C being lower than both 850 and 950 °C.

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Organisations: Department of Energy Conversion and Storage, Proton conductors, Tantaline A/S
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Web of Science (2016): Indexed yes
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Source: FindIt
Source-ID: 2303440580
Research output: Contribution to journal › Journal article – Annual report year: 2016 › Research › peer-review
Specific electrical conductivity in molten potassium dihydrogen phosphate \( \text{KH}_2\text{PO}_4 \) - An electrolyte for water electrolysis at \( \sim 300^\circ\text{C} \)

The conductivity of pure molten \( \text{KH}_2\text{PO}_4 \) salt and four mixtures with more or less water (\( \text{KH}_2\text{PO}_4\cdot\text{H}_2\text{O} \) and \( \text{KH}_2\text{PO}_4\cdot\text{KPO}_3 \) systems, respectively) were measured at temperatures of 240-320\(^\circ\text{C}\) and under their own water vapor pressures. Molten \( \text{KH}_2\text{PO}_4 \) has been proven to be a promising electrolyte for an elevated temperature pressurized water electrolyzer demonstrating high conductivity of \( \sim 0.30\text{Scm}^{-1} \) at 300\(^\circ\text{C}\). The conductivity data are given as polynomial functions of temperature and composition. The melting point of the pure salt under its own water vapor pressure was determined to be \( \sim 272^\circ\text{C} \).

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Source-ID: 2304164866
Research output: Contribution to journal › Journal article – Annual report year: 2016 › Research › peer-review

Understanding ternary poly(potassium benzimidazolide)-based polymer electrolytes
Poly(2,20-(m-phenylene)-5,50-bisbenzimidazole) (m-PBI) can dissolve large amounts of aqueous electrolytes to give materials with extraordinary high ion conductivity and the practical applicability has been demonstrated repeatedly in fuel cells, water electrolysis and as anion conducting component in fuel cell catalyst layers. This work focuses on the chemistry of m-PBI in aqueous potassium hydroxide. Equilibration in aqueous KOH with concentrations of 15e20 wt.% was found to result in ionization of the polymer, causing released intermolecular hydrogen bonding. This allowed for extensive volume swelling, high electrolyte uptake, dramatic plasticization and increase of the ion conductivity for the formed poly(potassium benzimidazolide)-based structure. Further increasing the concentration of the bulk solution to 50 wt.% resulted in dehydration and extensive crystallization of the polymer matrix as evidenced by X-ray diffraction, increased density and enhanced elastic modulus. © 2016 Elsevier Ltd. All rights reserved.

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Organisations: Department of Energy Conversion and Storage, Proton conductors
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Water vapor pressure over molten KH₂PO₄ and demonstration of water electrolysis at ∼300°C

A new potentially high-efficiency electrolyte for water electrolysis: molten monobasic potassium phosphate, KH₂PO₄ or KDP has been investigated at temperatures ∼275–325 °C. At these temperatures, KH₂PO₄ was found to dissociate into H₂O gas in equilibrium with a melt mixture of KH₂PO₄—K₂H₂P₂O₇—KPO₃—H₂O. The water vapor pressure above the melt, when contained in a closed ampoule, was determined quantitatively vs. temperature by use of Raman spectroscopy with methane or hydrogen gas as an internal calibration standard, using newly established relative ratios of Raman scattering cross sections of water and methane or hydrogen to be 0.40 ± 0.02 or 1.2 ± 0.03. At equilibrium the vapor pressure was much lower than the vapor pressure above liquid water at the same temperature. Electrolysis was realized by passing current through closed ampoules (vacuum sealed quartz glass electrolysis cells with platinum electrodes and the electrolyte melt). The formation of mixtures of hydrogen and oxygen gases as well as the water vapor was detected by Raman spectroscopy. In this way it was demonstrated that water is present in the new electrolyte: molten KH₂PO₄ can be split by electrolysis via the reaction 2H₂O → 2H₂ + O₂ at temperatures ∼275–325 °C. At these temperatures, before the start of the electrolysis, the KH₂PO₄ melt gives off H₂O gas that pressurizes the cell according to the following dissociations: 2KH₂PO₄ ↔ K₂H₂P₂O₇ + H₂O ↔ 2KPO₃ + 2H₂O. The spectra show however that the water by virtue of hydrogen-bonding has a high affinity for remaining in the melt. The formed hydrogen and oxygen gasses were detected by means of the characteristic Raman gas-phase spectra.
CsH$_2$PO$_4$/NdPO$_4$ Composites as Proton Conducting Electrolytes for Intermediate Temperature Fuel Cells

Composite proton conducting materials based on cesium dihydrogen phosphate and neodymium phosphate hydrate were prepared and investigated in terms of X-ray diffraction, thermogravimetry, conductivity, stability and fuel cell performance. At 150°C the conductivity was 1.8 × 10$^{-6}$ S cm$^{-1}$ for the pristine cesium dihydrogen phosphate and 0.8 × 10$^{-4}$ S cm$^{-1}$ for neodymium phosphate hydrate, while that of the composite containing 29 mol% neodymium phosphate and 71 mol% cesium dihydrogen phosphate was 0.4 × 10$^{-2}$ S cm$^{-1}$. It was proposed that the interaction between the two components establishes a dynamic hydrogen bonding network enabling efficient proton conduction long before the development of the extensive phase disordering of the superprotonic transition. The presence of thermally stable hydrate water present in neodymium phosphate may also play a role in improving both conductivity and stability of the solid acid. The electromotive force, open circuit voltage and fuel cell performance were measured as demonstration of the material application.

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Contributors: Anfimova, T., Jensen, A. H., Christensen, E., Jensen, J. O., Bjerrum, N. J., Li, Q.
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Peer-reviewed: Yes

Fe$_3$C-based oxygen reduction catalysts: synthesis, hollow spherical structures and applications in fuel cells

We present a detailed study of a novel Fe$_3$C-based spherical catalyst with respect to synthetic parameters, nanostructure formation, ORR active sites and fuel cell demonstration. The catalyst is synthesized by high temperature autoclave pyrolysis using decomposing precursors. Below 500 °C, melamine-rich microspheres are first developed with uniformly dispersed amorphous Fe species. During the following pyrolysis at temperatures from 600 to 660 °C, a small amount of Fe$_3$C phase with possible Fe–Nx/C active sites are formed, however, with moderate catalytic activity, likely limited by the low conductivity of the catalyst. At high pyrolytic temperatures of 700–800 °C, simultaneous formation of Fe$_3$C nanoparticles and encasing graphitic layers occur within the morphological confinement of the microspheres. With negligible surface nitrogen or iron functionality, the thus-obtained catalysts exhibit superior ORR activity and stability. A new ORR active phase of Fe$_3$C nanoparticles encapsulated by thin graphitic layers is proposed. The activity and durability of the catalysts are demonstrated in both Nafion-based low temperature and acid doped polybenzimidazole-based high temperature proton exchange membrane fuel cells.

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Organisations: Department of Energy Conversion and Storage, Proton conductors, Imaging and Structural Analysis, Institut National de la Recherche Scientifique, Chinese Academy of Sciences
Contributors: Hu, Y., Jensen, J. O., Zhang, W., Fernandez, S. M., Chenitz, R., Pan, C., Xing, W., Bjerrum, N. J., Li, Q.
Pages: 1752-1760
Publication date: 2015
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Porous poly(perfluorosulfonic acid) membranes for alkaline water electrolysis

Poly(perfluorosulfonic acid) (PFSA) is one of a few polymer types that combine excellent alkali resistance with extreme hydrophilicity. It is therefore of interest as a base material in separators for alkaline water electrolyzers. In the pristine form it, however, shows high cation selectivity. To increase its ion conductivity in aqueous KOH, a method for the preparation of porous PFSA membranes was developed. It was based on an approach where PFSA was co-cast with poly(vinylpyrrolidone) (PVP) at different ratios to give transparent and colorless blend membranes. The PVP was subsequently dissolved and washed out and the obtained porous materials allowed for swelling to reach water contents up to $\lambda=85\,\text{[H}_2\text{O]}\,\text{[−SO}_3\text{K]}^{-1}$. After equilibration in 22 wt% aqueous KOH, ion conductivity of 0.2 S cm$^{-1}$ was recorded for this membrane type at room temperature, which is significantly higher than 0.01 S cm$^{-1}$ for the unmodified membrane. The technological feasibility was demonstrated by testing the membranes in an alkaline water electrolysis cell with encouraging performance.

Pt-Si Bifunctional Surfaces for CO and Methanol Electro-Oxidation

Bimetallic surfaces offer activity benefits derived from synergistic effects among active sites with uniquely different functions, which is particularly important for the development of highly effective heterogeneous catalysts for specific technological applications, such as energy conversion and storage. Here we report on Pt-Si bulk samples prepared by arc-melting, for the first time, with high activities toward the electro-oxidation of CO and methanol. Increasing the Si concentration on the surface was correlated with the shifts of onset oxidation potentials to lower values and higher activities for CO and methanol electro-oxidation. It is proposed that the reaction on the Pt-Si catalyst could follow a Langmuir-Hinshelwood type of mechanism, where substantially enhanced catalytic activity is attributed to the fine-tuning of the surface Pt-Si atomic structure.
Space-confined preparation of high surface area tungsten oxide and tungsten nitride inside the pores of mesoporous silica SBA-15

For the direct preparation of high surface area nitride materials, a lack of suitable precursors exists. Indirect preparation by gas phase nitridation (e.g. by ammonia) requires high temperatures and often results in sintering. The present work demonstrates that the space-confined preparation of W2N inside the pores of ordered mesoporous silica SBA-15 offers a possibility to reduce sintering phenomena and thus to obtain smaller particles, porous structures and a higher surface area material. The preparation was pursued in a two-step approach. First, WO3 was introduced into the channels of SBA-15 and second, ammonolysis was conducted for its conversion to W2N. When performed in the presence of the exo-template, SBA-15 acts as a stabilizer and small W2N particles (6-7 nm) with a high specific surface area (40 m² g⁻¹) are obtained after template removal. When the template is, however, removed before nitridation, it cannot stabilize the W2N particles and enhanced sintering occurs. (C) 2015 Elsevier Inc. All rights reserved.
Specific Electrical Conductivity in Molten Potassium Dihydrogen Phosphate KH2PO4 Electrolyte at ~300 °C

The effect of preparation method on the proton conductivity of indium doped tin pyrophosphates

Indium doped tin pyrophosphates were prepared by three synthetic routes. A heterogeneous synthesis from metal oxides with excess phosphoric acid produces crystalline phosphate particles with a phosphorus rich amorphous phase along the grain boundaries. The amorphous phase prevents the agglomeration of particles, hydrolyzes in moist atmosphere as revealed by FT-IR and solid state NMR, and facilitates a high proton conductivity (above 2.5 × 10⁻² S cm⁻¹) with high stability at above 120 °C under a water partial pressure of 0.15 atm. This phase can be removed by washing with water, resulting in a dramatic decrease in conductivity as well as significant agglomeration of the particles, as evident in TEM and from particle size distribution measurements. Homogeneous synthesis with soluble metal acetates or chlorides as precursors results in a single crystalline phase with a small particle size, but strongly agglomerated, and a low conductivity at 10⁻⁷-10⁻⁶ S cm⁻¹ level. Further impregnation of the agglomerates with phosphoric acid does not lead to formation of the phosphorus rich amorphous layers on the surface of the crystals. An intermediate conductivity of 10⁻³ S cm⁻¹ was observed for the acid treated phosphates from the chloride synthesis but no improvement for the acid treated phosphates from the acetate synthesis was observed.

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The stability of poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole) membranes in aqueous potassium hydroxide

In the form of membranes, poly(2,2′-(m-phenylene)-5,5′-bibenzimidazole) (mPBI) is known to exhibit high ionic conductivity when doped with aqueous KOH, which makes it interesting as electrolyte in e.g. alkaline fuel cells and water electrolyzers. The conductivity peaks at KOH concentrations around 25wt%. This work is devoted to a comprehensive stability study of mPBI in aqueous KOH of different concentrations for up to 200 days under conditions relevant for electrochemical energy conversion technologies. The polymer membranes were kept at 88°C in aqueous KOH with concentrations ranging from 0 to 50wt%, and the chemical and physicochemical changes were monitored. The degradation was connected to the hydrolysis of the polymer backbone and the degradation rate increased with increasing KOH concentration. In the lower concentration range mPBI proved to be stable but exhibited low ionic conductivity (10−4 Scm−1). The preparation of a porous mPBI matrix was demonstrated as an effective approach to increase the ionic conductivity in the lower KOH concentration range, with great potential for further improvement through optimization of the porous structure.

Transition metal carbides (WC, Mo2C, TaC, NbC) as potential electrocatalysts for the hydrogen evolution reaction (HER) at medium temperatures

One limitation for large scale water electrolysis is the high price of the Pt cathode catalyst. Transition metal carbides, which are considered as some of the most promising non-Pt catalysts, are less active than Pt at room temperature. The present work demonstrates that the situation is different at medium temperatures (200-400 degrees C). By introducing a new setup which makes use of molten KH2PO4 as electrolyte, a model system for solid acid membrane electrolyser cells was obtained. Metal carbide coated wires prepared by a two-step oxidation carburization reaction of the metal wire surfaces were used as electrodes and allowed the measurement of the intrinsic catalytic properties of different transition metal carbides in direct comparison to Pt at 260 degrees C. Under these conditions, the activity in the hydrogen evolution reaction (HER) followed the order WC > Pt approximate to Mo2C > NbC > TaC. Copyright (C) 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.
Advances in the chemical vapor deposition (CVD) of Tantalum

The chemical stability of tantalum in hot acidic media has made it a key material in the protection of industrial equipment from corrosion under such conditions. The Chemical Vapor Deposition of tantalum to achieve such thin corrosion resistant coatings is one of the most widely mentioned examples of CVD processes; however very little information on the process and its characteristics can be found. This work presents the state of the art on the CVD of tantalum in long narrow channels and a reaction mechanism is suggested based on a rudimentary model. The effects of the system pressure, temperature and process-setup on the deposition rates and material distribution are also presented.
A Stability Study of Alkali Doped PBI Membranes for Alkaline Electrolyzer Cells

Polybenzimidazole membranes in a linear, a crosslinked and a thermally cured form were subjected to aging in 6 M aqueous KOH at 85 °C for periods of up to 176 days. The aged membranes were characterized with respect to weight loss, mechanical properties and ionic conductivity. The area specific conductivity was similar to a commercial Zirfon membrane and suitable for a water electrolyzer. Some chemical degradation was seen during the aging period, but the crosslinked and the cured materials were both integral after 176 days of aging. A simplified electrolyzer test cell was operated successfully.

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Development of Non-Platinum Catalysts for Intermediate Temperature Water Electrolysis

Water electrolysis is recognized as an efficient energy storage (in the form of hydrogen) supplement in renewable energy production. However, industrial alkaline water electrolyzers are rather ineffective and space requiring for a commercial use in connection with energy storage. The most effective modern water electrolyzers are based on polymeric proton-conducting membrane electrolytes (PEM), e.g. Nafion®, a perfluorocarbon-sulfonic acid polymer. These electrolyzers work at temperatures up to around 80 °C, and, in extreme cases, up to 130-140 °C. The most developed PEM electrolyzers are at the stage of commercial development. However, there is a great challenge for their widespread commercialization: high cost and low abundance of the electrocatalytic materials (Pt, IrO2) and use of Ti or other expensive construction materials. On the cathode side, the most active catalyst is Pt exhibiting the best compromise in metal-hydrogen bond strength1,2. Due to economic reasons there is a huge interest in replacing Pt by cheaper alternatives and much effort have been made in finding novel catalysts for Hydrogen Evolution Reaction (HER)3,4. Many anhydrous proton conductors have been investigated as electrolytes for the intermediate temperature applications, such as CsHSO4, KHSO45. The most successful systems have been developed with CsH2PO4 (solid acid fuel cells (SAFCs) and Sn0.9In0.1P2O7 electrolytes6,7. While developing materials for the promising medium temperature electrolysis systems it is important to simulate conditions of those presented in the assembled operational electrolyzer. In this work a molten KH2PO4 will be used as an electrolyte while screening performance of various transition metals and their carbides at higher temperature (Figure 1). In this work will be shown that coatings of transition metal carbides not only improve the stability of pure metals but also enhance electrocatalytic efficiency of materials towards HER and Oxygen Evolution Reaction (OER) at intermediate temperatures (Figure 2). The increase of the electrocatalytic activity of tungsten carbide in the electrochemical hydrogen reduction between 120 and 150 °C was recently demonstrated to be several times more...

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Direct Dimethyl Ether High Temperature Fuel Cells

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Direct Dimethyl Ether High Temperature PEM Fuel Cells

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Direct Synthesis of Fe3C-Functionalized Graphene by High Temperature Autoclave Pyrolysis for Oxygen Reduction

We present a novel approach to direct fabrication of few-layer graphene sheets with encapsulated Fe3C nanoparticles from pyrolysis of volatile non-graphitic precursors without any substrate. This one-step autoclave approach is facile and potentially scalable for production. Tested as an electrocatalyst, the graphene-based composite exhibited excellent catalytic activity towards the oxygen reduction reaction in alkaline solution with an onset potential of ca. 1.05 V (vs. the reversible hydrogen electrode) and a half-wave potential of 0.83 V, which is comparable to the commercial Pt/C catalyst.

Highly active and stable Pt electrocatalysts promoted by antimony-doped SnO2 supports for oxygen reduction reactions

Alternative composite supports for platinum catalysts were synthesized from antimony doped tin dioxide (ATO) nanoparticles. In the range of the antimony content from 0 to 11mol%, the highest electrical conductivity of 1.1Scm⁻¹ at 130°C was obtained for the 5mol% Sb ATO, from which composite supports composed of oxides and carbon and supported platinum catalysts were prepared. Using the pure oxide support, the Pt/ATO catalyst displayed superior specific activity and stability for the oxygen reduction reactions (ORRs). Low surface area of ATO caused poor dispersion of Pt particles compared to composite supports, which limited the mass activity of the supported catalysts. When the ATO composites were used as supports, the Pt/C-ATO catalysts showed significantly enhanced catalytic activity and durability for the ORR, attributable to the high ECSA and modified electronic structure of Pt by the ATO phase in the catalyst support. © 2013.
High Molecular Weight Polybenzimidazole Membranes for High Temperature PEMFC

High temperature operation of proton exchange membrane fuel cells under ambient pressure has been achieved by using phosphoric acid doped polybenzimidazole (PBI) membranes. To optimize the membrane and fuel cells, high performance polymers were synthesized of molecular weights from 30 to 94 kDa with good solubility in organic solvents. Membranes fabricated from the polymers were systematically characterized in terms of oxidative stability, acid doping and swelling, conductivity, mechanical strength and fuel cell performance and durability. With increased molecular weights the polymer membranes showed enhanced chemical stability towards radical attacks under the Fenton test, reduced volume swelling upon the acid doping and improved mechanical strength at acid doping levels of as high as about 11 mol H3PO4 per molar repeat polymer unit. The PBI-78kDa/10.8PA membrane, for example, exhibited tensile strength of 30.3 MPa at room temperature or 7.3 MPa at 130 °C and a proton conductivity of 0.14 S cm–1 at 160 °C. Fuel cell tests with H2 and air at 160 °C showed high open circuit voltage, power density and a low degradation rate of 1.5 μV h–1 at a constant load of 300 mA cm–2.

High Surface Area Tungsten Carbides: Synthesis, Characterization and Catalytic Activity towards the Hydrogen Evolution Reaction in Phosphoric Acid at Elevated Temperatures

Tungsten carbide powders were synthesized as a potential electrocatalyst for the hydrogen evolution reaction in phosphoric acid at elevated temperatures. With ammonium metatungstate as the precursor, two synthetic routes with and
without carbon templates were investigated. Through the intermediate nitride route and with carbon black as template, the obtained tungsten carbide samples had higher BET area. In 100% H3PO4 at temperatures up to 185°C, the carbide powders showed superior activity towards the hydrogen evolution reaction. A deviation was found in the correlation between the BET area and catalytic activity; this was attributed to the presence of excess amorphous carbon in the carbide powder. TEM imaging and TGA-DTA results revealed a better correlation of the activity with the carbide particle size.

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Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers as Oxygen Reduction Catalysts
Nonprecious metal catalysts for the oxygen reduction reaction are the ultimate materials and the foremost subject for low-temperature fuel cells. A novel type of catalysts prepared by high-pressure pyrolysis is reported. The catalyst is featured by hollow spherical morphologies consisting of uniform iron carbide (Fe3C) nanoparticles encased by graphitic layers, with little surface nitrogen or metallic functionalities. In acidic media the outer graphitic layers stabilize the carbide nanoparticles without depriving them of their catalytic activity towards the oxygen reduction reaction (ORR). As a result the catalyst is highly active and stable in both acid and alkaline electrolytes. The synthetic approach, the carbide-based catalyst, the structure of the catalysts, and the proposed mechanism open new avenues for the development of ORR catalysts.

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Hollow Spheres of Iron Carbide Nanoparticles Encased in Graphitic Layers as Oxygen Reduction Catalysts

Nonprecious metal catalysts for the oxygen reduction reaction are the ultimate materials and the foremost subject for low-temperature fuel cells. A novel type of catalysts prepared by high-pressure pyrolysis is reported. The catalyst is featured by hollow spherical morphologies consisting of uniform iron carbide (Fe3C) nanoparticles encased by graphitic layers, with little surface nitrogen or metallic functionalities. In acidic media the outer graphitic layers stabilize the carbide nanoparticles without depriving them of their catalytic activity towards the oxygen reduction reaction (ORR). As a result the catalyst is highly active and stable in both acid and alkaline electrolytes. The synthetic approach, the carbide-based catalyst, the structure of the catalysts, and the proposed mechanism open new avenues for the development of ORR catalysts.

Hydrogen evolution activity and electrochemical stability of selected transition metal carbides in concentrated phosphoric acid

Alternative catalysts based on carbides of Group 5 (niobium and tantalum) and 6 (chromium, molybdenum and tungsten) metals were prepared as films on the metallic substrates. The electrochemical activities of these carbide electrodes towards the hydrogen evolution reaction (HER) in concentrated phosphoric acid were investigated in a temperature range from 80 to 170°C. A significant dependence of the activities on temperature was observed for all five carbide samples. Through the entire temperature range Group 6 metal carbides showed higher activity than that of the Group 5 metal carbides, attributable to the different electronic structures. Tungsten carbide among the studied electrode samples exhibited the highest HER activity. Upon anodic potential scans in the presence of oxygen, chromium, tantalum and tungsten carbides displayed passivation due to the formation of stable surface layers whereas niobium and molybdenum carbides seemed to undergo corrosion.
Intermediate Temperature Fuel Cell Using CsH₂PO₄/ZrO₂-Based Composite Electrolytes

Proton conductors operating at intermediate temperatures are receiving significant attention due to their advantages over conventionally used materials in proton exchange membrane fuel cells. CsH₂PO₄ has proven to be proton conducting above 230°C, however within a narrow temperature range of the superprotonic phase. In the present work CsH₂PO₄-ZrO₂ composite electrolytes were prepared and investigated in the temperature range from 120°C to 300°C. As a result of improved thermal and mechanical stability the composite electrolyte exhibited high proton conductivities preserved to higher temperatures up to 280°C under low atmospheric humidification. Higher open circuit voltage and stability in the extended temperature range were achieved with composite electrolytes with a CsH₂PO₄ to ZrO₂ molar ratio of 2.

Invited: A Stability Study of Alkali Doped PBI Membranes for Alkaline Electrolyzer Cells

Alkaline fuel cells and electrolyzers are attracting increasing interest. This is to a large extent due to the broad selection of catalyst materials not based on resource limited and expensive noble metals. The first fuel cells in practical use were Francis Thomas Bacon's based on an alkaline electrolyte. The system has been quite successful with good oxygen kinetics, but the electrolyte suffers from carbonization when operated in normal CO₂ containing air and this has limited the application to space technology and similar niches. The alkaline electrolyzer on the other hand has been the state of art commercial choice for decades and the carbonization problem is absent since oxygen is produced, not consumed. However, the demand for high voltage efficiency has been limited and the alkaline electrolyzer has been optimized in the direction of robustness and long lifetime instead. Today it has become obvious that an energy system based on renewable energy will need conversion of a large amount of electrical energy to fuel for storage and for transport. We believe that from a materials perspective the alkaline electrolyzer has the strongest potential for meeting the manufacturing cost targets given, but voltage efficiency and rate capability must be improved significantly. One important component with room for improvement is the electrolyte which traditionally fills a gap of up to several mm between the electrodes. The resistance can be much reduced if a thin anion conducting membrane or a porous diaphragm is used instead in direct contact with both electrodes (zero gap). In proton exchange membrane (PEM) electrolyzers proton conducting membranes like in PEM fuel cells have been very successful, but for the equivalent anion exchange membranes a similar conductivity has not yet been demonstrated; in contrast it is typically about an order of magnitude lower, which is
insufficient [1]. The aromatic fluorine free polymer polybenzimidazole (PBI) has been very successful as a high temperature fuel cell membrane when doped with phosphoric acid [2] and it has been shown by Xing and Savadogo [3] that it can also be doped with potassium hydroxide and serve as electrolyte for alkaline fuel cells. See figure 1. In this work the stability of PBI doped with aqueous KOH was studied after storage in 6 M KOH at 85 °C for up to 176 days, i.e. close to half a year [4]. The pristine polymer was supplied by Danish Power Systems ApS and solution cast from DMAC. Three different variants of the PBI were used. 1) The pristine linear PBI, 2) PBI crosslinked by dibromoparaxylene and 3) PBI thermally cured at 350 °C. Tensile strength and elastic modulus decreased somewhat during storage, but all membranes remained integral throughout the entire storage period with the exception of the linear untreated sample which disintegrated when handled after the full 176 days. A gradual weight loss was seen for all membranes but the effect was much reduced for the crosslinked and the cured pieces. The thermally cured membrane lost less than 10 mass %. Viscosity measurement on the linear PBI (the only one soluble) showed a decreasing molecular weight over time of storage. The materials were also examined by IR, NMR and TGA. Finally, electrolysis tests were made including comparison with a commercial diaphragm material (Zirfon). The conductivity of the alkali doped PBI samples was around 0.05 S cm-2 at 85 °C, while that of Zirfon was ca. 0.2 S cm-2, but since Zirfon is much thicker to ensure a low bubble point pressure the practical area specific resistances were more or less equal and the cells showed very similar polarization characteristics. [1] G. Merle, M. Wessling and K. Nijmeijer. J. Membrane Sci. 377 (2011) 1– 35 [2] Q. F. Li, J. O. Jensen, R. F. Savinell and N. J. Bjerrum. Prog. Polym. Sci. 34(2009) 449 [3] B. Xing, O. Savadogo, Electrochemistry Communications 2(2000) 697-702 [4] D. Aili, M. K. Hansen, R.F. Renzaho, Q. F. Li, E. Christensen, J. O. Jensen and N. J..Bjerrum. J. Membrane Sci. 447 (2013) 424–432

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**Novel non-platinum metal catalyst material**

The present invention relates to a novel non-platinum metal catalyst material for use in low temperature fuel cells and electrolysers and to fuel cells and electrolysers comprising the novel non-platinum metal catalyst material. The present invention also relates to a novel method for synthesizing the novel non-platinum metal catalyst material.

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Oxygen evolution catalysts on supports with a 3-D ordered array structure and intrinsic proton conductivity for proton exchange membrane steam electrolysis

Proton exchange membrane steam electrolyzers suffer from insufficient catalyst activity and durability due to the slow reaction kinetics for oxygen evolution reaction (OER) and poor durability under harsh operating environments. Aiming at enhancement of oxygen electrode kinetics and durability, composite support materials for iridium oxide are synthesized via in situ phosphorization reaction on tin doped indium oxide and possess functionalities of high electronic and intrinsic proton conductivity. At 130 °C under a water vapor atmosphere an overall conductivity of 0.72 S cm−1 is achieved with a contribution of around 10−2 S cm−1 proton conductivity. The support structure of three-dimensionally ordered hexagonal arrays displays a high specific surface area of 180 m² g−1. Benefiting from the mixed conductivities and porous structure in the composite support materials, the supported IrO₂ catalysts exhibit about five times enhancement of the OER activity in acidic electrolytes. The improved catalytic performance for the OER was further confirmed by PEM electrolyzer tests at 130 °C. A test of such a steam electrolyzer cell at 350 mA cm−2 shows good durability within a period of up to 1150 hours.

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Perovskites As Electrocatalysts for Alkaline Water Electrolysis
Water electrolysis is a promising technology for the production of hydrogen as a sustainable energy storage source, combined with solar or wind power. In this work various electrocatalysts for the Oxygen Evolution Reaction (OER) electrode were synthesized and characterized by several techniques such as X-ray diffraction, electrical conductivity, scanning electron microscopy (SEM), energy dispersive microscopy (EDX) and rotating disk electrode. The perovskites tested in this work were both produced by a ball-milling technique and by an auto-combustion synthesis, which appeared to be a fast and robust method for synthesis of perovskites with various chemical compositions1. The electrochemical performance of the materials was tested through pellet pressing of the perovskite powders. This involved in some case a time consuming preparation process. Furthermore the technique should show the adequate reproducibility.2 In this work we show the development of the method, which was further used to compare the activity of various electrocatalysts (Figures 1,2). The electrocatalytic activity of all prepared perovskites was tested in 1M KOH at 80 °C, using an ink consisting of potassium exchanged Nafton®. All tests were performed in the potential window 0-700 mV on a glassy carbon electrode. All the tested perovskites were characterized by their overpotential , measured current at 650 mV, obtained kinetic current and Tafel slopes. It was also shown that this technique do not depend on the initial powder electric conductivity which varied by several orders of magnitude, as shown on Figure 3. 1 H. Nijjar, J. Lamonier, O. Mentr'e, J. Giraudon, H. Batis, Appl. Catal. B, 106, 149–159, 2011 2 J.O'M. Bockris and T. Otagawa J. Phys. Chem. 87:2960-2971, 1983.

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Phosphate-Doped Carbon Black as Pt Catalyst Support: Co-catalytic Functionality for Dimethyl Ether and Methanol Electro-oxidation

Niobium-phosphate-doped (NbP-doped) carbon blacks were prepared as the composite catalyst support for Pt nanoparticles. Functionalities of the composite include intrinsic proton conductivity, surface acidity, and interfacial synergistic interactions with methanol and dimethyl ether (DME). The supported Pt catalysts show significant improvement in catalytic activity towards the direct oxidation of methanol and DME, attributable to the enhanced adsorption and dehydrogenation of methanol and DME, as well as the presence of activated OH species in the catalysts. The latter is demonstrated to facilitate the removal of CO intermediates formed during the oxidation reactions.

The Electrochemical Behavior of Phosphoric-Acid-Doped Poly(perfluorosulfonic Acid) Membranes

Highly conductive phosphoric-acid-doped poly(perfluorosulfonic acid) membranes have long been known to malfunction in fuel cells. This is investigated and found to be due to failure of the anode, in which a limiting current is observed in the very low current-density range. It is proposed that the strongly acidic sulfonic acid groups protonate the phosphoric acid under anhydrous conditions, forming excess proton defects that are involved in proton conduction by means of the vehicle mechanism. The slow back-diffusion of phosphoric acid molecules as proton carriers thus limits the long-range conductivity of the membranes during fuel cell operation. The hypothesis is experimentally verified using a specially designed halfcell test.
Thermal Stability and Proton Conductivity of Rare Earth Orthophosphate Hydrates

Hydrated orthophosphate powders of three rare earth metals, lanthanum, neodymium and gadolinium, were prepared and studied as potential proton conducting materials for intermediate temperature electrochemical applications. The phosphates undergo a transformation from the rhabdophane structure to the monazite structure upon dehydration. The thermal stability of the hydrate is studied and found to contain water of two types, physically adsorbed and structurally bound hydrate water. The adsorbed water is correlated to the specific surface area and can be reversibly recovered when dehydrated as long as the rhabdophane structure is preserved. The bound hydrate water is accommodated in the rhabdophane structure and is stable at temperatures of up to 650 °C. The thermal stability of the hydrate water and the phosphate structure are of significance for the proton conductivity. The LaPO₄·0.6H₂O and NdPO₄•0.5H₂O exhibited the structure dependence of the proton conductivity while the GdPO₄•0.5H₂O showed a large effect of the phosphate morphology.

Water steam electrolysis at intermediate temperature with Sn₀.₉In₀.₁P₂O₇ solid electrolyte

Water steam electrolysis at intermediate temperature with Sn₀.₉In₀.₁P₂O₇ solid electrolyte.
Activity and Durability Studies of Nanoparticulate, Thin Film and Bulk Electro catalysts and they Supporting Materials for PEM and DMFCs

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Antimony doped tin oxide modified carbon nanotubes as catalyst supports for methanol oxidation and oxygen reduction reactions

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Benzimidazole grafted polybenzimidazoles for proton exchange membrane fuel cells

High molecular weight polybenzimidazole (PBI) was synthesized and grafted with benzimidazole pendant groups. The high molecular weight of PBI resulted in good film-forming properties and superior tensile strength. With a phosphoric acid doping level (ADL) of 13.1, a tensile strength of 16 MPa was achieved at room temperature. Grafting of benzimidazole moieties onto the PBI macromolecular chain introduced additional basic sites which allowed the membrane to achieve higher phosphoric acid uptakes. A molar acid conductivity, defined as the specific conductivity of each mole of doping acid, was proposed to evaluate the effective conductivity contributed from the doping acids. With a grafting degree of 5.3% and an ADL of 13.1, the PBI membranes exhibited a total conductivity of 0.15 S cm-1. A H2-air fuel cell based on this membrane showed a peak power density of 378 mW cm-2 at 180 °C without humidification. © 2013 The Royal Society of
Catalyst Degradation in High Temperature Proton Exchange Membrane Fuel Cells Based on Acid Doped Polybenzimidazole Membranes

Degradation of carbon supported platinum catalysts is a major failure mode for the long term durability of high temperature proton exchange membrane fuel cells based on phosphoric acid doped polybenzimidazole membranes. With Vulcan carbon black as a reference, thermally treated carbon black and multi-walled carbon nanotubes were used as supports for electrode catalysts and evaluated in accelerated durability tests under potential cycling at 150 °C. Measurements of open circuit voltage, area specific resistance and hydrogen permeation through the membrane were carried out, indicating little contribution of the membrane degradation to the performance losses during the potential cycling tests. As the major mechanism of the fuel cell performance degradation, the electrochemical active area of the cathodic catalysts showed a steady decrease in the cyclic voltammetric measurements, which was also confirmed by the post TEM and XRD analysis. A strong dependence of the fuel cell performance degradation on the catalyst supports was observed. Graphitization of the carbon blacks improved the stability and catalyst durability though at the expense of a significant decrease in the specific surface area. Multi-walled carbon nanotubes as catalyst supports showed further significant improvement in the catalyst and fuel cell durability.

Catalyst Degradation in High Temperature Proton Exchange Membrane Fuel Cells Based on Acid Doped Polybenzimidazole Membranes

Degradation of carbon supported platinum catalysts is a major failure mode for the long term durability of high temperature proton exchange membrane fuel cells based on phosphoric acid doped polybenzimidazole membranes. With Vulcan carbon black as a reference, thermally treated carbon black and multi-walled carbon nanotubes were used as supports for electrode catalysts and evaluated in accelerated durability tests under potential cycling at 150 °C. Measurements of open circuit voltage, area specific resistance and hydrogen permeation through the membrane were carried out, indicating little contribution of the membrane degradation to the performance losses during the potential cycling tests. As the major mechanism of the fuel cell performance degradation, the electrochemical active area of the cathodic catalysts showed a steady decrease in the cyclic voltammetric measurements, which was also confirmed by the post TEM and XRD analysis. A strong dependence of the fuel cell performance degradation on the catalyst supports was observed. Graphitization of the carbon blacks improved the stability and catalyst durability though at the expense of a significant decrease in the specific surface area. Multi-walled carbon nanotubes as catalyst supports showed further significant improvement in the catalyst and fuel cell durability.
Conductivity of Composite Material Based on System NdPO₄·nH₂O-CsH₂PO₄

The goal of the present study was to obtain a comprehensive knowledge about synthesis conditions, structure, thermal behavior and conductivity properties of neodymium orthophosphates in order to analyze their use in intermediate temperature fuel cells due to their thermal and chemical stability properties. The impedance spectroscopy technique (IS) was used to measure the conductivity. The conductivity of composites observed to be lower than conductivity of pure CsH₂PO₄ but had improved sufficiently conductivity of pure NdPO₄·nH₂O.

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Corrosion behavior of construction materials for intermediate temperature steam electrolyzers

Different corrosion resistant stainless steels, nickel-based alloys, pure nickel, Ta-coated stainless steel (AISI 316L), niobium, platinum and gold rods were evaluated as possible materials for use in the intermediate temperature (200-400 °C) acidic water electrolyzers. The corrosion resistance was measured under simulated conditions (molten KH₂PO₄) corresponding to the proton-conducting solid acids or transition metal phosphates as electrolytes. It was shown that, unlike at temperatures below 200 °C, gold is unstable with respect to corrosion in molten KH₂PO₄. Platinum demonstrated high corrosion resistance and the anodic and cathodic limits were for the first time found for the electrolyte. Nickel, niobium, Inconel®625, Hastelloy®C-276 and Ta-coated stainless steel (AISI 316L) demonstrated high corrosion stability and can be recommended as construction materials for bipolar plates. © (2013) Trans Tech Publications, Switzerland.

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Covalently Cross-Linked Sulfone Polybenzimidazole Membranes with Poly(Vinylbenzyl Chloride) for Fuel Cell Applications

Covalently cross-linked polymer membranes were fabricated from poly(aryl sulfone benzimidazole) (SO(2) PBI) and poly(vinylbenzyl chloride) (PVBCl) as electrolytes for high-temperature proton-exchange-membrane fuel cells. The cross-linking imparted organo insolubility and chemical stability against radical attack to the otherwise flexible SO(2) PBI membranes. Steady phosphoric acid doping of the cross-linked membranes was achieved at elevated temperatures with little swelling. The acid-doped membranes exhibited increased mechanical strength compared to both pristine SO(2) PBI and poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] (mPBI). The superior characteristics of the cross-linked SO(2) PBI membranes allowed higher acid doping levels and, therefore, higher proton conductivity. Fuel-cell tests with the cross-linked membranes demonstrated a high open circuit voltage and improved power performance and durability.

Crosslinked Hexafluoropropylidene Polybenzimidazole Membranes with Chloromethyl Polysulfone for Fuel Cell Applications

Hexafluoropropylidene polybenzimidazole (F6PBI) was synthesized with excellent chemical stability and improved solubility. When doped with phosphoric acid, however, the F6PBI membranes showed plastic deformation at elevated temperatures. Further efforts were made to covalently crosslink F6PBI membranes with chloromethyl polysulfone as a polymeric crosslinker. Comparing with linear F6PBI and mPBI membranes, the polymer crosslinked F6PBI membranes exhibited little organo solubility, excellent stability towards the radical oxidation, high resistance to swelling in concentrated phosphoric acid solutions, and improved mechanical strength, especially at elevated temperatures. The superior characteristics of crosslinked membranes allowed for higher acid doping levels and therefore increased proton conductivity as well as significantly improved fuel cell performance and durability, as compared with the linear F6PBI and mPBI membranes.
Development and Study of Tantalum and Niobium Carbides as Electrocatalyst Supports for the Oxygen Electrode for PEM Water Electrolysis at Elevated Temperatures

Polymer electrolyte membrane (PEM) water electrolysis is a prospective method of producing hydrogen. We focused on one of its issues – the lack of a suitable support material for the anode electrocatalyst. TaC and NbC were studied as possible electrocatalyst supports for the PEM water electrolysis. Resistance to oxidation of the TaC and NbC was investigated by exposing them to air at 84 and 150 °C. Subsequently, their electrical conductivity was measured as the indicator of oxidation. Change in specific surface area and conductivity was measured after different periods of ball milling. We found that the TaC was significantly more resistant to oxidation than the NbC. Eventually, both materials retained relatively high electrical conductivity even with the oxidized surface. TaC can thus be recommended as an electrocatalyst support for the oxygen evolution reaction and both materials are proposed to be tested as alternative electrocatalyst supports for the hydrogen evolution reaction.

Fabrication and Characterizations of Materials and Components for Intermediate Temperature Fuel Cells and Water Electrolysers

The worldwide development of fuel cells and electrolysers has so far almost exclusively addressed either the low temperature window (20-200 °C) or the high temperature window (600-1000 °C). This work concerns the development of key materials and components of a new generation of fuel cells and electrolysers for operation in the intermediate temperature range from 200 to 400 °C. The intermediate temperature interval is of importance for the use of renewable fuels. Furthermore electrode kinetics is
significantly enhanced compared to when operating at low temperature. Thus non-noble metal catalysts might be used. One of the key materials in the fuel cell and electrolyser systems is the electrolyte. Proton conducting materials such as cesium hydrogen phosphates, zirconium hydrogen phosphates and tin pyrophosphates have been investigated by others and have shown interesting potential.

**General information**
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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Jensen, A. H., Prag, C. B., Li, Q., Christensen, E., Bjerrum, N. J.
Number of pages: 1
Publication date: 2013
Peer-reviewed: No
Event: Poster session presented at International Symposium on Water Electrolysis and Hydrogen as part of the future Renewable Energy System, Copenhagen, Denmark.

**Abstract**

**Poster**
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Source-ID: u::7391
Research output: Contribution to conference › Poster – Annual report year: 2013 › Research

**Heterogeneous anion conducting membranes based on linear and crosslinked KOH doped polybenzimidazole for alkaline water electrolysis**

Polybenzimidazole is a highly hygroscopic polymer that can be doped with aqueous KOH to give a material with high ion conductivity in the 10−2Scm−1 range, which in combination with its low gas permeability makes it an interesting electrolyte material for alkaline water electrolysis. In this study membranes based on linear and crosslinked polybenzimidazole were evaluated for this purpose. Extensive characterization with respect to spectroscopic and physicochemical properties during aging in 6molL−1 KOH at 85°C for up to 176 days indicated structural stability of the high molecular weight specialty polymer, however, with limitations with respect to hydrolytic stability. The gradual decay of the average molecular weight resulted in a severe deterioration of the mechanical properties over time. Membranes based on crosslinked polybenzimidazole showed better stability than the membranes based on their linear counterpart. The technical feasibility of the membranes was evaluated by the preliminary water electrolysis tests showing performance comparable to that of commercially available cell separators with great potential of further improvement.

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Organisations: Department of Energy Conversion and Storage, Proton conductors, Siemens A/S
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**Publication information**
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Scopus rating (2013): CiteScore 5.38 SJR 2.451 SNIP 1.994
Web of Science (2013): Impact factor 4.908
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
Original language: English
Keywords: Polybenzimidazole, Ion conductivity, KOH, Stability, Water electrolysis
DOIs:
10.1016/j.memsci.2013.07.054
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Source-ID: n:oai:DTIC-ART:elsevier/391395088::31540
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**Indium doped niobium phosphates as intermediate temperature proton conductors**

Indium doped niobium phosphates were prepared from precursors of trivalent indium oxide, pentavalent niobium oxide and phosphoric acid. The obtained materials were characterized by X-ray diffraction, impedance spectroscopy, FT-IR spectroscopy and scanning electron microscopy. It was found that the indium doping promoted formation of the cubic
Nb2P4O15 phase instead of the monoclinic Nb5P7O30 phase in the pristine niobium phosphates and enhanced the preservation of OH functional groups in the phosphates. The preserved OH functionalities in the phosphates after the heat treatment at 650 °C contributed to the anhydrous proton conductivity. The Nb0.9In0.1 phosphate exhibited a proton conductivity of five times higher than that of the un-doped analog at 250 °C. The conductivity was stabilized at a level of above 0.02 S cm−1 under dry atmosphere at 250 °C during the stability evaluation for 3 days.

Oxidative degradation of acid doped polybenzimidazole membranes and fuel cell durability in the presence of ferrous ions

Phosphoric acid doped polybenzimidazole membranes have been explored as proton exchange membranes for high temperature polymer electrolyte membrane fuel cells. Long-term durability of the membrane is of critical concern and has been evaluated by accelerated degradation tests under Fenton conditions. In this study effects of phosphoric acid and ferrous ions were investigated by measurements of the weight loss, intrinsic viscosity and size exclusion chromatography (SEC) of the polymer membranes. Ferrous ions resulted in, as expected, catalytic formation of peroxide radicals and hence the accelerated polymer degradation in terms of weight loss and molecular weight decrease. The presence of phosphoric acid as an inevitable dopant of the membranes, on the other hand, significantly impeded the membrane degradation by means of metal ion complexing, decreased pH, and acid–base interactions with the amino groups of the polymer. Fuel cell durability tests with contaminations of ferrous ions did show considerable performance degradation, however, primarily due to the catalyst deterioration rather than the membrane degradation.
Platinum Activated IrO2/SnO2 Nanocatalysts and Their Electrode Structures for High Performance Proton Exchange Membrane Water Electrolysis

In order to improve proton exchange membrane water electrolysis performance, anode catalyst and catalyst layer were examined in this work. SnO2 supported IrO2 nanocatalyst and its analogue with platinum enhancement were firstly synthesized for the oxygen evolution reaction. The effect of the introduction of Pt on the properties of the composites was explored by X-ray diffraction (XRD) and electrochemical test. Interaction between the introduced Pt nanoparticles and the bulk IrO2/SnO2 was evidenced in XRD. Electrochemical characterization showed the enhanced activity for the Pt activated IrO2/SnO2, which was attributed to the cooperative effects of improved electric conductivity and synergistic effect of Pt and IrO2/SnO2. Furthermore, catalyst layers based on IrO2/SnO2 catalysts were optimized with respect to microstructures, pore volume and pore size distribution. The performance was obviously improved due to the appropriate porosity and pore size distribution. The highest electrolyser performance of 1.63 V at 2 A cm\(^{-2}\) was achieved at 80 °C for optimized catalyst layers containing platinum activated IrO2/SnO2 catalyst.

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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Xu, J., Li, Q., Christensen, E., Wang, X., Bjerrum, N. J.
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Publication information
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Volume: 8
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ISSN (Print): 1452-3981
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Web of Science (2013): Impact factor 1.956
ISI indexed (2013): ISI indexed yes
Web of Science (2013): Indexed yes
Original language: English
Keywords: Catalysts, Water Electrolysis, Oxygen evolution reactions, Xrays diffraction, Electrochemical analysis, Platinum
Research output: Contribution to journal › Journal article – Annual report year: 2013 › Research › peer-review

Synthesis of self-supported non-precious metal catalysts for oxygen reduction reaction with preserved nanostructures from the polyaniline nanofiber precursor

Non-precious metal catalysts (NPMCs) for the oxygen reduction reaction (ORR) are an active subject of recent research on proton exchange membrane fuel cells. In this study, we report a new approach to preparation of self-supported and nano-structured NPMCs using pre-prepared polyaniline (PANI) nanofibers as both nitrogen and carbon precursors. The synthesized NPMCs possess nanoworm structures preserved from the PANI precursor and exhibit high onset potential of 0.905 V vs. RHE and selective activity of nearly four-electron ORR pathways. A significant enhancement in the intrinsic activity and onset potential for the ORR is observed when the Fe content in the precursor is increased from 0 to 3.0 wt.% while further addition to 10.0 wt.% results in a decrease in the catalytic activity.

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Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, CAS - Changchun Institute of Applied Chemistry
Pages: 129-136
Publication date: 2013
Peer-reviewed: Yes
A Direct DME High Temperature PEM Fuel Cell

Dimethyl ether (DME) has been identified as an alternative to methanol for use in direct fuel cells. It combines the advantages of hydrogen in terms of pumpless fuel delivery and high energy density like methanol, but without the toxicity of the latter. The performance of a direct dimethyl ether fuel cell suffers greatly from the very low DME-water miscibility. To cope with the problem polybenzimidazole (PBI) based membrane electrode assemblies (MEAs) have been made and tested in a vapor fed system. PtRu on carbon has been used as anode catalyst and air at ambient pressure was used as oxidant. A power density of 79 mW/cm² has been achieved at 200 °C.
Anion conducting polymer membranes for hydrogen production through alkaline water electrolysis

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Aili, D., Li, Q., Christensen, E., Jensen, J. O., Bjerrum, N.
Pages: 78-78
Publication date: 2012

Antimony doped tin oxides and their composites with tin pyrophosphates as catalyst supports for oxygen evolution reaction in proton exchange membrane water electrolysis

Proton exchange membrane water electrolyser operating at typically 80 °C or at further elevated temperatures suffer from insufficient catalyst activity and durability. In this work, antimony doped tin oxide nanoparticles were synthesized and further doped with an inorganic proton conducting phase based on tin pyrophosphates as the catalyst support. The materials showed an overall conductivity of 0.57 S cm⁻¹ at 130 °C under the water vapor atmosphere with a contribution of the proton conduction. Using this composite support, iridium oxide nanoparticle catalysts were prepared and characterized in sulfuric and phosphoric acid electrolytes, showing much enhanced catalytic activity. Electrolyzer tests were conducted at both 80 °C with an Aquivion™ membrane and at 130 °C with a phosphoric acid doped Aquivion™ membrane. Significant improvement in the anodic kinetics was achieved on the composite supported catalysts at 130 °C although the electrolyzer cells showed higher ohmic resistance primarily from the membrane and catalyst layer. A durability test of electrolyzer cells was carried out at 130 °C under a current density of 400 mA cm⁻² in a period of up to 760 h, showing rather good stability of the system.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, University of Science and Technology of China
Pages: 18629-18640
Publication date: 2012
Peer-reviewed: Yes
Bifunctional Pt-Si Alloys for Small Organic Molecule Electro-oxidation

Designing highly active catalysts for electro-oxidation of small organic molecules can help to reduce the anodic overpotential for more efficient utilization of hydrocarbon fuels. The challenge in developing more active electrocatalysts for electro-oxidation reactions is to satisfy the stringent bifunctional requirement, which demands both adsorption and water oxidation sites. In this contribution, we explore the possibility of using Pt-Si alloys to fulfill this bifunctional requirement. Silicon, a highly oxophillic element, is alloyed into Pt as a site for water oxidation, while Pt serves as a CO adsorption site. We will discuss the enhanced activity of Pt-Si alloys for small organic molecule oxidation, which can be attributed to the improved CO electro-oxidation kinetics on Pt-Si.

Conductive Properties of Neodymium Phosphate composites Investigated by Electrochemical Impedance Spectra

Conductivity of NdPO₄-CsH₂PO₄ composites investigated by electrochemical impedance spectroscopy
Corrosion behavior of construction materials for intermediate temperature steam electrolysers

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Nikiforov, A., Petrushina, I., Jensen, J. O., Bjerrum, N.
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Corrosion Behavior of Construction Materials for Intermediate Temperature Steam Electrolysers

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Nikiforov, A., Petrushina, I., Jensen, J. O., Bjerrum, N.
Number of pages: 1
Publication date: 2012

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Title of host publication: ECS Meeting Abstracts
Publisher: The Electrochemical Society
Electronic versions:
Corrosion_behavior_of_construction_materials.pdf
URLs:
http://ma.ecsdl.org/site/archive/MA2012-02.xhtml
Source: dtu
Source-ID: u::5870
Research output: Chapter in Book/Report/Conference proceeding › Conference abstract in proceedings – Annual report year: 2012 › Research › peer-review

Development and study of tantalum and niobium carbides as catalyst supports for the oxygen evolution reaction (OER) for PEM water electrolysis at elevated temperatures

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Nikiforov, A., Petrushina, I., Prag, C. B., Polonsky, J., Christensen, E., Bjerrum, N.
Development of Refractory Ceramics for The Oxygen Evolution Reaction (OER) Electrocatalyst Support for Water Electrolysis at elevated temperatures

Commercial TaC and Si3N4 powders were tested as possible electrocatalyst support materials for the Oxygen Evolution Reaction (OER) for PEM water electrolysers, operating at elevated temperatures. TaC and Si3N4 were characterised by thermogravimetric and differential thermal analysis for their thermal stability. The Adams fusion method was implemented to deposit IrO2 on the support surfaces. A series of electrocatalysts was prepared with a composition of (IrO2)x(TaC/ Si3N4)1-x, where x represents the mass fraction of IrO2 and was equal to 0.1 (only for TaC), 0.3, 0.5, 0.7, 0.9 and 1. The thin-film method was used for electrochemical analysis of the prepared electrocatalysts. SEMEDX, BET and powder conductivity measurements were used as complementary techniques to complete characterisation of the electrocatalysts. Additionally, they were compared in their properties with previously reported data for a SiC-Si support. The stability of the electrocatalysts was assessed by estimation of reversibility of the anodic/cathodic processes. © The Electrochemical Society

Direct dimethyl ether fueling of a high temperature polymer fuel cell

Direct dimethyl ether (DME) fuel cells suffer from poor DME–water miscibility and so far peak powers of only 20–40 mW cm⁻² have been reported. Based on available literature on solubility of dimethyl ether (DME) in water at ambient pressure it was estimated that the maximum concentration of DME at 80 °C will be 300–600 times lower than the ratio 1 to 3 which is the stoichiometric ratio for full conversion to CO2. To overcome this dilution problem a high temperature polymer fuel cell was operated on DME–water vapor at ambient pressure and with air as oxidant. A peak power density of 67 mW cm⁻² was measured at 200 °C. A series of performance curves at temperatures ranging from 150 to 250 °C showed a pronounced temperature effect on the performance. Comparison was made between performances as direct DME and direct methanol cells and the difference was not as large as normally seen with conventional liquid fed cells below 100 °C.
Direct dimethyl ether high temperature polymer electrolyte membrane fuel cells

A high temperature polybenzimidazole (PBI) polymer fuel cell was fed with dimethyl ether (DME) and water vapour mixture on the anode at ambient pressure with air as oxidant. A peak power density of 79 mW/cm² was achieved at 200°C. A conventional polymer based direct DME fuel cell is liquid fed and suffers from low DME solubility in water. When the DME-water mixture is fed as vapour miscibility is no longer a problem. The increased temperature is more beneficial for the kinetics of the direct oxidation of DME than of methanol. The Open Circuit Voltage (OCV) with DME operation was 50 to 100 mV higher than that of methanol, indicating less fuel crossover.

Direct dimethyl ether high temperature polymer electrolyte membrane fuel cells with improved performance

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Vassiliev, A., Jensen, J. O., Li, Q., Bjerrum, N.
Number of pages: 1
Publication date: 2012
Peer-reviewed: No
Event: Poster session presented at Energieffektivisering for fremtiden, Kgs.Lyngby, Denmark.
Electronic versions:
Direct_dimethyl_ether.pdf
Source: dtu
Source-ID: u::6531
Research output: Contribution to conference › Poster – Annual report year: 2012 › Research
Efficient electrocatalytic oxygen reduction over selfsupported polyaniline-based non-precious metal catalyst

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, CAS - Changchun Institute of Applied Chemistry
Pages: 96-96
Publication date: 2012

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http://carisma2012.com
Research output: Chapter in Book/Report/Conference proceeding › Conference abstract in proceedings – Annual report year: 2012 › Research › peer-review

Energy Dispersive X-ray Analysis used to quantify the Phosphoric Acid Doping Level in Polybenzimidazole based Fuel Cells

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Danish Power Systems ApS
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http://carisma2012.com
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Fabrication and characterization of proton conducting composite materials for electrolytes in intermediate temperature fuel cells and water electrolysers

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry
Contributors: Jensen, A. H., Elsøe, K., Anfimova, T., Christensen, E., Barner, J. H. V., Bjerrum, N.
Pages: 75-75
Publication date: 2012

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Research output: Chapter in Book/Report/Conference proceeding › Conference abstract in proceedings – Annual report year: 2012 › Research › peer-review
Fabrication and Characterization of Proton Conducting Phosphate Electrolytes for Intermediate Temperature Fuel Cell Assembling

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry
Contributors: Jensen, A. H., Li, Q., Anfimova, T., Christensen, E., Barner, J. H. V., Bjerrum, N. J.
Number of pages: 1
Publication date: 2012
Peer-reviewed: Yes
Event: Abstract from Nordic Conference on Ceramic and Glass Technology, Roskilde, Denmark.
Electronic versions: Fabrication_and_Characterization.pdf

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Source-ID: u::7393
Research output: Contribution to conference » Conference abstract for conference – Annual report year: 2013 » Research peer-review

High Temperature Polymer Fuel Cells: From laboratory towards commercialization

General information
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Organisations: Department of Chemistry, Department of Energy Conversion and Storage, Proton conductors
Publication date: 2012
Peer-reviewed: No
Research output: Contribution to conference » Paper – Annual report year: 2012 » Research

Metal Phosphates as Intermediate Temperature Proton Conducting Electrolytes
A series of metal phosphates were synthesized and screened as potential proton conductor electrolytes for fuel cells and electrolysers operational at intermediate temperatures. Among the selected, niobium and bismuth phosphates exhibited a proton conductivity of $10^{-2}$ and $10^{-7}$ S cm$^{-1}$, respectively, under anhydrous atmosphere at 250 °C, showing close correlation with the presence of hydroxyl groups in the phosphate phases. At the water partial pressure of above 0.6 atm, both phosphates possessed a proton conductivity to a level of above $3 \times 10^{-2}$ S cm$^{-1}$. Reasonable stability of the proton conductivity was observed under either a constant low water partial pressure or under a humidity cycling test within a period of more than 80 hours.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Huang, Y., Li, Q., Pan, C., Anfimova, T., Jensen, J. O., Bjerrum, N.
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Journal: E C S Transactions
Volume: 45
Issue number: 1
ISSN (Print): 1938-5862
Ratings:
BFI (2012): BFI-level 1
Scopus rating (2012): CiteScore 0.29 SJR 0.241 SNIP 0.26
ISI indexed (2012): ISI indexed no
Original language: English
DOIs:
Nickel and its alloys as perspective materials for intermediate temperature steam electrolysers operating on proton conducting solid acids as electrolyte

Several stainless steels, nickel-based alloys, Ta-coated stainless steel, niobium, nickel, platinum and gold were evaluated as possible materials for use in the intermediate temperature water electrolysers. The corrosion resistance was measured in molten KH2PO4 as simulated conditions corresponding to protonconducting solid acids or transition metal phosphates as electrolytes. It was shown that Au is subject to corrosion in molten KH2PO4 during polarisation. However, Ni and Ta-coated stainless steel (AISI 316L) demonstrated high corrosion stability and can be recommended as a construction material for bipolar plates and cell housing. It was shown, that nickel, high-nickel alloys and austenitic stainless steels containing small amounts of Ti have high corrosion resistance in this media. © The Electrochemical Society.

Niobium phosphates as an intermediate temperature proton conducting electrolyte for fuel cells

A new proton conductor based on niobium phosphates was synthesized using niobium pentoxide and phosphoric acid as precursors. The existence of hydroxy groups in the phosphates was confirmed and found to be preserved after heat treatment at 500 °C or higher, contributing to an anhydrous proton conductivity of 1.6 × 10−2 S cm−1 at 250 °C. The conductivity increased with water content in the atmosphere and reached 5.8 × 10−2 S cm−1 under pure water vapour at the same temperature. The conductivity showed good stability in the low water partial pressure range of up to 0.05 atm. The metal phosphates are of high interest as potential proton conducting electrolytes for fuel cells operational in an intermediate temperature range.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, CAS - Changchun Institute of Applied Chemistry
Contributors: Huang, Y., Li, Q., Jensen, A. H., Yin, M., Jensen, J. O., Christensen, E., Pan, C., Bjerrum, N., Xing, W.
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Publication date: 2012
Peer-reviewed: Yes

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Journal: Journal of Materials Chemistry
Volume: 22
Issue number: 42
ISSN (Print): 0959-9428
Ratings:
Niobium Phosphates as Intermediate Temperature Proton Conductor

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Huang, Y., Li, Q., Pan, C., Jensen, J. O., Christensen, E., Cleemann, L. N., Jensen, A. H., Anfimova, T., Bjerrum, N.
Pages: 77-77
Publication date: 2012

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Electronic versions:
URLs:
http://carisma2012.com
Research output: Chapter in Book/Report/Conference proceeding – Annual report year: 2012

Novel Ceramic Materials for Polymer Electrolyte Membrane Water Electrolysers’ Anodes
Tantalum carbide was evaluated as a possible new support for the IrO2 for use in anodes of polymer electrolyte membrane water electrolysers. A series of supported electrocatalysts varying in mass content of iridium oxide was prepared. XRD, powder conductivity measurements and cyclic and linear sweep voltammetry were used to characterise the electrocatalysts. The most performing composition was found to lie between 50 and 90 wt.% IrO2 on TaC

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Institute of Chemical Technology in Prague
Contributors: Polonsky, J., Bouzek, K., Prag, C. B., Nikiforov, A., Petrushina, I., Christensen, E., Bjerrum, N.
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Publication date: 2012

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Publisher: Prague Institute of Chemical Technology
Editors: Krysa, J., Kluson, P.
Source: dtu
Source-ID: u::5939
Research output: Chapter in Book/Report/Conference proceeding – Annual report year: 2012
PEM steam electrolysis at 130 °C using a phosphoric acid doped short side chain PFSA membrane
Steam electrolysis test with a phosphoric acid doped Aquivion™ membrane was successfully conducted and current densities up to 775 mA cm⁻² at 1.8 V was reached at 130 °C and ambient pressure. A new composite membrane system using a perfluorosulfonic acid membrane (Aquivion™) as matrix and phosphoric acid as proton conducting electrolyte was developed. Traditional perfluorosulfonic acid membranes do not possess sufficient dimensional stability and proton conductivity to be used at elevated temperatures and ambient pressures. The elevated temperature, high potentials and acidic conditions implied that a new and highly corrosion resistant construction material was needed. Tantalum coated stainless steel felt was tested and found suitable as the anode gas diffusion layer.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Department of Energy Conversion and Storage, Proton conductors, Tantaline A/S
Pages: 10992-11000
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Publication information
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ISSN (Print): 0360-3199
Ratings:
BFI (2012): BFI-level 2
Scopus rating (2012): CiteScore 3.96 SJR 1.499 SNIP 1.708
Web of Science (2012): Impact factor 3.548
ISI indexed (2012): ISI indexed yes
Web of Science (2012): Indexed yes
Original language: English
Keywords: Water electrolysis, High temperature, Tantalum coating, Proton exchange membrane, PEMEC
DOI: 10.1016/j.ijhydene.2012.04.125
Source: dtu
Source-ID: u::4325
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Poly(aryl sulfone benzimidazole) and its copolymers as high temperature membrane electrolyte foe fuel cells

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Yang, J., Li, Q., Cleemann, L. N., Jensen, J. O., Pan, C., Bjerrum, N., He, R.
Publication date: 2012
Peer-reviewed: No

Bibliographical note
Oral presentation
Research output: Contribution to conference › Paper – Annual report year: 2012 › Research

Poly(benzimidazole)–functionalized graphene as a stable and durable support for PEM fuel cell electrocatalysts

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Permyakova, A. A., Jensen, J. O., Li, Q., Bjerrum, N.
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Poly(benzimidazole)-functionalized graphene supported Pt electrocatalyst and its application in high temperature PEM fuel cells

General information
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Contributors: Permyakova, A. A., Jensen, J. O., Li, Q., Bjerrum, N.
Number of pages: 1
Publication date: 2012

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Title of host publication: Abstract book - Pacific Rim Meeting on Electrochemical and Solid-State Science: 222nd Meeting of ECS — The Electrochemical Society and 2012 Fall Meeting of The Electrochemical Society of Japan
Article number: Abstract #1424
Electronic versions: Permyakova_1424.pdf
Source: PublicationPreSubmission
Source-ID: 97476862
Research output: Chapter in Book/Report/Conference proceeding › Conference abstract in proceedings – Annual report year: 2012 › Research › peer-review

Polybenzimidazoles – Synthesis, characterizations and applications in the form of membranes

General information
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Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Li, Q., Aili, D., Rudbeck, H. C., Yang, J., Jensen, J. O., Bjerrum, N.
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Publication date: 2012

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Publisher: Nova Science Publishers
Editor: Wythers, M. C.
(Advances in Materials Science Research, Vol. 14).
Research output: Chapter in Book/Report/Conference proceeding › Book chapter – Annual report year: 2012 › Research › peer-review

Proton Conductive Niobium Phosphates as Electrolytes for Fuel Cells Operating with Renewable Biofuels

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Huang, Y., Li, Q., Anfimova, T., Jensen, A. H., Jensen, J. O., Christensen, E., Bjerrum, N.
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Peer-reviewed: Yes
Research output: Contribution to conference › Paper – Annual report year: 2012 › Research › peer-review

Proton Conductivity of Refractory Metal Phosphates at Intermediate Temperatures

General information
Synthesis and properties of poly(aryl sulfone benzimidazole) and its copolymers for high temperature membrane electrolytes for fuel cells

Poly(aryl sulfone benzimidazole) (SO2PBI) and its copolymers with poly[2,2′-p-(phenylene)-5,5′-bibenzimidazole] (pPBI), termed as Co-SO2PBI, were synthesized with varied feeding ratios of 4,4′-sulfonyldibenzoic acid (SDBA) to terephthalic acid (TPA). Incorporation of the stiff para-phenylene and flexible aryl sulfone linkages in the macromolecular structures resulted in high molecular weight copolymers with good solubility. The chemical stability towards radical oxidation was improved for SO2PBI and its copolymer membranes due to the electron-withdrawing sulfone functional groups. Upon acid doping, the membrane swelling was reduced and the mechanical strength was improved, as compared with their meta structured analogues. At an acid doping level of 11 mol H3PO4 per average molar repeat unit, the Co-20%SO2PBI membrane exhibited a tensile strength of 16 MPa at room temperature and an H2-air fuel cell peak power density of 346 mW cm−2 at 180 °C at ambient pressure. Durability tests with the membrane under a constant current density of 300 mA cm−2 at 160 °C showed a degradation rate of 6.4 μV h−1 during a period of 2400 h, which was significantly lower than that for meta PBI membranes with a similar acid doping level.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Energy and Materials, Functional organic materials, Department of Chemistry, Newcastle University, Northeastern University
Contributors: Yang, J., Li, Q., Cleemann, L. N., Xu, C., Jensen, J. O., Pan, C., Bjerrum, N., He, R.
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Publication date: 2012
Peer-reviewed: Yes

Publication information
Tantalum carbide as a novel support material for anode electrocatalysts in polymer electrolyte membrane water electrolysers

Iridium oxide (IrO₂) currently represents a state of the art electrocatalyst for anodic oxygen evolution. Since iridium is both expensive and scarce, the future practical application of this process makes it essential to reduce IrO₂ loading on the anodes of PEM water electrolysers. In the present study an approach to utilising a suitable electrocatalyst support was followed. Of the materials selected from a literature review, TaC has proved to be stable under the conditions of the accelerated stability test proposed in this study. The test involved dispersing each potential support material in a mixture of trifluoromethanesulfonic acid (TFMSA) and hydrogen peroxide at 130 °C. The liquid phase was subsequently analysed using ICP-MS with respect to the occurrence of ions potentially originating from the support material tested. The TaC support selected was additionally characterised by thermogravimetric and differential thermal analysis to prove its thermal stability. A modified version of the Adams fusion method was used to deposit IrO₂ on the support surface. A series of electrocatalysts was prepared with a composition of (IrO₂)x(TaC)1−x, where x represents the mass fraction of IrO₂ and was equal to 0.1, 0.3, 0.5, 0.7, 0.9 and 1. The thin-film method was used for electrochemical characterisation of the electrocatalysts prepared. SEM–EDX analysis, X-ray diffraction, N₂ adsorption (BET) and powder conductivity measurements were used as complementary techniques to complete characterisation of the electrocatalysts prepared. The electrocatalysts with x ≥ 0.5 showed stable specific activity. This result is consistent with the conductivity measurements.
Thermal curing of PBI membranes for high temperature PEM fuel cells

Phosphoric acid doped polybenzimidazole (PBI) has emerged as one of the most promising electrolyte materials for proton exchange membrane (PEM) fuel cells operating under anhydrous conditions at temperatures of up to 200 °C. The limited long-term durability of the membrane electrode assemblies (MEAs) is currently hampering the commercial viability of the technology. In the present study, thermoset PBI membranes were prepared by curing the membranes under inert atmosphere at temperatures of up to 350 °C prior to the acid doping. The systematic membrane characterizations with respect to solubility, phosphoric acid doping, radical-oxidative resistance and mechanical strength indicated that the PBI membranes were irreversibly cured by the thermal treatment. After curing, the PBI membranes demonstrated features that are fundamental characteristics of a thermoset resin including complete insolubility, high resistance to swelling and improved mechanical toughness. Additionally, the thermal treatment was found to increase the degree of crystallinity of the membranes. The improved physicochemical characteristics of the membranes after curing were further illustrated by a dramatically improved long-term durability of the corresponding fuel cell MEAs. During continuous operation for 1800 h at 160 °C and 600 mA cm⁻², the average cell voltage decay rate of the MEA based on the cured membrane was 43 μV h⁻¹. This should be compared with an average cell voltage decay rate of 308 μV h⁻¹ which was recorded for the MEA based on its non-cured counterpart.

General information
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Organisations: Department of Chemistry, Energy and Materials, Department of Chemistry
Contributors: Aili, D., Cleemann, L. N., Li, Q., Jensen, J. O., Christensen, E., Bjerrum, N. J.
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Source-ID: n:oai:DTIC-ART:rsc/320979018::15406
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Transition metal carbides as electrode materials for HT PEM systems

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors
Contributors: Tomás García, A. L., Li, Q., Bjerrum, N. J.
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Publication date: 2012

Host publication information
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Electronic versions:
Tungsten carbide promoted Pd and Pd-Co electrocatalysts for formic acid electrooxidation

Tungsten carbide (WC) promoted palladium (Pd) and palladium–cobalt (Pd–Co) nanocatalysts are prepared and characterized for formic acid electrooxidation. The WC as the dopant to carbon supports is found to enhance the CO tolerance and promote the activity of the Pd-based catalysts for formic acid oxidation. Alloying of Pd with Co further improves the electrocatalytic activity and stability of the WC supported catalysts, attributable to a synergistic effect of the carbide support and PdCo alloy nanoparticles.

Water Electrolysis using Polymeric Electrolyte Membranes at Elevated Temperatures
WC as a non-platinum hydrogen evolution electrocatalyst for high temperature PEM water electrolysis

Tungsten carbide (WC) nanopowder was tested as a non-platinum cathode electrocatalyst for polymer electrolyte membrane (PEM) water electrolyzers, operating at elevated temperatures. It was prepared in thermal plasma reactor with confined plasma jet from WO3 precursor in combination with CH4 carburizing agent. The results of the investigation showed that the activity of tungsten carbide as cathode electrocatalyst increases significantly with temperature and this effect is more pronounced than for platinum, especially, at 150 °C.

Corrosion behaviour of construction materials for high temperature steam electrolysers

Different types of commercially available stainless steels, Ni-based alloys as well as titanium and tantalum were evaluated as possible metallic bipolar plates and construction materials. The corrosion resistance was measured under simulated conditions corresponding to the conditions in high temperature proton exchange membrane (PEM) steam electrolysers. Steady-state voltammetry was used in combination with scanning electron microscopy and energy-dispersive X-ray spectroscopy to evaluate the stability of the mentioned materials. It was found that stainless steels were the least resistant to corrosion under strong anodic polarisation. Among alloys, Ni-based showed the highest corrosion resistance in the simulated PEM electrolyser medium. In particular, Inconel 625 was the most promising among the tested corrosion-resistant alloys for the anodic compartment in high temperature steam electrolysis. Tantalum showed outstanding resistance to corrosion in selected media. On the contrary, passivation of titanium was weak, and the highest rate of corrosion among all tested materials was observed for titanium at 120 degrees C.
Crosslinking of polybenzimidazole membranes by divinylsulfone post-treatment for high-temperature proton exchange membrane fuel cell applications

Phosphoric acid-doped polybenzimidazole (PBI) has been suggested as a promising electrolyte for proton exchange membrane fuel cells operating at temperatures up to 200 °C. This paper describes the development of a crosslinking procedure for PBI membranes by post-treatment with divinylsulfone. The crosslinking chemistry was studied and optimized on a low-molecular weight model system and the results were used to optimize the crosslinking conditions of PBI membranes. The crosslinked membranes were characterized with respect to chemical and physiochemical properties, showing improved mechanical strength and oxidative stability compared with their linear analogues. Fuel cell tests were further conducted in order to demonstrate the feasibility of the crosslinked membranes.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Aili, D., Li, Q., Christensen, E., Jensen, J. O., Bjerrum, N.
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Web of Science (2011): Impact factor 1.902
ISI indexed (2011): ISI indexed yes
Web of Science (2011): Indexed yes
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DOIs:
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Source-ID: 314187
Research output: Contribution to journal › Journal article – Annual report year: 2010 › Research › peer-review
High temperature proton exchange membranes based on polybenzimidazole and clay composites for fuel cells

dispersion of modified laponite clay was achieved in polybenzimidazole (PBI) solutions which, when cast and allowed to dry, resulted in homogeneous and transparent composite membranes containing up to 20 wt% clay in the polymer. The clay was organically modified using a series of ammonium and pyridinium salts with varying polarity and hydrogen-bonding capacity. Clay modification by ion-exchange reactions involving replacement of interlayer inorganic cations was confirmed using X-ray photoelectron and infrared spectroscopy techniques. The cast PBI membranes were characterized by their water uptake, acid doping and swelling, tensile strength, conductivity and hydrogen permeability as well as by fuel cell tests. For the composite membranes, high acid doping levels were achieved with sufficient mechanical strength and improved dimensional stability or reduced membrane swelling. At an acid doping level of 12 mol H3PO4 per monomer unit, proton conductivity as high as 0.12 S cm−1 was obtained at 150 °C and 12% relative humidity. The composite membranes exhibited hydrogen permeability ranging from 0.6 to 1.2 × 10−10 mol cm−1 s−1 bar−1 from 100 to 200 °C, which was five times lower than that of acid-doped pristine PBI membranes. In accordance with the hydrogen permeability measurements, fuel cell tests exhibited high open circuit voltages (i.e., 1.02 V) at room temperature as well as high I–V
performance compared with normal PBI membranes.

Method of operating a direct dme fuel cell system
The present invention relates to a method of operating a fuel cell system comprising one or more fuel cells with a proton exchange membrane, wherein the membrane is composed of a polymeric material comprising acid-doped polybenzimidazole (PBI). The method comprises adjusting the operating temperature of the fuel cell to between 120 and 250 degrees C, supplying an oxidant stream to the cathode, and supplying a humidified fuel stream to the anode, said fuel stream comprising dimethyl ether, wherein dimethyl ether is directly oxidised at the anode.

Oxidative degradation of polybenzimidazole membranes as electrolytes for high temperature proton exchange membrane fuel cells
Polybenzimidazole membranes imbibed with acid are emerging as a suitable electrolyte material for high-temperature polymer electrolyte fuel cells. The oxidative stability of polybenzimidazole has been identified as an important issue for the long-term durability of such cells. In this paper the oxidative degradation of the polymer membrane was studied under the Fenton test conditions by the weight loss, intrinsic viscosity, size exclusion chromatography, scanning electron microscopy and Fourier transform infrared spectroscopy. During the Fenton test, significant weight losses depending on the initial molecular weight of the polymer were observed. At the same time, viscosity and SEC measurements revealed a steady decrease in molecular weight. The degradation of acid doped PBI membranes under Fenton test conditions is proposed to
start by the attack of hydroxyl radicals at the carbon atom linking imidazole ring and benzenoid ring, which may eventually lead to the imidazole ring opening and formation of small molecules and terminal groups for further oxidation by an endpoint oxidation. Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Preparation and study of IrO2/SiC–Si supported anode catalyst for high temperature PEM steam electrolysers

A novel catalyst material for oxygen evolution electrodes was prepared and characterised by different techniques. IrO2 supported on a SiC–Si composite was synthesised by the Adams fusion method. XRD and nitrogen adsorption experiments showed an influence of the support on the surface properties of the IrO2 particles, affecting the IrO2 particle size. The prepared catalysts were electrochemically characterised by cyclic voltammetry experiments at 25, 80, 120 and 150 °C. In accordance with the observed variation in particle size, a support loading of up to 20% improved the activity of the catalyst. Powder conductivity measurements were also performed, which showed the influence of the support particles in the packing of IrO2 particles, perhaps favouring the formation of channels and pores between particles, thus increasing the catalyst utilisation.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Nikiforov, A., Tomás García, A. L., Petrushina, I., Christensen, E., Bjerrum, N.
Pages: 5797-5805
Publication date: 2011
Peer-reviewed: Yes
SiC-Si as a support material for oxygen evolution electrode in PEM steam electrolysers

The need of higher energy efficiency in hydrogen production has promoted the research on improved catalysts for water electrolysis. In this work, a novel supported catalyst for oxygen evolution electrodes was prepared and characterized with different techniques. IrO$_2$ supported on a SiC/Si composite was synthesized following the Adams fusion method. The obtained powder was characterized with different techniques. XRD and Nitrogen adsorption experiments showed the influence of the support particles in the surface properties of the IrO$_2$ particles, mainly affecting the IrO$_2$ particle size. The prepared catalysts were electrochemically characterized by cyclic voltammetry experiments at 25, 80, 120 and 150°C. The results indicate an improvement in catalyst activity with the addition of the support. This was attributed to the mentioned variation in particle size and a different packing of catalyst particles, which could favor the formation of channels and pores between particles, thus increasing the catalyst utilization. Electric conductivity tests were performed on the powder samples, showing a very low conductivity of the support compared to the active phase. The conductivity of the supported catalysts seems to depend strongly on the density of contacts between IrO$_2$ particles, with the support particles disrupting the conduction paths through the powders.

1.7 nm Platinum Nanoparticles: Synthesis with Glucose Starch, Characterization and Catalysis

Monodisperse platinum nanoparticles (PtNPs) were synthesized by a green recipe. Glucose serves as a reducing agent and starch as a stabilization agent to protect the freshly formed PtNP cores in buffered aqueous solutions. Among the ten buffers studied, 2-(N-morpholino)ethanesulfonic acid (MES), ammonium acetate and phosphate are the best media for PtNP size control and fast chemical preparation. The uniform sizes of the metal cores were determined by transmission electron microscopy (TEM) and found to be 1.8 +/- 0.5, 1.7 +/- 0.2 and 1.6 +/- 0.5 nm in phosphate, MES and ammonium acetate buffer, respectively. The estimated total diameter of the core with a starch coating layer is 5.8-6.0 nm, based on thermogravimetric analysis (TGA). The synthesis reaction is simple, environmentally friendly, highly reproducible, and easy to scale up. The PtNPs were characterized electrochemically and show high catalytic activity for reduction of dioxygen and hydrogen peroxide as well as for oxidation of dihydrogen. The PtNPs can be transferred to carbon support materials with little demand for high specific surface area of carbon. This enables utilization of graphitized carbon blacks to prepare well-dispersed Pt/C catalysts, which exhibit significantly improved durability in the accelerated aging test under fuel cell mimicking conditions.
A direct DME fuel cell based on acid doped PBI

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Ingemann Olsen, M., Li, Q., Vassiliev, A., Pan, C., Steenberg, T., Bjerrum, N.
Publication date: 2010
Peer-reviewed: Yes
Event: Abstract from Progress MEA 2010, La Grande Motte, France.
Source: orbit
Source-ID: 270209
Research output: Contribution to journal → Journal article – Annual report year: 2010 → Research → peer-review

A Medical Delivery Device
The present invention relates to a medical delivery device comprising at least two membrane electrode assembly units each of which comprises three layers: an upper and a lower electrode and a selective ionic conductive membrane provided there-between. At least one of the three layers are shared by the two MEA units which are individually controllable.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Novo Nordisk AS
Contributors: Nielsen, O. C., Jensen, J. O., Nielsson, M. S., Bjerrum, N., Hennesø, E.
Publication date: 2010

Publication information
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Development and Characterizations of High Performance MEAs For High Temperature PBI Fuel Cells

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Organisations: Department of Chemistry
Publication date: 2010
Peer-reviewed: Yes
Event: Abstract from Progress MEA 2010, La Grande Motte, France.
Source: orbit
Durability Issues and Status of High Temperature Proton Exchange Membrane Fuel Cells Based on Acid Doped Polybenzimidazole Membranes

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Li, Q., Jensen, J. O., Pan, C., Liao, J., Rudbeck, H. C., Cleemann, L. N., Bjerrum, N.
Publication date: 2010

Event information
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Location: Vancouver, Canada
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Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2010 › Research

High Temperature PEMFC and Its Integration with Fuel Processors - An Approach to Portable Fuel Cells

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Li, Q., Jensen, J. O., Bjerrum, N.
Publication date: 2010

Event information
Event: International Symposium on Portable Fuel Cells
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Source: orbit
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Introduktion til højtemperatur PEM brændselsceller

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
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Source: orbit
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Nafion®-Polybenzimidazole-Zirconium Phosphate composite membranes for steam electrolysis applications

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Aili, D., Hansen, M. K., Li, Q., Bjerrum, N.
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Peer-reviewed: Yes
Source: orbit
Source-ID: 271821
Research output: Contribution to conference › Poster – Annual report year: 2010 › Research › peer-review
Ongoing Efforts Addressing Degradation of High Temperature PEMFC

**General information**
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Organisations: Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
Publication date: 2010

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PEM fuel cells, Towards higher working temperature

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Contributors: Jensen, J. O., Li, Q., Bjerrum, N.
Publication date: 2010

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Polymer Degradation and Catalyst Sintering in High Temperature PEMFC Based on Acid Doped Polybenzimidazole Membranes

**General information**
Publication status: Published
Organisations: Department of Chemistry, University of Stuttgart
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Event: Abstract from Progress MEA 2010, La Grande Motte, France.
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Research output: Contribution to conference › Conference abstract for conference – Annual report year: 2010 › Research › peer-review

Possibilities of High Temperature PEMFC as Compared with Conventional PEMFC

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
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**Event information**
Event: “Proton conducting materials at high temperature and their applications” HyFC Academy Workshop
Location: Department of Chemistry, Technical University of Denmark
Source: orbit
Source-ID: 272176
Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2010 › Research
Properties, degradation and high temperature fuel cell test of different types of PBI and PBI blend membranes

Polybenzimidazoles (PBIs) with synthetically modified structures and their blends with a partially fluorinated sulfonated aromatic polyether have been prepared and characterized for high temperature proton exchange membrane fuel cells. Significant improvement in the polymer chemical stability in terms of the oxidative weight loss, molecular weight decrease and onset temperatures for the thermal SO2 and CO splitting-off was achieved with the electron-deficient polybenzimidazoles containing -S(O)(2)- and -C(CF3)(2)- bridging groups. Ionical cross-linking in the form of acid-base blends was found to further improve the polymer stability and assist maintaining the membrane integrity. Upon acid doping the membrane swelling was reduced for the modified PBI and their blend membranes, which, in turn, results in enhancement of the mechanical strength, proton conductivity and high temperature fuel cell performance. (C) 2009 Elsevier B.V. All rights reserved.

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Organisations: Energy and Materials, Department of Chemistry, University of Stuttgart
Contributors: Li, Q., Rudbeck, H. C., Chromik, A., Jensen, J. O., Pan, C., Steenberg, T., Calverley, M., Bjerrum, N., Kerres, J.
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10.1016/j.memsci.2009.10.032
Source: orbit
Source-ID: 257576
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Properties, Degradation and High Temperature Fuel Cell Test of Different Types of PBI and PBI Blend Membranes

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, University of Stuttgart
Contributors: Kerres, J. A., Li, Q., Rudbeck, H. C., Chromik, A., Jensen, J. O., Pan, C., Steenberg, T., Calverley, M., Bjerrum, N.
Publication date: 2010
Peer-reviewed: Yes
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Source-ID: 272812
Research output: Contribution to conference › Conference abstract for conference – Annual report year: 2010 › Research › peer-review

Recent advances with high temperature PEMFC in Denmark

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Organisations: Department of Chemistry, Danish Power Systems ApS
Contributors: Jensen, J. O., Li, Q., Pan, C., Rudbeck, H. C., Steenberg, T., Bjerrum, N.
Publication date: 2010

Event information
Event: the 8h International Symposium on New Materials for Electrochemical Systems
Silicon carbide-silicon as a support material for oxygen evolution reaction in PEM steam electrolyser

There is a demand to develop a corrosion resistant and conductive substrate for the anode electrocatalyst, which can assist in the reducing of noble catalyst loading without a significant loss of performance. It was shown that SiC can act as a support material for platinum electrocatalyst in fuel cells. In the present work a commercial SiC-Si, produced by the Acheson process, with a fraction of free silicon around 20% wt. was investigated as a catalyst support for anode electrocatalyst in PEM steam electrolyser. This electrocatalyst system was characterized using several techniques such as XRD, cyclic voltammetry, SEM, EDX and steady state electrochemical polarisation in a working PEM steam electrolyser. Several SiC-Si-IrO2 electrodes have been prepared and tested. The iridium oxide content at the electrode active layer varied from x=0.2 to x=1, corresponding to the general formula (1-x)(SiC-Si)-x(IrO2). Compositions in this range were tested with the step difference in x=0.1. A diameter of about 5-6 nm of individual IrO2 crystallites was measured by X-ray diffraction and calculated from the Scherrer equation. The particle size distribution of SiC-Si was measured by the X-Ray sedimentation technique and the average particle diameter of silicon carbide-silicon was found to be in the range of 5-10 µm, while its specific surface area was about 5 sq.m/g. The oxygen evolution reaction was studied by the cyclic voltammetry technique in 85% phosphoric acid solution at temperatures between 22 and 150 degrees C in a conventional three-electrode cell. Fig. 1 shows cyclic voltammograms, recorded with the prepared supported and unsupported iridium oxide on tantalum electrodes. There was an evident increase in associated voltammetric capacitance value corresponding to the supported catalyst compared to the pure oxide catalyst material. This indicates a relatively higher number of active sites deduced from the charge transferred when cycling the potential between two preselected values. Based on the above results, the SiC-Si compound is a potential candidate as a support for the anode electrocatalyst for phosphoric acid doped membrane steam electrolyser.

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Organisations: Energy and Materials, Department of Chemistry
Contributors: Nikiforov, A., Petrushina, I., Christensen, E., Tomás García, A. L., Bjerrum, N.
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Abstract
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Research output: Contribution to conference › Poster – Annual report year: 2010 › Research

Strategic surface topographies for enhanced lubrication in sheet forming of stainless steel

Strategic stainless steel surfaces have been developed for which the tribological properties are significantly improved for sheet-metal forming compared with the as-received surfaces. The improvements have been achieved by modification of the surface to promote Micro-Plasto Hydrodynamic Lubrication (MPHL) by increasing the ratio of closed lubricant pockets and modifying the pocket geometry. These factors influence the retention and subsequent escape of lubricant during forming thus enhancing lubricant permeability to the contact between flattened workpiece asperities and contacting tool. The technique, which has been developed, is based on an electrochemical treatment changing the topography of the stainless steel surface. Comparative testing of the new surface topographies in ironing and deep drawing of stainless steel sheet shows significant improvements and possibilities of replacing chlorinated paraffin oils with environmentally friendly plain mineral oil.

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Manufacturing Engineering, Energy and Materials, Manufacturing Engineering, Department of Mechanical Engineering
Pages: 68-79
Publication date: 2010
Peer-reviewed: Yes

Publication information
Journal: International Journal of Surface Science and Engineering
Volume: 4
Issue number: 1
The energy efficiency of onboard hydrogen storage

Global warming resulting from the use of fossil fuels is threatening the environment and energy efficiency is one of the most important ways to reduce this threat. Industry, transport and buildings are all high energy-using sectors in the world and even in the most technologically optimistic perspectives energy use is projected to increase in the next 50 years. How and when energy is used determines society’s ability to create long-term sustainable energy systems. This is why this book, focusing on energy efficiency in these sectors and from different perspectives, is sharp and also important for keeping a well-founded discussion on the subject.

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Organisations: Energy and Materials, Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Bjerrum, N.
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Publication date: 2010

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URLs:
http://www.intechopen.com/books/show/title/energy-efficiency

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The Energy Efficiency of Onboard Hydrogen Storage

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Organisations: Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Bjerrum, N.
Publication date: 2010

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Location: Uppsala, Sweden
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CHEMISTRY, ELECTROCHEMISTRY, AND ELECTROCHEMICAL APPLICATIONS: Aluminum
Corrosion behavior of highly austenitic stainless steels and Ni-based alloys at elevated temperatures in concentrated phosphoric acid solutions

Degradation of high temperature PEM fuel cells

Durability Issues of High Temperature Proton Exchange Membrane Fuel Cells Based on Acid Doped Polybenzimidazole Membranes

To achieve high temperature operation of proton exchange membrane fuel cells (PEMFC), preferably under ambient pressure, phosphoric acid doped polybenzimidazole (PBI) membrane represents an effective approach, which in recent years has motivated extensive research activities with great progress. As a critical concern, issues of long term durability of PBI based fuel cells are addressed in this talk, including oxidative degradation of the polymer, mechanical failures of the membrane, acid leaching out, corrosion of carbon support and sintering of catalysts particles. Excellent polymer durability has observed under continuous operation with hydrogen and air at 150-160°C, with a fuel cell performance degradation rate of 5-10 µV/h. Improvement of the membrane performance such as mechanical strength, swelling and oxidative stability has achieved by exploring the polymer chemistry, i.e. covalently or ionically cross-linking and structure
moderation With load, thermal or startup-shutdown cycling, the performance loss was found to be much bigger, about 300 µV per cycle or 40 µV per operating hour, due to the increased acid loss and catalyst support corrosion, particularly under open circuit voltage operation. Further efforts are outlined to the future work.

**General information**
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Organisations: Energy and Materials, Department of Chemistry
Contributors: Li, Q., Jensen, J. O., Pan, C., Bjerrum, N.
Publication date: 2009

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Location: Beijing, China
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Source-ID: 257734
Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2009 › Research

**Durable Catalysts for High Temperature Proton Exchange Membrane Fuel Cells**
Durability of proton exchange membrane fuel cells (PEMFCs) is recognized as one of the most important issues to be addressed before the commercialization. The failure mechanisms are not well understood, however, degradation of carbon supported noble metal catalysts is identified as a major failure mode of PEMFCs. Under idle, load-cycling or start-up/shutdown modes of operation, which are prerequisite for automobile applications, the cathode will experience significantly higher potentials and therefore suffer from serious carbon corrosion, especially at the presence of platinum. The carbon corrosion, in turn, triggers the agglomeration of platinum particles resulting in reduction of the active surface area and catalytic activity. This is a major mechanism of the catalyst degradation and a key challenge to the PEMFC long-term durability. High temperature PEMFC, on the other hand, has attached significant attention in recent years because of its potential advantages such as high CO tolerance, easy cooling, better heat utilization and possible integration with fuel processing units. However, the high temperature obviously aggravates the carbon corrosion and catalyst degradation. Based on thermally treated carbon black and structurally designed carbon nanotubes (CNTs) as support, highly dispersed and adhered platinum nanoparticles were prepared in this work. Surface functionalization and activation of the support materials were found to be able to boost the catalyst activity and improve the selectivity for platinum loading. Fuel cell durability tests in term of performance degradation were performed with acid doped polybenzimidazole membrane fuel cells at temperatures of up to 160°C. The tests were focused on catalyst degradation by means of a potential cycling protocol. The electrochemical active area of the electrode, hydrogen permeability of the membrane and the area specific resistance of the cell were also measured during the tests. Compared with active carbon black supported catalysts, significant improvement in the catalyst durability was achieved.

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Li, Q., Buazar, F., Cleemann, L. N., Pan, C., Jensen, J. O., Steenberg, T., Christensen, E., Bjerrum, N.
Publication date: 2009

**Event information**
Event: International Symposium on Electrochemistry for Energy Conversion and Storage
Location: The Three Gorges, Wuhan, China
Source: orbit
Source-ID: 257736
Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2009 › Research

**Electrochemical promotion in the CO,H2 /(Pt/Ru)/PBI(H3PO4)/Pt/H2 membrane fuel cell system at 150°C**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, Energy and Materials, Technical University of Denmark
Contributors: Petrushina, I., Cleemann, L. N., Li, Q., Bjerrum, N.
Pages: 67-70
Publication date: 2009

**Host publication information**
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Place of publication: France
Source: orbit
Electrochemical Behavior of Molten Imidazole with Strong Acids

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Bandur, V., Li, Q., Bjerrum, N.
Pages: Abstract 3071
Publication date: 2009

Host publication information
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Publisher: The Electrochemical Society
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Green Platinum Nanoparticles: Synthesis, Characterization and Function

General information
Publication status: Published
Organisations: Department of Chemistry, NanoChemistry, Department of Energy Conversion and Storage, Proton conductors, Technical University of Denmark
Contributors: Engelbrekt, C., Sørensen, K. H., Lübcke, T., Zhang, J., Li, Q., Pan, C., Bjerrum, N., Ulstrup, J.
Publication date: 2009
Peer-reviewed: Yes
Electronic versions:
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Source: PublicationPreSubmission
Source-ID: 101972358

High Temperature PEM Fuel Cells: From Membranes to Stacks

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
Publication date: 2009
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Event: Abstract from HySA Systems Seminar, Cape Town, South Africa.
Source: orbit
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High temperature PEM fuel cells in Denmark

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
High temperature PEM fuel cells in Denmark: Part I: Introduction to HT-PEMFC, selected results, Part II: Durability, Electrolysis, activities in Denmark

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
Publication date: 2009
Peer-reviewed: No
Source: orbit
Source-ID: 257544
Research output: Contribution to conference » Paper – Annual report year: 2009 » Research

To achieve high temperature operation of proton exchange membrane fuel cells (PEMFC), preferably under ambient pressure, acid–base polymer membranes represent an effective approach. The phosphoric acid-doped polybenzimidazole membrane seems so far the most successful system in the field. It has in recent years motivated extensive research activities with great progress. This treatise is devoted to updating the development, covering polymer synthesis, membrane casting, physicochemical characterizations and fuel cell technologies. To optimize the membrane properties, high molecular weight polymers with synthetically modified or N-substituted structures have been synthesized. Techniques for membrane casting from organic solutions and directly from acid solutions have been developed. Ionic and covalent cross-linking as well as inorganic–organic composites have been explored. Membrane characterizations have been made including spectroscopy, water uptake and acid doping, thermal and oxidative stability, conductivity, electro-osmotic water drag, methanol crossover, solubility and permeability of gases, and oxygen reduction kinetics. Related fuel cell technologies such as electrode and MEA fabrication have been developed and high temperature PEMFC has been successfully demonstrated at temperatures of up to 200 °C under ambient pressure. No gas humidification is mandatory, which enables the elimination of the complicated humidification system, compared with Nafion cells. Other operating features of the PBI cell include easy control of air flow rate, cell temperature and cooling. The PBI cell operating at above 150 °C can tolerate up to 1% CO and 10ppm SO2 in the fuel stream, allowing for simplification of the fuel processing system and possible integration of the fuel cell stack with fuel processing units. Long-term durability with a degradation rate of 5Vh−1 has been achieved under continuous operation with hydrogen and air at 150–160 °C. With load or thermal cycling, a performance loss of 300V per cycle or 40Vh−1 per operating hour was observed. Further improvement should be done by, e.g. optimizing the thermal and chemical stability of the polymer, acid–base interaction and acid management, activity and stability of catalyst and more importantly the catalyst support, as well as the integral interface between electrode and membrane.

General information
Publication status: Published
Organisations: Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry, Energy and Materials, Case Western Reserve University
Contributors: Li, Q., Jensen, J. O., Savinell, R. F., Bjerrum, N. J.
Modified PFSA Membranes for PEM Electrolysers at Elevated Temperatures

Nafion-Polybenzimidazole-Zirconium Phosphate composite membranes for fuel cell and steam electrolyser applications

PEM Fuel cells

Publication information
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BFI (2009): BFI-level 1
Scopus rating (2009): SJR 11.539 SNIP 8.14
Web of Science (2009): Indexed yes
Original language: English
Keywords: Durability, Polybenzimidazole (PBI), Cross-linking, Fuel cell, Phosphoric acid, High temperature proton exchange membrane

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DOIs:
10.1016/j.progpolymsci.2008.12.003
Source: orbit
Source-ID: 232784
Research output: Contribution to journal › Journal article – Annual report year: 2009 › Research › peer-review

Modified PFSA Membranes for PEM Electrolysers at Elevated Temperatures

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Christensen, E., Gu, Z., Aili, D., Li, Q., Bjerrum, N.
Publication date: 2009

Event information
Event: International Symposium on Electrochemistry for Energy Conversion and Storage
Location: The Three Gorges, Wuhan, China
Source: orbit
Source-ID: 272566
Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2009 › Research

Nafion-Polybenzimidazole-Zirconium Phosphate composite membranes for fuel cell and steam electrolyser applications

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Li, Q., Gu, Z., Aili, D., Christensen, E., Bjerrum, N.
Publication date: 2009

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PEM Fuel cells

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
Publication date: 2009
Peer-reviewed: No
PEM fuel cells at elevated temperature

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Jensen, J. O., Li, Q., Pan, C., Bjerrum, N.
Publication date: 2009
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Research output: Contribution to conference » Conference abstract for conference – Annual report year: 2009 » Research

Water electrolysis at elevated temperatures

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Nikiforov, A., Aili, D., Hansen, M. K., Petrushina, I., Christensen, E., Jensen, J. O., Li, Q., Bjerrum, N.
Publication date: 2009
Peer-reviewed: No
Source: orbit
Source-ID: 257610
Research output: Contribution to conference » Poster – Annual report year: 2009 » Research

A high temperature PEMFC integrated with a diesel reforming system

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Pages: 275-283
Publication date: 2008

Host publication information
Cross-linked polybenzimidazole membranes for high temperature proton exchange membrane fuel cells with dichloromethyl phosphinic acid as a cross-linker

Phosphoric acid doped polybenzimidazole (PBI) membranes have been covalently cross-linked with dichloromethyl phosphinic acid (DCMP). FT-IR measurements showed new bands originating from bonds between the hydrogen bearing nitrogen in the imidazole group of PBI and the CH2 group in DCMP. The produced cross-linked membranes show increased mechanical strength, making it possible to achieve higher phosphoric acid doping levels and therefore higher proton conductivity. Oxidative stability is significantly improved and thermal stability is sufficient in a temperature range of up to 250 degrees C, i.e. within the temperature range of operation of PBI-based fuel cells.

Partially fluorinated aarylene polyethers and their ternary blends with PBI and H3PO4. Part II. Characterisation and fuel cell tests of the ternary membranes

Ternary blend membranes based on sulphonated partially fluorinated arylene polyether, polybenzimidazole (PBI) and phosphoric acid were prepared and characterised as electrolyte for high temperature proton exchange membrane fuel cells. Partially fluorinated arylene polyether was first prepared from polycondensation of decafluorobiphenyl with 2,2-bis(4-hydroxyphenyl)hexafluoropropane, followed by sulphonation with H2SO4/60% SO3, based on which binary blends with PBI were prepared and further doped with concentrated phosphoric acid at temperatures of up to 130 degrees C. Acid doping levels as high as 10-13 mol phosphoric acid per PBI repeat unit can be reached, showing small swelling and excellent mechanical strength. At an acid doping level of 11, a conductivity of 0.12 S cm(-1) was obtained at 175 degrees C and 10% relative humidity. Such a membrane exhibits a tensile strength of 6 MPa, elongation of 220% and modulus of 50 MPa at 150 degrees C. Based on these ternary membranes large MEAs with an active area of 256 cm(2) have been prepared for a 2 kW(el) stack showing good performance and reproducibility.
Partially fluorinated arylene polyethers and their ternary blend membranes with PBI and H3PO4. Part I. Synthesis and characterisation of polymers and binary blend membranes

A partially fluorinated polyether ionomer from polycondensation of decafluorobiphenyl with 2,2'-bis(4-hydroxyphenyl)-hexafluoropropane, followed by sulphonation with H2SO4 (60% SO3), has been prepared and optimised in terms of molecular weight and sulphonation degree. The partially fluorinated ionomer has been blended with poly(2,2'-mphenylen-5,5'-bibenzimidazole) (PBI), yielding base-acid blends with PBI in excess. The base-acid blend membranes have been characterised in terms of solubility in DMAc, water uptake and oxidative stability by immersion in aqueous 5 wt.-% H2O2 solutions and Fenton's Reagent, respectively. Ionomers with molecular masses of up to 140,000 Da (non-sulphonated) and 178,000 Da (sulphonated) with excellent thermal stabilities and high sulphonation degrees of up to 2.06 SO3H groups per repeat unit have been produced. Their base-excess blend membranes, where the ionomer blend component served as acidic ionomeric cross-linker, showed excellent oxidative stabilities which were better than that of pure PBI and comparable to the oxidative stability of Nafion (R) in Fenton's Reagent.

Development of a high-pressure microbalance for hydrogen storage materials

Pressure-composition isotherms (PCIs) help to determine thermodynamic properties related to hydrogen uptake of materials. PCIs are normally obtained volumetrically with a Sieverts type apparatus or gravimetrically with a microbalance. A potential problem with the gravimetric technique is that the sample is momentarily exposed to air when transferring it to the system often causing unwanted changes such as oxidation and reaction with moisture in the air. In this study, a high-pressure microbalance was built from scratch inside a glove box with inert atmosphere. The system consists of an electromagnetic microbalance, pressure resistant casing for up to 100 bar hydrogen, a flow system for hydrogen and inert gas, heating elements for temperature control, and software for controlling the system. Thermal convection effects are observed and dampened by heating on both the sample and a counterweight. The precision of the mass measurements
for a 1 g sample was +/- 5 μg, and this range proved to be the same independent of pressure and temperature.

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Vestbø, A. P., Jensen, J. O., Bjerrum, N.
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Publication date: 31 Oct 2007
Peer-reviewed: Yes

**Publication information**
Journal: Journal of Alloys and Compounds
Volume: 446
Issue number: Special Issue
ISSN (Print): 0925-8388
Ratings:
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Web of Science (2007): Indexed yes
Original language: English
Keywords: gas-solid reactions, high-pressure, metal hydrides, hydrogen absorbing materials, thermodynamic properties
DOI:
10.1016/j.jallcom.2007.04.044
Source: orbit
Source-ID: 214660
Research output: Contribution to journal › Conference article – Annual report year: 2007 › Research › peer-review

**Corrosion monitoring in a straw-fired power plant using an electrochemical noise probe**
Electrochemical Noise Measurements have been carried out in situ in a straw-fired power plant using an experimental probe constructed from alumina and AISI 347 steel. Based on a framework of controlled laboratory experiments it has been found that electrochemical noise has the unique ability to provide in-situ monitoring of intergranular corrosion in progress. The probe had a lifetime of two months. It was shown that down-time corrosion in the boiler was negligible. Electrochemical noise data indicated that metal temperatures around 590°C should be avoided as the intergranular corrosion is at an increased level at this temperature, most likely because of favorable conditions for molten salt film condensation.

**General information**
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials, Department of Chemistry
Contributors: Cappeln, F. V., Bjerrum, N., Petrushina, I.
Pages: 588-593
Publication date: Aug 2007
Peer-reviewed: Yes

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Volume: 58
Issue number: 8
ISSN (Print): 0947-5117
Ratings:
Scopus rating (2007): SJR 0.703 SNIP 0.915
Web of Science (2007): Indexed yes
Original language: English
DOI:
10.1002/maco.200604045
Source: orbit
Source-ID: 207197
Research output: Contribution to journal › Journal article – Annual report year: 2007 › Research › peer-review

**Catalytic reduction of NO by methane using a Pt/C/polybenzimidazole/Pt/C fuel cell**
The catalytic NO reduction by methane was studied using a (NO,CH₄,Ar),Pt|polybenzimidazole(PBI)–H₃PO₄|Pt,(H₂,Ar) fuel cell at 135 and 165°C. It has been found that, without any reducing agent (like CH₄), NO can be electrochemically reduced in the (NO, Ar), Pt|PBI–H₃PO₄|Pt/C, (H₂, Ar) fuel cell with participation of H⁺ or electrochemically produced hydrogen. When added, methane partially suppresses the electrochemical reduction of NO. Methane outlet concentration monitoring has shown the CH₄ participation in the chemical catalytic reduction, i.e., methane co-adsorption with NO.
inhibited the electrochemical NO reduction and introduced a dominant chemical path of the NO reduction. The products of the NO reduction with methane were \( \text{N}_2 \), \( \text{C}_2\text{H}_4 \), and water. The catalytic NO reduction by methane was promoted when the catalyst was negatively polarized \((-0.2 \text{ V})\). Repeated negative polarization of the catalyst increased the NO conversion. Maximum NO conversion was 48%. This effect was explained as a result of the electrochemically produced hydrogen.

**Cross-linked polybenzimidazole membranes for fuel cells**

**General information**
- Publication status: Published
- Organisations: Energy and Materials, Department of Chemistry
- Contributors: Li, Q., Pan, C., Jensen, J. O., Precht Noyé, P., Bjerrum, N.
- Pages: 350-352
- Publication date: 2007
- Peer-reviewed: Yes

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- Journal: Chemistry of Materials
- Volume: 19
- Issue number: 3
- ISSN (Print): 0897-4756
- Ratings:
- Scopus rating (2007): SJR 3.11 SNIP 1.845
- Web of Science (2007): Indexed yes
- Original language: English
- DOIs: 10.1021/cm0627793
- Source: orbit
- Source-ID: 207151

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Source: orbit
Source-ID: 194364
Research output: Contribution to journal › Journal article – Annual report year: 2007 › Research › peer-review
Doping phosphoric acid in polybenzimidazole membranes for high temperature proton exchange membrane fuel cells

Polybenzimidazole (PBI) membranes were doped in phosphoric acid solutions of different concentrations at room temperature. The doping chemistry was studied using the Scatchard method. The energy distribution of the acid complexation in polymer membranes is heterogeneous, that is, there are two different types of sites in PBI for the acid doping. The protonation constants of PBI by phosphoric acid are found to be 12.7 L mol(-1) (K-1) for acid complexing sites with higher affinity, and 0.19 L mol(-1) (K-2) for the sites with lower affinity. The dissociation constants for the complexing acid onto these two types of PBI sites are found to be 5.4 X 10(-4) and 3.6 X 10(-2), respectively, that is, about 10 times smaller than that of aqueous phosphoric acid in the first case but 5 times higher in the second. The proton conducting mechanism is also discussed.

Electrochemical Promotion of Catalytic Reactions Using Pt/C/polybenzimidazole(H3PO4)/Pt/C fuel cell performed by the Energy and Materials Science Group (Technical University of Denmark) during the last 6 years[1-4]. The development of our understanding of the nature of the electrochemical promotion is also presented.

Electrochemical promotion of catalytic reactions with Pt/C (or Pt/Ru/C)//PBI catalysts

The paper is an overview of the results of the investigation on electrochemical promotion of three catalytic reactions: methane oxidation with oxygen, NO reduction with hydrogen at 135 degrees C and Fischer-Tropsch synthesis (FTS) at 170 degrees C in the [CH4/O-2(or NO/H-2 or CO/H-2)/Ar//Pt(or Pt/Ru)//PBI(H3PO4)/H-2, Ar] fuel cell. It has been shown that the partial methane oxidation to C2H2 and the C-2 selectivity were electrochemically promoted by the negative catalyst polarization. This was also the case in NO reduction with hydrogen for low NO and H-2 partial pressures. In both cases the catalytic reactions have been promoted by the electrochemically produced hydrogen. It has been found that the NO reduction with hydrogen on the Pt/PBI strongly depends on NO and hydrogen partial pressures in the working gas.
mixture. At higher NO and H-2 partial pressures the catalysis is promoted by the electrochemical pumping of H+ from the catalyst, i.e. at positive polarization. FTS demonstrated the highest methane production rate (11% of CO conversion) at zero fuel cell voltage.

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Petrushina, I., Bjerrum, N., Bandur, V., Cleemann, L. N.
Pages: 427-434
Publication date: 2007
Peer-reviewed: Yes

**High temperature PEMFC and the possible utilization of the excess heat for fuel processing**

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Fluid Mechanics, Department of Mechanical Engineering
Contributors: Jensen, J. O., Li, Q., Pan, C., Vestbø, A. P., Mortensen, K., Petersen, H. N., Sørensen, C. L., Clausen, T. N., Schramm, J., Bjerrum, N.
Pages: 1567-1571
Publication date: 2007
Peer-reviewed: Yes

**Preparation and operation of gas diffusion electrodes for high-temperature proton exchange membrane fuel cells**

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Pan, C., Li, Q., Jensen, J. O., He, R., Cleemann, L. N., Bjerrum, N., Zeng, Q.
Pages: 278-286
Publication date: 2007
Peer-reviewed: Yes
Recent Development of PBI Membranes for PEMFC

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Department of Chemistry
Contributors: Li, Q., Jensen, J. O., Precht Noyé, P., Pan, C., Bjerrum, N.
Pages: 1-10
Publication date: 2007

Host publication information
Title of host publication: Proceedings of World Hydrogen Technologies Convention

Bibliographical note
Plenary talk
Source: orbit
Source-ID: 207168
Research output: Chapter in Book/Report/Conference proceeding – Annual report year: 2007 – Research

The Energy Efficiency of Onboard Hydrogen Storage
A number of the most common ways of storing hydrogen are reviewed in terms of energy efficiency. Distinction is made between energy losses during regeneration and during hydrogen liberation. In the latter case, the energy might have to be provided by part of the released hydrogen, and the true storage density is then equivalently smaller. Systems covered include compressed and liquid hydrogen, reversible and irreversible metal hydrides, and methanol and ammonia.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Jensen, J. O., Vestbø, A. P., Li, Q., Bjerrum, N.
Pages: 723-728
Publication date: 2007
Peer-reviewed: Yes

Publication information
Journal: Journal of Alloys and Compounds
Volume: 446–447
ISSN (Print): 0925-8388
Ratings:
Scopus rating (2007): SJR 0.882 SNIP 1.209
Web of Science (2007): Indexed yes
Original language: English
Keywords: Hydrogen storage, Metal hydride, Compressed hydrogen, Liquid hydrogen, Efficiency
DOIs:
10.1016/j.jallcom.2007.04.051
Source: orbit
Source-ID: 194236
Research output: Contribution to journal – Conference article – Annual report year: 2007 – Research – peer-review
Bronsted acidic room temperature ionic liquids derived from N,N-dimethylformamide and similar protophilic amides

Development of a high-pressure microbalance for hydrogen storage materials

Examination of catalytic reduction of NO by CH₄ in a Pt-polybenimidazole membrane-Pt system with and without polarization
Gas Diffusion Electrodes for PBI Cells

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry
Contributors: Li, Q., Pan, C., Jensen, J. O., Nilsson, M. S., Bjerrum, N.
Pages: Abstract 541
Publication date: 2006

Host publication information
Title of host publication: Meeting Abstracts - Electrochemical Society
Publisher: The Electrochemical Society
Electronic versions:
Pan.pdf

Bibliographical note
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Source: orbit
Source-ID: 264240
Research output: Chapter in Book/Report/Conference proceeding › Conference abstract in proceedings – Annual report year: 2006 › Research › peer-review

Phosphoric acid doped Polybenzimidazole Composite Membranes for High temperature Proton Exchange Membrane Fuel Cells

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: He, R., Li, Q., Bjerrum, N.
Pages: 697-703
Publication date: 2006
Peer-reviewed: Yes

Publication information
Journal: Chinese Journal of Applied Chemistry
Volume: 23
Issue number: 7
Original language: English
Source: orbit
Source-ID: 192694
Research output: Contribution to journal › Journal article – Annual report year: 2006 › Research › peer-review

Physicochemical properties of phosphoric acid doped polybenzimidazole membranes for fuel cells
Polybenzimidazole (PBI) membranes have been prepared with different molecular weights. The water and acid swelling, mechanical strength, gas permeability and proton conductivity were studied for the pristine and acid doped PBI membranes. When doped with 5 mol of phosphoric acid per mole repeat unit of the polymer, a level necessary to obtain high enough proton conductivity for fuel cell uses, the polymer membrane exhibits a volume swelling by 118%, resulting in separation of the polymer backbones. The separation in turn reduces the mechanical strength of the membrane especially at high temperatures. Another consequence is the increased H2 and O2 permeability through the membrane. In the temperature range from 120 to 180 °C, the hydrogen permeability was found to be 1.6-4.3×10−17 and 1.2-4.0×10−15 mol cm cm−2 s−1 Pa−1 for pristine and acid doped PBI membranes, respectively, while for oxygen it was 5.0-10×10−19 and 3.0-9.4×10−16 mol cm cm−2 s−1 Pa−1, respectively. High molecular weights of the polymers improve the mechanical
strength but have little influence on the proton conductivity of the membranes.

Recent Progress in Preparation and Characterization of PBI Membranes for PEMFC

The Energy Efficiency of On-board Hydrogen Storage

100-200°C Polymer Fuel Cells for use with NaAlH4
200°C PEM Fuel Cells

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Bjerrum, N.
Publication date: 2005
Peer-reviewed: No
Source: orbit
Source-ID: 188088
Research output: Contribution to conference → Poster → Annual report year: 2005 → Research

Electrochemical and Spectroscopic Studies of the Chloro and Oxochloro Complex Formation of Nb(V) and Ta(V) in NaCl-AlCl₃ Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Barner, J. H. V., Bjerrum, N.
Pages: 9847-9851
Publication date: 2005
Peer-reviewed: Yes
Publication information
Journal: Inorganic Chemistry
Volume: 44
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2005): SJR 2.049 SNIP 1.434
Web of Science (2005): Indexed yes
Original language: English
Source: orbit
Source-ID: 185339
Research output: Contribution to journal → Journal article → Annual report year: 2005 → Research → peer-review

Electrochemical noise measurements of steel corrosion in the molten NaCl-K₂SO₄ system

Electrochemical noise measurements have been carried out on AISI347, 10CrMo910, 15Mo3, and X20CrMoV121 steels in molten NaCl-K₂SO₄ at 630 degrees C. Different types of current noise have been identified for pitting, intergranular and peeling corrosion. The corrosion mechanism was the so-called active corrosion (i.e., the corrosion proceeds with no passivation due to the influence of chlorine), characterized by the formation of volatile metal chlorides as a primary corrosion product. It was found possible to obtain an empirical separation of general and intergranular corrosion using kurtosis (a statistical parameter calculated from the electrochemical noise data). It was found that average kurtosis values above 6 indicated intergranular corrosion and average values below 6 indicated general corrosion. The response time for localized corrosion detection in in-plant monitoring was approximately 90 min on this basis. Approximate values of
polarization resistances of AISI347 and 15Mo3 steels were determined to be 250 and 100 Omega cm(2), respectively.

**General information**
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry
Contributors: Cappeln, F. V., Bjerrum, N., Petrushina, I.
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**Fuel cells: a promise of electrochemistry and challenges for electrochemists**

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**Fuel cells: a promise of electrochemistry and challenges for electrochemists**

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Organisations: Department of Chemistry, Department of Chemistry
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FURIM: Further improvement of high temperature PEM fuel cells

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Contributors: Jensen, J. O., Li, Q., Pan, C., Precht Noyé, P., Bjerrum, N.
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High Temperature PEMFC

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High temperature PEM fuel cells at Technical University of Denmark

General information
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Organisations: Department of Chemistry
Contributors: Jensen, J. O., Li, Q., Pan, C., Precht Noyé, P., Bjerrum, N.
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Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2005 › Research
Integration of high temperature PEM fuel cells with a methanol reformer

On-board generation of hydrogen by methanol reforming is an efficient and practical option to fuel PEMFC especially for vehicle propulsion purpose. The methanol reforming can take place at temperatures around 200°C with a nearly 100% conversion at a hydrogen yield of about 400 L–(h–kg catalyst)-1. The CO content in the reformate gas at this temperature is less than 0.2 vol%. The recently developed high temperature PEMFC based on acid doped PBI membranes can operate in the same temperature range and tolerate a few percent of CO in the feeding gas. The high CO tolerance makes it possible to use the reformate gas directly from the reformer without further CO removal. Integration of high temperature PEMFC with a reformer is expected to improve the system efficiency and simplify the system construction and operation. The present work has demonstrated this possibility. (c) 2005 Elsevier B.V. All rights reserved.

Phosphoric acid doped AB-PBI membranes and its applications in high temperature PEMFC

Poly(2,5-benzimidazole) (ab-PBI) was prepared from 3,4-diaminobenzoic acid via a polymerisation reaction. The obtained polymer exhibits excellent thermal stability in a temperature range ...... The membrane of ab-PBI when doped with phosphoric acid at room temperature presents high proton conductivity in a wide temperature range. The conductivity of the acid doped ab-PBI membranes was studied in a temperature range of 80°C to 200°C under different relative humidity and with different acid doping levels. PEMFC test results indicated that the fuel cell could be operated at temperatures up to 200°C with phosphoric acid doped ab-PBI as the electrolyte under atmospheric pressure at 200°C without humidification.
Proton Conductivity and Operational Features Of PBI-Based Membranes
As an approach to high temperature operation of PEMFCs, acid-doped PBI membranes are under active development. The membrane exhibits high proton conductivity under low water contents at temperatures up to 200°C. Mechanisms of proton conduction for the membranes have been proposed. Based on the membranes fuel cell tests have been demonstrated. Operating features of the PBI cell include no humidification, high CO tolerance, better heat utilization and possible integration with fuel processing units. Issues for further development are also discussed.

Proton Exchange Membranes for Fuel Cells: - Challenges and Recent Developments

Proton Exchange Membranes For Fuel Cells - Challenges And Recent Developments
Recent Progress in High Temperature PEMFC and the Possible Utilization of the Excess Heat for Fuel Processing

The FURIM Project

The FURIM Project (IP) - SES6-CT-2004-502782

100-200°C Polymer Fuel Cells for use with NaAlH4

A PEMFC operating at up to 200°C as a possible link to the complex metal hydrides like NaAlH4
Ca-Ni alloys and the search for lighter interstitial hydrides. New metal hydrides for hydrogen storage

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Bjerrum, N.
Publication date: 2004

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Research output: Non-textual form › Sound/Visual production (digital) – Annual report year: 2004 › Research

Development of strategic surface topographies for lubrication in sheet forming of stainless steel
Strategic stainless steel surfaces have been developed by which the tribological properties are significantly improved for sheet metal forming compared to as received surfaces. The improvements have been achieved by modification of the surface in order to promote micro-plasto hydrodynamic lubrication by increasing the ratio of closed lubricant pockets and modifying the pocket geometry. These factors influence the retention and subsequently escape of lubricant during forming thus enhancing lubricant permeability to the contact between flattened work piece asperities and contacting tool. The technique, which has been developed, is based on an electrochemical treatment changing the topography of the stainless steel surface. Comparative testing of the new surface topographies in ironing and deep drawing of stainless steel sheet shows significant improvements and possibilities of replacing chlorinated paraffin oils with environmentally friendly, plain mineral oil.

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Publication status: Published
Organisations: Department of Chemistry, Department of Management Engineering
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Iodine as catalyst for the direct oxidation of methane to methyl sulfates in oleum

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Gang, X., Zhu, Y., Birch, H., Hjuler, H., Bjerrum, N.
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Materials Issues and System Prospects of High Temperature PEMFC

General information
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PBI-based polymer membranes for high temperature fuel cells – preparation, characterizations and fuel cell demonstrations

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Organisations: Department of Chemistry
Contributors: Qingfeng, L., He, R., Jensen, J. O., Bjerrum, N.
Pages: 147-159
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Polymer Membranes for Fuel Cells

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Water Uptake and Acid Doping of Polybenzimidazoles as Electrolyte Membranes for Fuel Cells

Acid-doped polybenzimidazole (PBI) membranes have been demonstrated for fuel cell applications with advanced features such as high operating temperatures, little humidification, excellent CO tolerance, and promising durability. The water uptake and acid doping of PBI membranes have been studied. The water uptake of PBI from the vapour phase is only slightly increased as the atmospheric humidity increases up to unity (100%). Little difference is observed for the water uptake from vapour and liquid phases, behaving very differently from Nafion membranes. When doped with phosphoric acid at low levels (<2), the active sites of the imidazole ring are preferably occupied by the doping acid and the water uptake is consequently lower. At higher acid doping levels, the water uptake is influenced by the excess of hygroscopic acid and higher water uptake than for Nafion membranes is observed. Upon doping, the acid is found to be concentrated inside the polymer. Only two molecules of phosphoric acid are bonded to each repeat unit of PBI, corresponding to the two nitrogen sites available. Infrared and Raman spectra show the presence of strong hydrogen bonds between phosphoric acid and nitrogen atoms of the imidazole rings. The excessive doping acid is "free acid" that contributes to high conductivity but suffers from a fast washing out when adequate liquid is present. (C) 2004 Elsevier B.V. All rights reserved.

Acid-doped Polybenzimidazole Membranes as Electrolyte for Fuel Cells Operating Above 100°C

The technical achievement and challenges for the PEMFC technology based on perfluorosulfonic acid (PFSA) polymer membranes (e.g. Nafion®) are briefly discussed. The newest development in the field is alternative polymer electrolytes for operation above 100°C. As one of the successful approaches to high operational temperatures, the development and evaluation of acid doped PBI membranes are reviewed, covering polymer synthesis, membrane casting, acid doping, physiochemical characterization and fuel cell tests. A high temperature PEMFC system operational at up to 200°C is demonstrated with no gas humidification and high CO-tolerance up to 10 vol%. This high CO tolerance allows for a direct use of reformed hydrogen without further CO removal, which opens the possibility for an integrated reformer-fuel cell system. The content of this review is to a large extent based on research performed by the authors’ group.
Acid Doped Polybenzimidazole Membranes for Polymer Electrolyte Fuel Cells

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Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N., Li, Q., He, R., Jensen, J. O.
Publication date: 2003

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Research output: Chapter in Book/Report/Conference proceeding – Article in proceedings – Annual report year: 2003 – Research

Approaches and Recent Development of Polymer Electrolyte Membranes For Fuel Cells Operational Above 100°C: A Review

The state-of-the-art of polymer electrolyte membrane fuel cell (PEMFC) technology is based on perfluorosulfonic acid (PFSA) polymer membranes operating at a typical temperature of 80 °C. Some of the key issues and shortcomings of the PFSA-based PEMFC technology are briefly discussed. These include water management, CO poisoning, hydrogen, reformate and methanol as fuels, cooling, and heat recovery. As a means to solve these shortcomings, high-temperature polymer electrolyte membranes for operation above 100 °C are under active development. This treatise is devoted to a review of the area encompassing modified PFSA membranes, alternative sulfonated polymer and their composite membranes, and acid-base complex membranes. PFSA membranes have been modified by swelling with nonvolatile solvents and preparing composites with hydrophilic oxides and solid proton conductors. DMFC and H2/O2 (air) cells based on modified PFSA membranes have been successfully operated at temperatures up to 120 °C under ambient pressure and up to 150 °C under 3-5 atm. Alternative polymers are selected from silicon- and fluorine-containing inorganic polymers or aromatic hydrocarbon polymers and functionalized by sulfonation. The sulfonated hydrocarbons and their inorganic composites are potentially promising for high-temperature operation. High conductivities have been obtained at temperatures up to 180 °C. Acid-base complex membranes constitute another class of electrolyte membranes. A high-temperature PEMFC based on H3PO4-doped PBI has been demonstrated for operation at temperatures up to 200 °C under ambient pressure. The advanced features include high CO tolerance, simple thermal and water management, and possible integration with the fuel processing unit.
CO tolerance by the PEMFC operational at temperatures up to 200°C

The CO poisoning effect on carbon-supported platinum catalysts in polymer electrolyte membrane fuel cells has been investigated in a temperature range from 125 to 200°C with the phosphoric acid-doped polybenzimidazole membranes as electrolyte. The effect is very temperature-dependent and can be sufficiently suppressed at elevated temperature. By defining a poisoning factor as less than 2% of power loss due to the poisoning effect, it is evaluated that 3% CO in hydrogen can be tolerated at current densities up to 0.7 A/cm² at 200°C, while at 125°C 0.1% CO in hydrogen can be tolerated at current densities lower than 0.25 A/cm². For comparison, the tolerance is only 0.0025 % CO (25 ppm) at 80°C at current densities up to 0.15 A/cm². The effect of CO₂ in hydrogen was also studied. At 175°C, 25% CO₂ in the fuel stream showed only the dilution effect.

Electrochemical promotion of NO reduction by hydrogen on a platinum/polybenzimidazole catalyst

The electrochemical promotion of catalytic NO reduction by hydrogen was studied using a (NO, H₂, Ar), Pt polybenzimidazole (PBI)-H₃PO₄/Pt, (H₂, Ar) fuel cell at 135°C. A mixture of NO/H₂/Ar was used as the working mixture at one electrode and a mixture of H₂/Ar was used as reference and counter gas at the other electrode. Products of NO reduction (N₂ and H₂O) were analyzed by an on-line mass spectrometer. At high NO+H₂+Ar flow rate (17 mL/min; 17 and 354 mL/min, respectively, at atmospheric pressure) the maximum rate enhancement ratio was 4.65. At low NO+H₂+Ar flow rate (17 mL/min; 17 and 140 mL/min, respectively), NO reduction increased 20 times even without polarization compared to the high gas flow rate. The electrochemical promotion effect occurs at positive polarization with a maximum increase at approximately 0.08 V and with 1.5 times the zero polarization value. The promotion at the negative polarization can be attributed to the electrochemical production of the promoters. At low gas flow rates, a charge-induced change of the strength of chemisorptive bonds can take place.
HIGH TEMPERATURE POLYMER FUEL CELLS: HEAT UTILIZATION AND CO TOLERANCE
This paper will report recent results from our group on polymer fuel cells (PEMFC) based on the temperature resistant polymer polybenzimidazole (PBI), which allow working temperatures up to 200°C. The membrane has a water drag number near zero and need no water management at all. The high working temperature allows for utilization of the excess heat for fuel processing. Moreover, it provides an excellent CO tolerance of several percent, and the system needs no purification of hydrogen from a reformer. Continuous service for over 6 months at 150°C has been demonstrated.

Integration of high temperature PEMFC with a methanol reformer
NEW POLYMER ELECTROLYTE MEMBRANES FOR FUEL CELLS OPERATING ABOVE 100°C: APPROACHES AND RECENT PROGRESS

The state-of-the-art of PEMFC technology is based on perfluorosulfonic acid (PFSA) polymer membranes operating at a typical temperature of 80°C. The newest development in the field is alternative polymer electrolytes for operation above 100°C. This paper is devoted to a review on the development, which is classified into three groups: modified PFSA...
membranes, alternative sulfonated polymer and their inorganic composite membranes and acid-base complex membranes. High temperature PEMFC has been demonstrated with advanced features such as fast electrode kinetics, high CO tolerance, simple thermal and water management and possible integration with the fuel processing unit.

Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic proton conductors
Phosphoric acid doped polybenzimidazole (PBI) and PBI composite membranes have been prepared in the present work. The PBI composites contain inorganic proton conductors including zirconium phosphate (ZrP), (Zr(HPO4)2·nH2O), phosphotungstic acid (PWA), (H3PW12O40·nH2O) and silicotungstic acid (SiWA), (H4SiW12O40·nH2O). The conductivity of phosphoric acid doped PBI and PBI composite membranes was found to be dependent on the acid doping level, relative humidity (RH) and temperature. A conductivity of 6.8×10⁻² S cm⁻¹ was observed for PBI membranes with a H3PO4 doping level of 5.6 (mole number of H3PO4 per repeat unit of PBI) at 200 °C and 5% RH. A higher conductivity of 9.6×10⁻² S cm⁻¹ was obtained by composite of 15 wt.% of ZrP in a PBI membrane under the same conditions. Homogeneous membranes with good mechanical strength were prepared by introducing PWA (20–30 wt.%) and SiWA (20–30 wt.%) into PBI, and their conductivity were found to be higher than or comparable with that of the PBI membrane at temperatures up to 110 °C.

The CO poisoning effect in PEMFCs operational at temperatures up to 200 degrees C
The CO poisoning effect on carbon-supported platinum catalysts (at a loading of 0.5 mg Pt/cm(2) per electrode! in polymer electrolyte membrane fuel cells (PEMFCs) has been investigated in a temperature range from 125 to 200 degreesC with the phosphoric acid-doped polybenzimidazole membranes as electrolyte. The effect is very temperature-dependent and can be sufficiently suppressed at elevated temperature. By defining the CO tolerance as a voltage loss less than 10 mV, it is evaluated that 3% CO in hydrogen can be tolerated at current densities up to 0.8 A/cm(2) at 200 degreesC, while at 125 degreesC 0.1% CO in hydrogen can be tolerated at current densities lower than 0.3 A/cm(2). For comparison, the tolerance is only 0.0025% CO (25 ppm) at 80 degreesC at current densities up to 0.2 A/cm(2). The relative anode activity for hydrogen oxidation was calculated as a function of the CO concentration and temperature. The effect of CO2 in hydrogen was also studied. At 175 degreesC, 25% CO2 in the fuel stream showed only the dilution effect. (C) 2003 The Electrochemical Society.
A quasi-direct methanol fuel cell system based on blend polymer membrane electrolytes

On the basis of blend polymer electrolytes of polybenzimidazole and sulfonated polysulfone, a polymer electrolyte membrane fuel cell was developed with an operational temperature up to 200 degrees C. Due to the high operational temperature, the fuel cell can tolerate 1.0-3.0 vol % CO in the fuel, compared to less than 100 ppm CO for the Nafion-based technology at 80 degrees C. The high CO tolerance makes it possible to use the reformed hydrogen directly from a simple methanol reformer without further CO removal. That both the fuel cell and the methanol reformer operate at temperatures around 200 degrees C opens the possibility for an integrated system. The resulting system is expected to exhibit high power density and simple construction as well as efficient capital and operational cost.
Electrochemical promotion of oxidative coupling of methane on platinum/polybenzimidazole catalyst

The electrochemical promotion of catalytic methane oxidation was studied using a (CH4,O-2,Ar), Pt/polybenzimidazole (PBI)-H3PO4/Pt,(H-2,Ar) fuel cell at 135° degrees C. It has been found that C2H2, CO2, and water are the main oxidation products. Without polarization the yield of C2H2 was 0.9% and the yield of CO2 was 7.3%. This means that C-2 open-circuit selectivity was approximately 11%. Open-circuit voltage was around 0.6 V. It has been shown that the CH4 --> C2H2 catalytic reaction can be electrochemically promoted at negative polarization and exhibits a clear "volcano-type" promotion behavior, meaning that there was a maximum promotion effect at a polarization of -0.15 V, or 0.45 V catalyst potential vs. a hydrogen electrode (3.8% C2H2 yield). The catalytic rate enhancement ratio, r(C-2)/r(o)(C-2), at this maximum was 4.2. There was no C2H2 production at polarization greater than or equal to -0.1 and less than or equal to -0.3 V. The yield of C2H2 decreased with decreasing temperature. Dependence of CO2 yield on polarization also showed a "volcano-type" behavior with maximum yield of 8.3% at -0.15 V polarization. The catalytic rate enhancement ratio for CO2 production, r(CO2)/r(o)(CO2), at this maximum was 1.1, which means that this catalytic reaction is only slightly affected by the electrochemical polarization. This indicates that polarization especially affects the C-2 selectivity of the catalyst. The obtained data was explained by the electrochemical production of Pt-H active centers at the electrolyte-catalyst-gaseous reactant interface (lambda much greater than 1).
Stability of CaNi5Hx stored at temperatures between 20 and 150 degrees C

The stability of CaNi5Hx stored at different temperatures was studied as a function of time. In general AB(5) metal hydrides are known to be metastable with a tendency to disproportionate at elevated temperatures. In the present study samples of CaNi5 were stored in the hydrided state (as CaNi5Hsimilar to4.7) at temperatures between 20 and 150degreesC. After different periods of time, up to 120 days, the hydrogen absorption capacity was measured electrochemically. Significant capacity decays were observed at temperatures of 40degreesC and higher. The capacity decay with storage time tended to stop at a level of 147 mAh/g corresponding to 1.83 hydrogen atoms per calcium atom. X-ray diffraction revealed that the CaCu5 structure was preserved after the degradation. A mathematical model for the decay is proposed.

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Web of Science (2002): Indexed yes
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**Water Uptake and Acid Doping of Polybenzimidazole electrolyte Membranes for fuel Cells.**

**Development and characterization of acid-doped polybenzimidazole/sulfonated polysulfone blend polymer electrolytes for fuel cells**

Polymeric membranes from blends of sulfonated polysulfones (SPSF) and polybenzimidazole (PBI) doped with phosphoric acid were developed as potential high-temperature polymer electrolytes for fuel cells and other electrochemical applications. The water uptake and acid doping of these polymeric membranes were investigated. Ionic conductivity of the membranes was measured in relation to temperature, acid doping level, sulfonation degree of SPSF, relative humidity, and blend composition. The conductivity of SPSF was of the order of $10^{-3}$ S cm$^{-1}$. In the case of blends of PBI and SPSF, it was found to be higher than $10^{-2}$ S cm$^{-1}$. Much improvement in the mechanical strength is observed for the blend polymer membranes, especially at higher temperatures. Preliminary work has demonstrated the feasibility of these polymeric membranes for fuel-cell applications.

**Electrosynthesis of tantalum borides in oxygen-free and oxygen-containing fluoride melts**

Results of electrosynthesis of tantalum borides in fluoride and oxyfluoride melts are compared. It is shown that the single-phase X-ray-amorphous micro-layered coatings form only in the latter case. Linear and square-wave voltammetry, complemented by X-ray diffraction analysis, IR spectroscopy, and OC, reveals that the reason for their formation is the cathodic reduction of heteronuclear tantalum and boron complexes.
Phosphoric acid doped polybenzimidazole membranes: Physiochemical characterization and fuel cell applications [PEM fuel cells]

A polymer electrolyte membrane fuel cell operational at temperatures around 150-200 degrees C is desirable for fast electrode kinetics and high tolerance to fuel impurities. For this purpose polybenzimidazole (PBI) membranes have been prepared and H/sub 3/PO/sub 4/-doped in a doping range from 300 to 1600 mol%. Physiochemical properties of the membrane electrolyte have been investigated by measurements of water uptake, acid doping level, electric conductivity, mechanical strength and water drag coefficient. Electrical conductivity is found to be insensitive to humidity but dependent on the acid doping level. At 160 degrees C a conductivity as high as 0.13 S cm/sup -1/ is obtained for membranes of high doping levels. Mechanical strength measurements show, however, that a high acid doping level results in poor mechanical properties. At operational temperatures up to 190 degrees C, fuel cells based on this polymer membrane have been tested with both hydrogen and hydrogen containing carbon monoxide.
POLYMER ELECTROLYTE MEMBRANE FUEL CELLS
A method for preparing polybenzimidazole or polybenzimidazole blend membranes and fabricating gas diffusion electrodes and membrane-electrode assemblies is provided for a high temperature polymer electrolyte membrane fuel cell. Blend polymer electrolyte membranes based on PBI and various thermoplastic polymers for high temperature polymer electrolyte fuel cells have also been developed. Miscible blends are used for solution casting of polymer membranes (solid electrolytes). High conductivity and enhanced mechanical strength were obtained for the blend polymer solid electrolytes. With the thermally resistant polymer, e.g., polybenzimidazole or a mixture of polybenzimidazole and other thermoplastics as binder, the carbon-supported noble metal catalyst is tape-cast onto a hydrophobic supporting substrate. When doped with an acid mixture, electrodes are assembled with an acid doped solid electrolyte membrane by hot-press. The fuel cell can operate at temperatures up to at least 200 °C with hydrogen-rich fuel containing high ratios of carbon monoxide such as 3 vol% carbon monoxide or more, compared to the carbon monoxide tolerance of 10-20 ppm level for Nafion®-based polymer electrolyte fuel cells.

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The carbon monoxide poisoning effect on the performance of polymer electrolyte membrane fuel cells operational at temperatures up to 200°C

General information
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ISBN (Print): 3-9807963-0-2
Source: orbit
Anti corrosion layer for stainless steel in molten carbonate fuel cell - comprises phase vapour deposition of titanium nitride, aluminium nitride or chromium nitride layer then oxidising layer in molten carbonate electrolyte

Forming an anticorrosion protective layer on a stainless steel surface used in a molten carbonate fuel cell (MCFC) - comprises the phase vapour deposition (PVD) of a layer comprising at least one of titanium nitride, aluminium nitride or chromium nitride and then forming a protective layer in situ by replacement of the nitride ions with oxide ions in the molten carbonate electrolyte.

Cold Forging of Stainless Steel with FeCl₃ based lubricants

A lubricant system for cold forging of stainless steel based on FeCl₃ has been presented. a.o.

Corrosion Protection of Steel in Molten Li₂CO₃-K₂CO₃ and Na₂CO₃-K₂CO₃ Mixtures in a Hydrogen Containing Atmosphere

Ratings:
Scopus rating (2000): SJR 0.666 SNIP 1.007
Development of air metal hydride battery

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Contributors: Bjerrum, N., Jensen, J. O., al, E.
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Research output: Contribution to conference › Poster – Annual report year: 2000 › Research

Direct Oxidation of Methane to Methanol by Mercuric Sulfate Catalyst

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Web of Science (2000): Indexed yes
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Electrochemical promotion of sulfur dioxide catalytic oxidation
The effect of electrochemical polarization on the catalytic SO2 oxidation in the molten V2O5-K2S2O7 system has been studied using a gold working electrode in the temperature range 400-460 degrees C. A similar experiment has been performed with the industrial catalyst VK-58. The aim of the present investigation was to study a possible non-Faradaic electrochemical promotion of the liquid-phase catalytic reaction. It has been shown that there are two negative potential promotion areas with maximum effects at approximately -0.1 and -0.2 V, and one positive potential promotion area with the maximum effect between 0.1 and 0.3 V. There were no Faradaic reactions in the negative polarization region, and there was an anodic current which was less than 16% of the theoretical value for an exclusively Faradaic SO2 oxidation. Therefore the promotion effects at negative polarization are completely non-Faradaic. All the promotion effects have been explained as mainly due to charging of the electric double layer at the gold electrode. The effect at -0.2 V also depends on the V2O5 concentration and is more pronounced at higher V2O5 concentrations. This has been ascribed to a destruction of the vanadium polymeric chains caused by the negative charge on the electrode. The Faradaic part of the promoting effect under positive polarization has been explained as the electrochemical pushing of the V(V) V(IV) equilibrium in the direction of V(V) formation. It has also been shown that when using the industrial VK-58 catalyst the activity can be increased up to four times by using the negative polarization effect with maximum at -0.2 V. (C) 2000 The Electrochemical Society. S0013-1651(99)10-023-5. All rights reserved.

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Contributors: Petrushina, I., Bandur, V., Cappeln, F. V., Bjerrum, N.
Electrochemical studies of the molten system K2NbF7-Na2O-Nb-(LiF-NaF-KF)(eut) at 700 degrees C

Various voltammetric methods have been used to study FLINAK (LiF-NaF-KF eutectic melt 46.5-11.5-42 mol %) melts containing about 1 mol % niobium-fluoro and -oxofluoro complexes with Nb in oxidation states (V) and (IV) at 700 degrees C and varying amounts of Na2O in the range 0 <n(O)(0)/n(Nb)(0) <7. A slow, spontaneous reduction of Nb(V)-fluoro complexes to Nb(IV)-fluoro complexes was observed in the absence of Nb metal. With a stoichiometric amount of Nb metal, Nb(V) is reduced rapidly to Nb(IV) according to the reaction 4NbF(7)(2-) + Nb reversible arrow 5NbF(x)((x-4)-). The solubilities of Nb2O5, and KNbO3 in FLINAK were measured and found to be 1.8 and 0.13 mol %, respectively. The following reactions probably occur when increasing amounts of oxide are added to a melt originally containing NbFx(x-4)-: NbFx(x-4)- + O-2(-) reversible arrow Nb(IV)-mono-oxo-fluoride + fluoride, 5Nb(IV)-mono-oxo-fluoride + O-2(-) reversible arrow 4NbO(2)F(4)(3-) + Nb, and NbO2F43- + O-2(-) + Alk(+) reversible arrow AlkNbO(3)(s) + 4F(-) (Alk(+) = Li+, Na+, or K+). At oxide to niobium molar ratios higher than three, AlkNbO(3)(s) redissolves, and at n(O)(0)/n(Nb)(0) > 4, all Nb and O added are dissolved. Strong indications of the coexistence of the oxygen rich Nb(V)OF complexes and O-2(-) ions in FLINAK at n(O)(0)/n(Nb)(0) > 4 have been found. An equilibrium/sampling/analysis technique was also used to study this system without Nb metal added. The results mainly agree with the results of the voltammetric studies. However, no indications of spontaneous reduction of Nb(V) to Nb(IV) were observed, even after 24 h. (C) 2000 The Electrochemical Society. S0013-3651(99)12-112-8. All rights reserved.
Infrared and Raman Spectroscopic Investigations of the Nb(V) Fluoro and Oxofluoro Complexes in the LiF-NaF-KF (FLINAK) Eutectic Melt with Development of a Diamond IR-cell

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Andersen, K. B., Christensen, E., Berg, R. W., Bjerrum, N., Barner, J. H. V.
Pages: 3449-3454
Publication date: 2000
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 39
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2000): SJR 1.884 SNIP 1.379
Web of Science (2000): Indexed yes
Original language: English
Source: orbit
Source-ID: 176758
Research output: Contribution to journal › Journal article – Annual report year: 2000 › Research › peer-review

Matrix Isolated Al2OF62+ Ion in Molten and Solid FLINAK

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Brooker, M. H., Berg, R. W., Barner, J. H. V., Bjerrum, N.
Pages: 4725-4730
Publication date: 2000
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 39
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2000): SJR 1.884 SNIP 1.379
Web of Science (2000): Indexed yes
Original language: English
Source: orbit
Source-ID: 176734
Research output: Contribution to journal › Journal article – Annual report year: 2000 › Research › peer-review

Metalhydridbatterier og lavtemperaturbrændselsceller

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Metal hydride storage tank for demonstration in hydrogen vehicle

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Hennesø, E., Bjerrum, N.
Pages: 133-139
Publication date: 2000

Host publication information
Title of host publication: Proceedings of the Nordic Workshop on Materials for Energy Conversion : Bardøla Høyfjellshotel
Place of publication: Geilo, Norway
Publisher: Nordic Energy Research Programme
Source-ID: 188081
Research output: Chapter in Book/Report/Conference proceeding – Article in proceedings – Annual report year: 2000 – Research

Miscibility Behavior of Polybenzimidazole/Sulfonated Polysulfone Blends for Use in Fuel Cell Applications

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Deimede, V., Voyiatzis, G. A., Kallitsis, J. K., Qingfeng, L., Bjerrum, N.
Pages: 7609-7617
Publication date: 2000
Peer-reviewed: Yes

Publication information
Journal: Macromolecules
Volume: 33
ISSN (Print): 0024-9297
Ratings:
Scopus rating (2000): SJR 2.793 SNIP 2.012
Web of Science (2000): Indexed yes
Original language: English
Source-ID: 176755

On the chemical nature of boundary lubrication of stainless steel by chlorine - and sulfur-containing EP-additives

The nature of the extreme pressure (CEP) effect of the dialkylpolysulfides and chlorinated paraffins during the ironing of stainless steel AISI 304 has been studied. A strip reduction test was used in combination with differential thermal analysis (DTA), profilometry, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy analysis (AES).

Strip reduction tests, in which chlorinated paraffin and dialkyl sulfide were compared as EP-additives, have shown significantly stronger EP-effect of the chlorine containing lubricant, than for the sulfur containing lubricant. DTA analysis of the Me-powder (where Me = iron, chromium or nickel)-dialkylpolysulfide (or chlorinated paraffin) mixtures have shown that dialkylpolysulfide was chemically active with iron and nickel (the highest activity was with nickel). Chromium was practically nonactive with dialkylpolysulfide. Chlorinated paraffin was equally active with iron, chromium and nickel.
The better lubrication performance demonstrated by chlorinated paraffin compared to dialkylpolysulfides was attributed to the chemical activity of the chlorinated paraffin with all the main components of stainless steel.

The depth profiles of the stainless steel strips were examined before and after strip reduction by use of AES sputter profiling. Results imply that the chlorine containing lubricant enforces the formation of a thick oxide layer. (C) 2000 Elsevier Science S.A. All rights reserved.

**General information**
Publication status: Published
Organisations: Department of Chemistry, Department of Physics
Contributors: Petrushina, I., Christensen, E., Bergqvist, R. S., Møller, P. B., Bjerrum, N., Høj, J. W., Kann, G., Chorkendorff, I.
Pages: 98-105
Publication date: 2000
Peer-reviewed: Yes

**Publication information**
Journal: Wear
Volume: 246
Issue number: 1-2
ISSN (Print): 0043-1648
Ratings:
Scopus rating (2000): SJR 0.835 SNIP 1.161
Web of Science (2000): Indexed yes
Original language: English
DOIs:
10.1016/S0043-1648(00)00503-2
Source: orbit
Source-ID: 176756
Research output: Contribution to journal › Journal article – Annual report year: 2000 › Research › peer-review

**Oxygen reduction on carbon supported platinum catalysts in high temperature polymer electrolytes**
Oxygen reduction on carbon supported platinum catalysts has been investigated in H3PO4, H3PO4-doped Nafion and polybenzimidazole (PBI) polymer electrolytes in a temperature range up to 190 degrees C. Compared with pure H3PO4, the combination of H3PO4 and polymer electrolytes can significantly improve the oxygen reduction kinetics due to increased oxygen solubility and suppressed adsorption of phosphoric acid anions. Further enhancement of the catalytic activity can be obtained by operating the polymer electrolytes at higher temperatures. Efforts have been made to develop a polymer electrolyte membrane fuel cell based on H3PO4-doped PBI for operation at temperatures between 150 and 200 degrees C. (C) 2000 Elsevier Science Ltd. All rights reserved.

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Qingfeng, L., Hjuler, H. A., Bjerrum, N.
Pages: 4219-4226
Publication date: 2000
Peer-reviewed: Yes

**Publication information**
Journal: Electrochimica Acta
Volume: 45
Issue number: 25-26
ISSN (Print): 0013-4686
Ratings:
Scopus rating (2000): SJR 0.889 SNIP 1.161
Web of Science (2000): Indexed yes
Original language: English
Keywords: Oxygen reduction, Platinum, Nafion, Polybenzimidazole, Phosphoric acid
DOIs:
10.1016/S0013-4686(00)00554-5
Source: orbit
Source-ID: 174878
Research output: Contribution to journal › Journal article – Annual report year: 2000 › Research › peer-review
Raman Study of the Hexafluoroaluminate Ion in Solid and Molten FLINAK

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Brooker, M. H., Berg, R. W., Barner, J. H. V., Bjerrum, N.
Pages: 3682-3689
Publication date: 2000
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 39
ISSN (Print): 0020-1669
Ratings:
Scopus rating (2000): SJR 1.884 SNIP 1.379
Web of Science (2000): Indexed yes
Original language: English
Source: orbit
Source-ID: 176752
Research output: Contribution to journal › Journal article – Annual report year: 2000 › Research › peer-review

Stability of CaNi5HX stored at temperatures between 20 and 150°C

General information
Publication status: Published
Organisations: Department of Chemistry, Technical University of Denmark
Contributors: Jensen, J. O., Møller, T. S., Bjerrum, N.
Publication date: 2000
Peer-reviewed: No
Event: Abstract from 7th International Symposium on Metal-Hydrogen Systems, Noosa, Australia.
Source: orbit
Source-ID: 188080
Research output: Contribution to conference › Conference abstract for conference – Annual report year: 2000 › Research

Advanced Solid Polymer Fuel Cells for Operation at Temperatures up to 200°C

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N., Qingfeng, L.
Number of pages: 22
Publication date: 1999

Publication information
Original language: English
Source: orbit
Source-ID: 174666
Research output: Book/Report › Report – Annual report year: 1999 › Research › peer-review

Advanced Solid Polymer Fuel Cells for Operation at Temperatures up to 200°C (ASPEC)

General information
Publication status: Published
Organisations: Department of Chemistry, Novo Nordisk AS
Contributors: Bjerrum, N., Qingfeng, L., Hjuler, H. A., Bergqvist, R. S.
Number of pages: 16
Publication date: 1999

Publication information
Original language: English
Source: orbit
A PROCESS FOR THE CATALYTIC OXIDATION OF HYDROCARBONS

A process for producing an alcohol from a gaseous hydrocarbon, e.g. a lower alkane such as methane, via oxidative reaction of the hydrocarbon in a concentrated sulfuric acid medium in the presence of a catalyst employs an added catalyst comprising a substance selected from iodine, iodine compounds, titanium, titanium compounds, chromium and chromium compounds.

Complex formation during dissolution of metal oxides in molten alkali carbonates

Dissolution of metal oxides in molten carbonates relates directly to the stability of materials for electrodes and construction of molten carbonate fuel cells. In the present work the solubilities of PbO, NiO, Fe2O3,and Bi2O3 in molten Li/K carbonates have been measured at 650 degrees C under carbon dioxide atmosphere. It is found that the solubilities of NiO and PbO decrease while those of Fe2O3 and Bi2O3 remain approximately constant as the lithium mole fraction increases from 0.43 to 0.62 in the melt. At a fixed composition of the melt, NiO and PbO display both acidic and basic dissolution as the partial pressure of carbon dioxide varies. By combination of solubility and electromotive force measurements, a model is constructed assuming the dissolution involves complex formation. The possible species for lead are proposed to be [Pb(CO3)(2)](-2) and/or [Pb(CO3)(3)](-4). A similar complex chemistry for nickel oxide dissolution might be expected. (C) 1999 The Electrochemical Society. S0013-4651(98)11-017-0. All rights reserved.
Development and Characterization of Temperature-resistant Polymer Electrolytes

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Qingfeng, L., Hjuler, H. A., Bjerrum, N.
Publication date: 1999

Host publication information
Title of host publication: Proceedings of Workshop on Indirect and Direct Methanol Fuel Cells
Place of publication: Portorose
Source: orbit
Source-ID: 174656
Research output: Chapter in Book/Report/Conference proceeding

Development of Air Metal Hydride Battery (Amhbat): Fourth Periodic Report 1/12-98 til 30/11-99

General information
Publication status: Published
Organisations: Department of Chemistry
Number of pages: 81
Publication date: 1999

Publication information
Original language: English
Source: orbit
Source-ID: 174810
Research output: Book/Report

Development of Air Metal Hydride Battery (Amhbat): Mid-term Review

General information
Publication status: Published
Organisations: Department of Chemistry
Number of pages: 33
Publication date: 1999

Publication information
Original language: English
Source: orbit
Source-ID: 174812
Research output: Book/Report

Electrochemical Noise Measurements on Stainless Steel in the K2SO4-NaCl Molten System

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Cappeln, F. V., Petruchina, I., Bjerrum, N.
Pages: 1721-1721
Publication date: 1999

Host publication information
Title of host publication: Meeting Abstracts, The 1999 International Meeting
Place of publication: Honolulu
Publisher: The Electrochemical Society
Source: orbit
Source-ID: 174945
Electrochemical promotion of sulfur dioxide catalytic oxidation

General information
Publication status: Published
Organisations: Department of Chemistry, National Academy of Sciences of Ukraine
Contributors: Petruchina, I., Bandur, V., Cappeln, F. V., Bjerrum, N.
Pages: 2327-2327
Publication date: 1999

Estimation of temperature in the lubricant film during cold forging of stainless steel based on studies of phase transformation in the film

Changes in friction during backward can extrusion of stainless steel were observed for four different lubricant systems. The observed changes in friction are believed to be caused by phase transitions in the lubricant. The lubricant systems consisted of two different carrier coatings (crystalline Zn-3(PO4)(2). 4H2O and amorphous Zn1.5Ca1.5(PO4)(2)) lubricated with soap or MoS2. The temperature in the lubricant film during the process was estimated from changes in friction in correlation with observed phase transitions in the lubricant. Phase transitions in the carrier coatings as a function of pressure and temperature were investigated. Several previously unknown phase transitions were discovered. Four different crystal structures of Zn-3(PO4). xH2O were observed as a function of temperature. At 700-900 degrees C Zn-3(PO4)(2) becomes amorphous (depending on the pressure). Amorphous Zn1.5Ca1.5(PO4)(2) crystallises at 200-300 degrees C and a second phase transition is observed at 400-700 degrees C (depending on the pressure). It is estimated on the basis of the results from the backward can extrusion and analysis of the structure as a function of temperature that the temperature may reach in the excess of 450 degrees C at a height/diameter ratio of two. (C) 1999 Elsevier Science S.A. All rights reserved.

General information
Publication status: Published
Organisations: Department of Chemistry, University of Copenhagen
Contributors: Steenberg, T., Olsen, J., Christensen, E., Bjerrum, N.
Pages: 140-144
Publication date: 1999
Peer-reviewed: Yes

Publication information
Journal: Wear
Volume: 232
Issue number: 2
ISSN (Print): 0043-1648
Ratings:
Scopus rating (1999): SJR 0.833 SNIP 1.36
Original language: English
DOIs:
10.1016/S0043-1648(99)00137-4
Source: orbit
Source-ID: 174792
Research output: Contribution to journal › Journal article – Annual report year: 1999 › Research › peer-review

Højtemperaturkorrosion under Industrielle Forbrændingsprocesser

General information
Publication status: Published
Organisations: Department of Chemistry
Investigation of mercury-catalyzed oxidation of methane to methanol

Mechanisms of Lubrication and Compounds of Lubrication for Coldforging and Sheet Forging of Stainless Steel

Metal hydrides for electrodes: Towards higher capacity

Niobium Plating Processes in Alkali Chloride Melts
Oxygen reduction on carbon supported platinum catalysts in high temperature polymer electrolytes

Structural studies of disordered Mg$_2$NiH$_4$ formed by mechanical grinding

The low temperature phase of Mg$_2$NiH$_4$ was mechanically ground in argon atmosphere. The ordered monoclinic structure was destroyed to form the disordered cubic structure, previously only found above 510 K. With a Guinier-Hagg X-ray camera the cell parameter was determined to be $a=6.492(3)$ Å. By performing a Rietveld refinement on neutron diffraction data it was confirmed that the disordered structure is similar to the high temperature form of Mg$_2$NiH$_4$ (space group Fm$ar{3}$m). (© 1999 Elsevier Science S.A. All rights reserved.)
Systematic B-metal substitution in CaNi5
The aim of this work has been to study the effect of B metal substitutions in CaNi5 (AB(5)) which is known to suffer from poor cycling stability as a hydride electrode material. Systematic monosubstitutions of nickel with the most common other B metals (i.e. Al, Cr, Mn, Fe, Co, Cu, Zn and Sn) and Mg were performed. The overall composition was in all cases CaNi5-xMx (x=0.5 or 1) where M is the substituting element. The alloys were prepared by mechanical alloying. The hydrogen storage capacity was measured electrochemically ranging from 39 to 390 mAh/g, but none of the substitutions increased the cycling stability to any significant extend compared to pure CaNi5. X-ray diffraction patterns of the alloys revealed that only in a few cases the hexagonal CaCu5 structure of a true AB(5) alloy was preserved. In most cases diffraction patterns matching Ca2Ni7, CaNi3 or CaNi2 were seen. It can be concluded that CaNi5 is much less tolerant towards B-metal substitution than LaNi5. This fact makes it less possible that the problem with cycling stability of Ca-based hydride electrodes can be solved by substitutions. (C) 1999 Elsevier Science S.A. All rights reserved.

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Bjerrum, N.
Pages: 185-189
Publication date: 1999
Peer-reviewed: Yes

Publication information
Journal: Journal of Alloys and Compounds
Volume: 293-295
ISSN (Print): 0925-8388
Ratings:
Scopus rating (1999): SJR 0.744 SNIP 0.927
Original language: English
Keywords: Hydrides, CaNi5, Electrodes, Substitution, Hydrogen storage
DOI:
10.1016/S0925-8388(99)00418-1
Source: orbit
Source-ID: 174798
Research output: Contribution to journal › Journal article – Annual report year: 1999 › Research › peer-review
The Effect of the Melting Composition on Electrode Processes and Structure of Tantalum-Boride Coatings

General information
Publication status: Published
Organisations: Department of Chemistry, Institute of Chemistry
Contributors: Makarova, O., Polyakova, L., Polyakov, E., Bjerrum, N.
Pages: 2320-2320
Publication date: 1999

Host publication information
Title of host publication: Meeting Abstracts, The 1999 Joint International Meeting
Place of publication: Honolulu
Publisher: The Electrochemical Society
Source: orbit
Source-ID: 174784
Research output: Contribution to journal – Journal article – Annual report year: 1999 – Research – peer-review

The Solubility of metal oxides in molten carbonates - why the acid-basic chemistry fails?

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N., Qingfeng, L., Borup, F., Petruchina, I.
Pages: 48-52
Publication date: 1999

Host publication information
Title of host publication: Proceedings of The International George Papatheodorou Symposium
Place of publication: Patras
Publisher: ICE/HT
Source: orbit
Source-ID: 174661

The Study of Electrode Processes in LiF-NaF-KF-K2TaF7-KBF4 melt

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Russian Academy of Sciences
Contributors: Polyakova, L., Polyakov, E., Bjerrum, N.
Pages: 117-125
Publication date: 1999
Peer-reviewed: Yes

Publication information
Journal: Plasmas & Ions
Volume: 2
Issue number: 3-4
ISSN (Print): 1288-3255
Original language: English
Source: orbit
Source-ID: 246681
**Advanced Solid Polymer Fuel Cells for Operation at Temperatures up to 200°C (ASPEC): Technical report 1/2-98-30/6-98**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Technical University of Denmark
Contributors: Bjerrum, N., Qingfeng, L., Bergqvist, R. S.
Number of pages: 12
Publication date: 1998

**Publication information**
Original language: English
Source: orbit
Source-ID: 170599
Research output: Book/Report › Report – Annual report year: 1998 › Research › peer-review

**Characterization of Niobium Platings Obtained from NaCl-KCl Melts**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Gillesberg, B., Barner, J. H. V., Bjerrum, N.
Publication date: 1998

**Host publication information**
Title of host publication: Programme Abstracts of European Research Conferences, Molten Salts: From Structural Aspects to Waste Processing
Place of publication: Porquerolles
Publisher: Institut Universitaire des Systèmes Thermiques Industriels
Source: orbit
Source-ID: 170639
Research output: Chapter in Book/Report/Conference proceeding › Article in proceedings – Annual report year: 1998 › Research

**Chemical interactions between extreme pressure lubricants and stainless steel during ironing procedure.**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, Department of Management Engineering
Contributors: Møller, P. B., Petrushina, I., Christensen, E., Bjerrum, N., Høj, J., Kann, G., Andreasen, J. L., Bay, N.
Pages: 721-728
Publication date: 1998

**Host publication information**
Title of host publication: Proceed. 8th Int. Conf. Tribology, NORDTRIB'98
Publisher: Publisher unknown
URLs: http://www.ipl.dtu.dk/publikation/8881/dk/
Source: orbit
Source-ID: 187609
Research output: Chapter in Book/Report/Conference proceeding › Article in proceedings – Annual report year: 1998 › Research › peer-review

**Conversion of Methane**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Gang, X., Bjerrum, N.
Number of pages: 25
Publication date: 1998
Corrosion behavior of various steels in molten NaCl-K2SO4

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Cappeln, F. V., Petruchina, I., Bjerrum, N.
Publication date: 1998

Host publication information
Title of host publication: Proceedings of European Research Conferences, Molten Salts: From Structural Aspects to Waste Processing
Place of publication: Porquerolles
Publisher: Institut Universitaire des Systèmes Thermiques Industriel
Source: orbit
Source-ID: 170636

Development of Air Metal Hydride Battery (Amhbat): First Periodic Report 1/12-97 til 30/6-98

General information
Publication status: Published
Organisations: Department of Chemistry
Number of pages: 11
Publication date: 1998

Publication information
Original language: English
Source: orbit
Source-ID: 174809

Development of Air Metal Hydride Battery (Amhbat): Second Periodic Report 1/12-97 til 30/11-98

General information
Publication status: Published
Organisations: Department of Chemistry
Number of pages: 95
Publication date: 1998

Publication information
Original language: English
Source: orbit
Source-ID: 170606

Development of fuel cells

General information
Publication status: Published
Organisations: Department of Chemistry, Technical University of Denmark
Contributors: Hennesø, E., Bjerrum, N.
Number of pages: 85
Publication date: 1998
Electrochemical and Spectroscopic Investigation of Electrochemical Cells and Catalysts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Petrushina, I., Bjerrum, N.
Number of pages: 14
Publication date: 1998

Publication information
Original language: English
Source: orbit
Source-ID: 170602
Research output: Book/Report › Report – Annual report year: 1998 › Research › peer-review

Electrochemical and Spectroscopic Investigation of Electrochemical Cells and Catalysts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Petrushina, I., Bjerrum, N., Cappeln, F. V.
Pages: 3721-3728
Publication date: 1998
Peer-reviewed: Yes

Publication information
Journal: Journal of The Electrochemical Society
Volume: 145
Issue number: 11
ISSN (Print): 0013-4651
Original language: English
Electronic versions:
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DOIs:
10.1149/1.1838865
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http://dx.doi.org/10.1149/1.1838865

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Copyright The Electrochemical Society, Inc. [1998]. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, resold, distributed, or modified without the express permission of The Electrochemical Society (ECS).
Electrolytic depositions of amorphous and crystalline zink-calcium phosphates

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, Technical University of Denmark
Contributors: Olesen, P., Steenberg, T., Christensen, E., Bjerrum, N.
Pages: 3059-3063
Publication date: 1998
Peer-reviewed: Yes

Publication information
Journal: Journal of Materials Science
Volume: 33
ISSN (Print): 0022-2461
Original language: English
Source: orbit
Source-ID: 170590

Environmentally Safe Lubricants for Sheet Forming and Coldforging of Stainless Steel: Final Report for the Project

General information
Publication status: Published
Organisations: Department of Chemistry
Number of pages: 49
Publication date: 1998

Publication information
Publisher: Technical University of Denmark (DTU)
Original language: English
Source: orbit
Source-ID: 170604

Estimation of Temperature in the Lubricant Film during Cold Forging of Stainless steel

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, University of Copenhagen
Contributors: Steenberg, T., Olsen, J. S., Christensen, E., Bjerrum, N.
Pages: 695-701
Publication date: 1998

Host publication information
Title of host publication: Proceedings of the 8th International Conference on Tribology
Place of publication: Aarhus
Source: orbit
Source-ID: 170624

FeCl3 - A potential new lubricant for cold forging of stainless steel.

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Management Engineering
Contributors: Steenberg, T., Christensen, E., Bay, N., Bjerrum, N.
Publication date: 1998
METHOD FOR ELECTROCHEMICAL PHOSPHATING OF METAL SURFACES, PARTICULARLY STAINLESS STEEL, AND APPLICATION OF AN AQUEOUS PHOSPHATING SOLUTION FOR SUCH A METHOD

A method for electrochemical phosphating of metal surfaces, particularly stainless steel, in connection with cold forming of metal workpieces, which method provides the cold formed work-piece with a lubricant after phosphating, involves an electrochemical phosphating through a cathodic process applying an aqueous phosphating solution containing: 0.5 to 100 g Ca?2+¿/1, 0.5 to 100 g Zn?2+¿/1, 5 to 100 g PO¿4??3-¿/1, 0 to 100 g NO¿3??-¿/1, 0 to 100 g ClO¿3??-¿/1 and 0 to 50 g F?-¿ or Cl?-¿/1, by which the temperature of the solution is between 0 and 95 °C, the pH-value of the solution is between 0.5 and 5, and the current density is between 0.1 and 250 mA/cm?2¿. This gives a good lubrication effect, a good adhesion to the metal surface, particularly stainless steel, and a more expedient texture than ordinary phosphating.
**Systematic B-metal substitution in CaNi₅**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Bjerrum, N.
Publication date: 1998
Peer-reviewed: No
Source: orbit
Source-ID: 188077
Research output: Contribution to conference » Poster – Annual report year: 1998 » Research

**Tantalum Coating of Steel, Copper, Aluminum, and Titanium by Thermal Chemical Vapor Deposition (CVD)**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Christensen, E., Bjerrum, N.
Pages: 852-852
Publication date: 1998

**Host publication information**
Title of host publication: Meeting Abstracts, The 194 th Meeting of The Electrochemical Society
Place of publication: Boston
Publisher: The Electrochemical Society
Source: orbit
Source-ID: 170553
Research output: Chapter in Book/Report/Conference proceeding » Article in proceedings – Annual report year: 1998 » Research

**The Study of Electrode Processes During Electrochemical Synthesis of Tantalum Borides in Oxofluoride Melts**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Russian Academy of Sciences
Contributors: Polyakova, L., Makarova, O., Polyakov, E., Christensen, E., Barner, J. H. V., Bjerrum, N.
Pages: 58-58
Publication date: 1998

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Source-ID: 171039
Research output: Chapter in Book/Report/Conference proceeding » Article in proceedings – Annual report year: 1998 » Research

**The study of electrode processes during tantalum boride electrochemical synthesis in oxofluoride melts**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Russian Academy of Sciences, Institute of Chemistry
Contributors: Polyakov, E., Polyakova, L., Makarova, O., Kremenetsky, V., Christensen, E., Barner, J. H. V., Bjerrum, N.
Pages: 619-626
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**Publication information**
Developments of New Lubricants for Cold Forging of Stainless Steel

Two new lubricant systems for cold forging of stainless steel have been developed. The main component of these systems are FeCl₃ and ZnCa₂(PO₄)₂, respectively. Both lubricant systems have been tested using a backward extrusion test. The results show excellent lubricating properties with respect to obtainable height of cup and friction. It is proposed that the formation of FeCl₂ plays an important role in the lubrication mechanism of FeCl₃. The ZnCa₂(PO₄)₂ coating have been lubricated with sodium stearate and MoS₂ and the best results were obtained with sodium stearate.

Electrochemical and Spectroscopic Investigations of Lower Valent States of Niobium in Fluoride Melts

The electrochemical behavior of K₂S₂O₇-KHSO₄-V₂O₅, K₂S₂O₇-V₂O₄ and K₂S₂O₇-KHSO₄-V₂O₄ melts was studied in argon and SO₂/air atmospheres using a gold electrode. In order to identify the voltammetric waves due to KHSO₄, molten KHSO₄ and mixtures of K₂S₂O₇-KHSO₄ were investigated by voltammetry performed with Au and Pt electrodes in an argon atmosphere. It was shown that H⁺ reduction took place at 0.26 V vs. an Ag+/Ag reference electrode, i.e., at a potential in between the V(V) → V(IV) and V(IV) → V(III) reduction stages. The presence of KHSO₄ caused an increased concentration of V(III) species in the V₂O₅ containing molten electrolytes. This effect may be caused either by protonic promotion of the V(IV) → V(III) reduction (VO₂⁺ + 2H(+) + e⁻ → V³⁺ + H₂O) or by chemical reduction of V(IV) complexes with hydrogen, formed from H⁺ as the product of the electrochemical reduction. Both the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation remained one-electron electrochemical reactions after the addition of KHSO₄ (or water) to the H₂S₂O₇-V₂O₅ melt. Water had no noticeable effect on the V(V) → V(IV) reduction but the V(IV) → V(V) oxidation proceeded at higher polarizations in the water-containing melts in both argon and SO₂/air atmospheres. This effect may be explained by participation of the water molecules in the V(IV) active complexes.

Electrochemical Behavior of Molten V₂O₅-K₂S₂O₇-KHSO₄ Systems

The electrochemical behavior of K₂S₂O₇-KHSO₄-V₂O₅, K₂S₂O₇-V₂O₄ and K₂S₂O₇-KHSO₄-V₂O₄ melts was studied in argon and SO₂/air atmospheres using a gold electrode. In order to identify the voltammetric waves due to KHSO₄, molten KHSO₄ and mixtures of K₂S₂O₇-KHSO₄ were investigated by voltammetry performed with Au and Pt electrodes in an argon atmosphere. It was shown that H⁺ reduction took place at 0.26 V vs. an Ag+/Ag reference electrode, i.e., at a potential in between the V(V) → V(IV) and V(IV) → V(III) reduction stages. The presence of KHSO₄ caused an increased concentration of V(III) species in the V₂O₅ containing molten electrolytes. This effect may be caused either by protonic promotion of the V(IV) → V(III) reduction (VO₂⁺ + 2H(+) + e⁻ → V³⁺ + H₂O) or by chemical reduction of V(IV) complexes with hydrogen, formed from H⁺ as the product of the electrochemical reduction. Both the V(V) → V(IV) reduction and the V(IV) → V(V) oxidation remained one-electron electrochemical reactions after the addition of KHSO₄ (or water) to the H₂S₂O₇-V₂O₅ melt. Water had no noticeable effect on the V(V) → V(IV) reduction but the V(IV) → V(V) oxidation proceeded at higher polarizations in the water-containing melts in both argon and SO₂/air atmospheres. This effect may be explained by participation of the water molecules in the V(IV) active complexes.
Electrochemical investigation on the redox chemistry of niobium in LiCl-KCl-KF-Na2O melts

The system LiCl-KCl-KF-1 mole percent K2NbF7 (molar ration F-/Nb = 8) has been investigated in the temperature range 370 to 725 degrees C by cyclic and square wave voltammetry. In the temperature range from 370 to 520 degrees C Nb(V) was reduced to Nb(III) in two reversible steps: Nb(V) --> Nb(IV) --> Nb(III). At these temperatures subvalent halides of niobium were formed at more negative potentials. At temperatures above 660 degrees C metallic niobium was formed during reduction. When oxide (molar ratio O2-/Nb = 1.1) was introduced in the melt at 725 degrees C only minor changes were observed in the voltammograms. It is suggested that oxide addition mainly leads to precipitation of oxide containing compounds.

General information
Publication status: Published
Organisations: Department of Chemistry, Universite Pierre et Marie Curie
Contributors: Gillesberg, B., Bjerrum, N., Barner, J. H. V., Lantelme, F.
Pages: 3435-3441
Publication date: 1997
Peer-reviewed: Yes
Electrodeposition of Tantalum-boride Coatings From Oxofluoride Melts.

Environmentally Safe Lubricants for Sheet Forming and Coldforging of Stainless Steel

FeCl₃·6H₂O-A Potential New Lubricant for Cold Forging of Stainless Steel
**Nature of Alkali Metal Promotion and Electrochemical Promotion of the Catalytic SO\textsubscript{2} Oxidation**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Petruchina, I., Bjerrum, N., Cappeln, F. V.
Publication date: 1997

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Place of publication: Frankfurt am Main
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**New Surface Treatment Technique**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Technical University of Denmark, Esti Chem A/S, Houghton Denmark A/S
Contributors: Petruchina, I., Bjerrum, N., Christensen, E., Møller, P., Mathiesen, T., Petersen, S.
Publication date: 1997

**Publication information**
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Original language: Danish
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**Production of Tantalum Coatings on Steel by Thermal Activated Vapor Deposition (CVD)**

**General information**
Publication status: Published
Organisations: Department of Chemistry
Contributors: Eriksen, S., Christensen, E., Bjerrum, N.
Number of pages: 10
Publication date: 1997

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Research output: Chapter in Book/Report/Conference proceeding – Article in proceedings – Annual report year: 1997 – Research

**Screening the performance of lubricants for ironing of stainless steel with a strip reduction test**

A laboratory strip reduction test simulating the tribological conditions of an ironing process is proposed. The test is capable of simulating varying process conditions such as reduction, drawing speed, tool temperature and sliding length. The test makes it possible to quantify the onset of breakdown of the lubricant film and subsequent galling. Experimental investigations of stainless steel show the influence of varying process conditions and the performance of different lubricants.

**General information**
Publication status: Published
Organisations: Department of Management Engineering, Department of Chemistry, Department of Chemistry
Contributors: Andreasen, J. L., Bay, N., Andersen, M. M., Christensen, E., Bjerrum, N.
Pages: 1-5
Publication date: 1997
Peer-reviewed: Yes
Screening the performance of lubricants for ironing of stainless steel with a strip reduction test.

General information
Publication status: Published
Organisations: Department of Management Engineering, Department of Chemistry
Contributors: Andreasen, J. L., Bay, N., Andersen, M., Christensen, E., Bjerrum, N.
Publication date: 1997

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CaNi5 prepared by mechanical alloying

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Jensen, J. O., Berg, R. W., Bjerrum, N.
Publication date: 1996

Host publication information
Place of publication: Friburg
Publisher: MH96, Institut of Physics, University of Friburg
Source: orbit
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Research output: Chapter in Book/Report/Conference proceeding – Article in proceedings – Annual report year: 1996 – Research

Characterization of La1-xSrxCrO3±d (x = 0.2, d 0) Powders by X-ray Powder Diffraction

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Berg, R., Andersen, M. M., Bjerrum, N.
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Publication date: 1996

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Electrochemical and spectroscopic behaviour of iron in the molten NaCl-K2SO4 mixture

General information
Publication status: Published
Organisations: Department of Chemistry, National Academy of Sciences of Ukraine
Pages: 27
Publication date: 1996
Peer-reviewed: Yes

Publication information
Journal: Ukrainian Chemical Journal
Issue number: 62
Original language: English
Source: orbit
Source-ID: 166497

Electrochemical behavior of boron in LiF-NaF-KF- melts
The electrochemical reduction of B(III) to B(0) in KBF4-LiF-NaF-KF melts has been studied by voltammetric and chronopotentiometric methods. Glassy carbon, Pt, and Ag were used as working electrode materials. Only in the case of Ag was the reduction not complicated by interaction between boron and the electrode material. On a silver electrode B(III) was reduced to B(0) in a single irreversible step in the KBF4 concentration range up to 5.7 x 10(-2) mole percent (m/o). The cathodic half-wave potential was -1.34 V vs, an Ag/AgCl reference electrode at 700 degrees C. The diffusion coefficient of BF4- at 700 degrees C was determined to be 2.06 X 10(-5) cm(2) s(-1). Further increase of the KBF4 concentration above 5.7 x 10(-2) m/o leads to a change in the reduction process. An ohmic resistance control becomes the limiting factor of the boron electroreduction process. The "apparent surface resistance" changes from 3.0 to 21.6 Ohm cm(2) as the temperature decreases from 700 to 550 degrees C, respectively. Furthermore at KBF4 concentrations higher than 5.7 x 10(-2) m/o a second reduction peak and a corresponding anodic peak appeared on the voltammograms. These peaks were attributed to formation of alkali metal borides.

General information
Publication status: Published
Organisations: Department of Chemistry, Russian Academy of Sciences
Contributors: Polyakova, L., Bukatova, G., Polyakova, E., Christensen, E., Barner, J. H. V., Bjerrum, N.
Pages: 3178-3186
Publication date: 1996
Peer-reviewed: Yes

Publication information
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Source: orbit
Source-ID: 166491

Research output: Contribution to journal › Journal article – Annual report year: 1996 › Research › peer-review
Investigation of the Possibilities for Introduction of Environmental Lubricants for Plastic Modelling of Stainless Steel, Incl. Test and Methods of Analysis

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N.
Number of pages: 5
Publication date: 1996

Report Concerning Explosion Accident at Department of Chemistry, University of Copenhagen

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N.
Number of pages: 3
Publication date: 1996

The redox chemistry of niobium(V) fluoro and oxofluoro complexes in LiF-NaF-KF melts
The electrochemical behavior of niobium(V) fluoro and oxofluoro complexes in eutectic LiF-NaF-KF (FLINAK) melts at 700 degrees C has been studied by cyclic voltammetry. The fluoro complexes NbF72-, introduced into the melt by the addition of K2NbF7, can be reduced to niobium metal in two reversible steps involving one and four electrons, respectively. At 700 degrees C the diffusion constants of the fluoro niobate complexes involved in these reduction steps, i.e., NbF72- and Nb(IV)F-x((x-4)-), were determined to be 8.3 x 10(-6) and 3.4 x 10(-5) cm(2)/s, respectively. Titration with equivalent amounts of oxide ions, introduced as Na2O, leads to a conversion of NbF72- to oxofluoro complexes of the type NbOFn(n-3-) and NbO2F43-. At 700 degrees C the conversion of NbF72- to NbOFn(n=3) is not complete, and the degree of conversion is shown to depend strongly on temperature. Thus, at 645 degrees C the conversion is more nearly complete than at 700 degrees C, while the presence of NbOFn(n=3-) complexes cannot be identified in cyclic voltammograms obtained at 795 degrees C. It is concluded that the degree of conversion decreases with increasing temperature. At Na2O/K2NbF7 molar ratios equal to three, electroactivity is still observed in the melt, indicating the presence of solute species. The products of reduction of the oxofluoro complexes have not been identified because the reduction of NbOFn(n=3-) ions cannot be obtained without simultaneous reduction of Nb(IV)F-x((x-4)-) ions, and at Na2O/K2NbF7 molar ratios exceeding two, no deposits are obtained. The reduction of the oxofluoro complex NbO2F43-, and complexes formed at Na2O/K2NbF7 molar ratios exceeding two always proceed in one step.

General information
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Organisations: Department of Chemistry, Department of Chemistry, Grundfos DK AS
Contributors: Matthiesen, F., Christensen, E., Barner, J. H. V., Bjerrum, N.
Pages: 1793-1799
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Peer-reviewed: Yes

The redox chemistry of niobium(V) fluoro and oxofluoro complexes in LiF-NaF-KF melts
The electrochemical behavior of niobium(V) fluoro and oxofluoro complexes in eutectic LiF-NaF-KF (FLINAK) melts at 700 degrees C has been studied by cyclic voltammetry. The fluoro complexes NbF72-, introduced into the melt by the addition of K2NbF7, can be reduced to niobium metal in two reversible steps involving one and four electrons, respectively. At 700 degrees C the diffusion constants of the fluoro niobate complexes involved in these reduction steps, i.e., NbF72- and Nb(IV)F-x((x-4)-), were determined to be 8.3 x 10(-6) and 3.4 x 10(-5) cm(2)/s, respectively. Titration with equivalent amounts of oxide ions, introduced as Na2O, leads to a conversion of NbF72- to oxofluoro complexes of the type NbOFn(n=3-) and NbO2F43-. At 700 degrees C the conversion of NbF72- to NbOFn(n=3) is not complete, and the degree of conversion is shown to depend strongly on temperature. Thus, at 645 degrees C the conversion is more nearly complete than at 700 degrees C, while the presence of NbOFn(n=3-) complexes cannot be identified in cyclic voltammograms obtained at 795 degrees C. It is concluded that the degree of conversion decreases with increasing temperature. At Na2O/K2NbF7 molar ratios equal to three, electroactivity is still observed in the melt, indicating the presence of solute species. The products of reduction of the oxofluoro complexes have not been identified because the reduction of NbOFn(n=3-) ions cannot be obtained without simultaneous reduction of Nb(IV)F-x((x-4)-) ions, and at Na2O/K2NbF7 molar ratios exceeding two, no deposits are obtained. The reduction of the oxofluoro complex NbO2F43-, and complexes formed at Na2O/K2NbF7 molar ratios exceeding two always proceed in one step.

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, Grundfos DK AS
Contributors: Matthiesen, F., Christensen, E., Barner, J. H. V., Bjerrum, N.
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Electrochemical Investigation of The Catalytical Processes During Sulfuric Acid Production.

The electrochemical behavior of molten K2S2O7 and its mixtures with V2O5 [2–20 mole percent (m/o) V2O5] was studied at 440°C in argon, by using cyclic voltammetry on a gold electrode. The effect of the addition of sulfate and lithium ions on the electrochemical processes in the molten potassium pyrosulfate was also investigated. The potential window for pure K2S2O7 was estimated as 2.1 V, being limited by the S2O7\(^{2-}\) oxidation and reduction. The oxidation of SO\(^{4-}\) to oxygen is irreversible in the basic melt. It is found that V(V) electroreduction proceeds in two steps. The first reduction stage [V(V) \(\rightarrow\) V(IV)], starting at 0.7–0.8 V vs. Ag+/Ag, is reversible for V2O5 concentrations lower than 5 m/o and at potential scan rates less than 200 mV/s. For all studied compositions, the first reduction stage is a one-electron reaction. The second reduction stage [V(IV) \(\rightarrow\) V(III)], starting at 0.1–0.2 V, is irreversible and under ohmic control at all studied V2O5 concentrations. The presence of Li2SO4 causes a noticeable depolarization effect on the V(V) reduction and the V(IV) oxidation.

Hydrogen Oxidation on Gas Diffusion Electrodes for Phosphoric Acid Fuel Cells in the Presence of Carbon Monoxide and Oxygen

Hydrogen oxidation has been studied on a carbon-supported platinum gas diffusion electrode in a phosphoric acid electrolyte in the presence of carbon monoxide and oxygen in the feed gas. The poisoning effect of carbon monoxide present in the feed gas was measured in the temperature range from 80 to 150°C. It was found that throughout the temperature range, the potential loss due to the CO poisoning can be reduced to a great extent by the injection of small amounts of gaseous oxygen into the hydrogen gas containing carbon monoxide. By adding 5 volume percent (v/o) oxygen, an almost CO-free performance can be obtained for carbon monoxide concentrations up to 0.5 v/o CO at 130°C, 0.2 v/o CO at 100°C, and 0.1 v/o CO at 80°C, respectively.
Oxygen Reduction on Gas-Diffusion Electrodes for Phosphoric Acid Fuel Cells by a Potential Decay Method

The reduction of gaseous oxygen on carbon supported platinum electrodes has been studied at 150 degrees C with polarization and potential decay measurements. The electrolyte was either 100 weight percent phosphoric acid or that acid with a fluorinated additive, potassium perfluorohexanesulfonate (C6F13SO3K). The pseudo-Tafel curves of the overpotential vs. log (i/(L)/(i(L) - i)) show a two-slope behavior, probably due to different adsorption mechanisms. The potential relaxations as functions of log (t + tau) and log (-d eta/dt) have been plotted. The variations of these slopes and the dependence of the double-layer capacitance on the overpotential depended on the electrode manufacture and the kind of electrolyte (whether containing the fluorinated additive or not).

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Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Department of Chemistry
Contributors: Li, Q., Gang, X., Hjuler, H. A., Berg, R. W., Bjerrum, N.
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Source: orbit
Source-ID: 248388
Research output: Contribution to journal › Journal article – Annual report year: 1995 › Research › peer-review
Use of Vibrational Spectroscopy to Determine Oxide Content of Alkali Metal Fluoride-Tantalum Melts.

Electrochemical Study of Tantalum in Fluoride and Oxofluoride Melts

The electrochemical behavior of tantalum in the form of K2TaF7 in an LiF-NaF-KF eutectic melt has been studied by linear voltammetry in the temperature range of 560 to 815-degrees-C with and without additions of Na2O. An amperometric titration has been performed by measuring the heights of the cathodic and the anodic peaks. It was shown that at a molar ratio Na2O/K2TaF7 = 1 the predominating complex in the melt is TaO2F5(2-), whereas with an Na2O/K2TaF7 molar ratio of 2 it is TaO2F(x)(x-1-), probably in the form of TaO2F4(3-). Increase in the Na2O/K2TaF7 molar ratio in excess of two leads to a decrease of tantalum concentration in the melt, and precipitation of KTaO3 occurs. Both the fluoro complex and the monooxofluoro complex were reduced to metal in a single five-electron step. The fluoro complexes, in the temperature range 625 to 815-degrees-C with potential scan rates 0.5 V . s-1 they discharge irreversibly. Monooxofluoro complexes discharge irreversibly at all temperatures and scan rates studied. The diffusion coefficient of the tantalum fluoro complex depends on the temperature as log D = -2.55 - 2044/T with an activation energy of 39.1 kJ . mol-1. For the tantalum monooxofluoro complex the dependence is log D = -2.35 - 2293/T with an activation energy of 43.9 kJ . mol-1.
Limiting Current of Oxygen Reduction on Gas-Diffusion Electrodes for Phosphoric Acid Fuel Cells

Various models have been devoted to the operation mechanism of porous diffusion electrodes. They are, however, suffering from the lack of accuracy concerning the acid-film thickness on which they are based. In the present paper the limiting current density has been measured for oxygen reduction on polytetrafluorine-ethyl bonded gas-diffusion electrodes in phosphoric acid with and without fluorinated additives. This provides an alternative to estimate the film thickness by combining it with the acid-adsorption measurements and the porosity analysis of the catalyst layer. It was noticed that the limiting current density can be accomplished either by gas-phase diffusion or liquid-phase diffusion, and it is the latter that can be used in the film-thickness estimation. It is also important to mention that at such a limiting condition, both the thin-film model and the filmed agglomerate model reach the same expression for the limiting current density. The acid-film thickness estimated this way was found to be of 0.1 mum order of magnitude for the two types of electrodes used in phosphoric acid with and without fluorinated additives at 150-degrees-C.

The Influence of Oxide on the Electrodeposition of Niobium from Alkali Fluoride Melts

Electrodeposit of niobium metal from K2NbF7-LiF-NaF-KF-Na2O melts at 700-degrees-C has been investigated. It was found that the equilibrium oxidation state of niobium was four for initial O2-/Nb(V) ratios of up to at least one. On the other hand when a niobium metal sheet was used for the reduction, average oxidation states close to five were obtained. Cyclic voltammetry showed that NbF72- is reduced in two steps. A mechanism Nb(V) --> Nb(IV) --> Nb(0) is proposed. When oxide is present, new waves due to reduction of niobium mono-oxofluoro and dioxofluoro complexes are observed at -0.6 and -0.74 V, respectively. In addition plating experiments were also performed. The substrates in our work were low-carbon steel, the anodes niobium metal, and the current density was around 90 mA/cm2. It was found that the presence of at least 1 mole percent of oxide was necessary to obtain current efficiencies higher than 30%. The highest current efficiencies obtained were around 95%. For oxide/Nb(V) molar ratios equal to or higher than one, partially nonmetallic surface layers were deposited.
Complex Formation in Pyrosulfate Melts. 4. Density, Potentiometry, Calorimetry and Conductivity of the Systems Cs2S2O7-V2O5, Cs2S2O7-Cs2SO4 and Cs2S2O7-Cs2SO4-V2O5 in the Temperature Range 340-550°C

Crystal Structure and Spectroscopic Characterization of CsV(SO4)2 Evidence for an Electronic Raman Transition

Electrolyte Additives for Phosphoric Acid Fuel Cells

Electrochemical characteristics of a series of modified phosphoric acid electrolytes containing fluorinated carbon compounds and silicone fluids as additives are presented. When used in phosphoric acid fuel cells, the modified electrolytes improve the performance due to the enhanced oxygen reduction rate. Among useful additives we found
potassium perfluorohexanesulfonate (C₆F₁₃SO₃K), potassium nonafluorobutanesulfonate (C₄F₉SO₃K), perfluorotributylamine [(C₄F₉)₃N], and polymethylsiloxanes [(-Si(CH₃)₂O-)ₙ]. The wettability of the electrodes by the modified electrolytes also is discussed, as a fuel-cell performance with the modified electrolytes. Specific conductivity measurements of some of the modified phosphoric acid electrolytes are reported. At a given temperature, the conductivity of the C₄F₉SO₃K-modified electrolyte decreases with an increasing amount of the additive; the conductivity of the remains at the same value as the conductivity of the pure phosphoric acid. At a given composition, the conductivity of any modified electrolyte increases with temperature. We conclude that the improved cell performance for modified electrolytes is not due to any increase in conductivity.

Mechanism of Reaction in NaAlCl₄ Molten Salt Batteries with Nickel Felt Cathodes and Aluminum Anodes. Part II: Experimental Results and Comparison with Model Calculations.

The battery systems: Al/NaCl-AlCl₃-Al(2)X(3)/Ni-felt (X = S, Se, Te) and the corresponding system without chalcogen have been studied experimentally at 175 degrees C. Charge/discharge experimental performed on cells with NaCl saturated melts, show that advantages with regard to rate capability and cyclability can be obtained with systems containing dissolved chalcogen compared with the chalcogen-free system. Exchange of chalcogen between cathode and electrolyte during cycling was confirmed by performing gravimetric analysis and Raman spectroscopy of the electrolytes. Cathode reactions were studied by coulometric titrations (performed on cells with slightly acidic NaCl-AlCl₃ melts and small amounts of chalcogen) and compared with model calculations. Cells containing chalcogen revealed at least three voltage plateaus during cycling. The lowest plateau is associated with formation/decomposition of essentially Ni₄Sₓ and Ni₄Seₙ in the sulfide and selenide system, respectively. Cells containing selenide revealed extra capacity below the Ni₄Seₙ-plateau, most probably associated with a AlvNi₄Seₙ compound. On the second plateau of sulfide systems NiCl₂ or a Ni₄SₙCl₂y-2z compound with y > (4.4 +/- 0.2). z is formed during charging. Reduction of the formed compound to Ni takes place via consumption of sodium chloride. For acidic melts, sulfide at the cathode was found to be present as...

A theoretical description of the thermodynamic properties of the battery systems: Al/NaCl-AlCl₃-Al(2)X(3)/Ni-felt (X = S, Se, Te) and the corresponding system without chalcogen has been provided for cells with basic to slightly acidic NaCl-AlCl₃ melts containing small amounts of chalcogen. The model developed describes the equilibrium concentrations of constituent species in the electrolyte and equilibrium potentials of the electrodes vs. number of coulombs passed through the cells. For cells without chalcogen curves were calculated under the assumption of NiCl₂ formation showing corresponding variation of anode potential, cathode potential, and cell voltage as a function of electrolyte composition. For sulfide containing cells the plateau of lowest potential has been found to be associated with essentially pure nickel sulfide, NixS ninja. A procedure for model fitting to the cathode potential curve-form of the NixS plateau is presented. A general equation is proposed for the reaction taking place along the second plateau.

Molten Triazolium Chloride Systems as New Aluminum Battery Electrolytes

The possibility of using molten mixtures of 1,4-dimethyl-1,2,4-triazolium chloride (DMTC) and aluminum chloride (AlCl₃) as secondary battery electrolytes was studied, in some cases extended by the copresence of sodium chloride. DMTC-AlCl₃ mixtures demonstrated high specific conductivity in a wide temperature range. The equimolar system is most conductive and has kappa values between 4.02 x 10(-5) and 7.78 x 10(-2) S cm⁻¹ in the range from -31 to 123-degrees-C.
respectively. The electrochemical window of DMTC-containing sodium tetrachloroaluminate melts varied in the region of 2.5 to 2.2 V (150-170-degrees-C) depending on melt acidity and anode material. DMTC, being specifically adsorbed and reduced on the tungsten electrode surface, had an inhibiting effect on the aluminum reduction, but this effect was suppressed on the aluminum substrate. An electrochemical process with high current density (tens of milliamperes per square centimeter) was observed at 0.344 V on the acidic sodium tetrachloroaluminate background, involving a free triazolium radical mechanism. Molten DMTC-AlCl₃ electrolytes are acceptable for battery performance and both the aluminum anode and the triazolium electrolyte can be used as active materials in the acidic DMTC-AlCl₃ mixtures.
Electrochemical and Spectroscopic Studies of Tantalum in NaCl-AlCl₃ Melts at 160-300°C.

Conductivity, Thermal Analysis, and Phase Diagram of the System Cs₂S₂O₇-V₂O₅. Spectroscopic Characterization of the Compound, Cs₄(VO₂)₂(SO₄)₂S₂O₇

ESR-Investigations of Sulfuric Acid Catalyst Deactivation
Influence of Substrates on the Electrochemical Deposition and Dissolution of Aluminum in NaAlCl₄ Melts.

The deposition and dissolution of aluminum in NaAlCl₄ melts saturated with NaCl have been investigated by voltammetry and potentiometry for different electrode materials at 175°C. The tungsten and glassy carbon electrodes are shown to be electrochemically inert in the melts, whereas copper is electrochemically active; it dissolves into the melts at a low anodic potential. On a nickel substrate, nickel dichloride will be formed at a potential of ca. 1.0 V vs. an aluminum reference electrode. The reversibility (of deposition and dissolution of aluminum) is found to be strongly affected by current density and the coulombic charges used for glassy carbon electrodes, mainly because of poor adhesion of the deposits to the substrate. The reversibility is noticeably affected by the magnitude of deposition current density for the tungsten electrodes, while it remains high on the nickel electrode under all conditions investigated. Nickel and, to some extent, tungsten electrodes proved to be appropriate as working anodes in the Al/NaCl-AlCl₃/Ni battery system.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Li, Q., Hjuler, H. A., Berg, R. W., Bjerrum, N.
Pages: 763-766
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Peer-reviewed: Yes

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Source: orbit
Source-ID: 248625
Research output: Contribution to journal › Journal article – Annual report year: 1991 › Research › peer-review

The Crystal Structure of NaV(SO₄)₂

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Boghosian, S., Papatheodorou, G., Nielsen, K., Berg, R. W., Bjerrum, N.
Pages: 961-964
Publication date: 1991
Peer-reviewed: Yes

Publication information
Journal: Acta Chemica Scandinavica
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Original language: English
Source: orbit
Source-ID: 248622
Research output: Contribution to journal › Journal article – Annual report year: 1991 › Research › peer-review
Vibrational Spectra of Nb(V) Fluoro and Oxofluoro Complexes Formed in Alkali-Metal Fluoride Melts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Barner, J. H. V., Christensen, E., Bjerrum, N., Gilbert, B.
Pages: 561-566
Publication date: 1991
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 30
ISSN (Print): 0020-1669
Original language: English
Source: orbit
Source-ID: 248631
Research output: Contribution to journal › Journal article – Annual report year: 1991 › Research › peer-review

Crystal Structure and Vibrational Spectra of Na2VO(SO4)2

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Boghosian, S., Papatheodorou, G., Nielsen, K., Berg, R. W., Bjerrum, N.
Pages: 3294-3298
Publication date: 1990
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 29
ISSN (Print): 0020-1669
Original language: English
Source: orbit
Source-ID: 248635
Research output: Contribution to journal › Journal article – Annual report year: 1990 › Research › peer-review

Electrochemical Deposition and Dissolution of Aluminum in NaAlCl4 Melts: Influence of MnCl2 and Sulfide Addition

Effects of the additives MnCl2, sulfide, and their combined influence on aluminum deposition and dissolution in NaAlCl4 saturated with NaCl have been studied by polarization measurements, galvanostatic deposition, and current reversal chronopotentiometry (CRC). The solubility of MnCl2 was found to be 0.086 ± 0.006 m/o in the melt at 175°C. Aluminum-manganese alloys can be deposited in NaAlCl4 saturated with both NaCl and MnCl2, resulting in a slight increase in cathodic overpotentials. The codeposition of the binary alloys at current densities below 4 mA/cm2 gave rise to formation of deposits so compact that their specific average volumes are of the theoretical value. The content of manganese in the alloy deposits was found to be between 8–11 a/o. It was found that the manganese content in the deposits did not depend on the current efficiency. The presence of sulfide in NaAlCl4 results in the formation of more spongy deposits at low current densities, and thus destroys the beneficial effects of MnCl2 when both additives are present, but prevents formation of dendritic deposits at high current densities. Coulombic ratios of dissolution to deposition were found by CRC measurementsto be affected by the nature of the substrate.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Technical University of Denmark
Contributors: Li, Q., Hjuler, H., Berg, R. W., Bjerrum, N.
Pages: 2794-2798
Publication date: 1990
Peer-reviewed: Yes

Publication information
Journal: Journal of The Electrochemical Society
Volume: 137
Issue number: 9
Electrochemical Deposition of Aluminum from NaCl-AlCl₃ Melts

Electrochemical deposition of aluminum from NaAlCl₄ melts saturated with NaCl onto a glassy carbon electrode at 175°C has been studied by voltammetry, chronoamperometry, and constant current deposition. The deposition of aluminum was found to proceed via a nucleation/growth mechanism, and the nucleation process was found to be progressive. The morphology of aluminum deposits was examined with photomicroscopy. It was shown that depending on the current densities (c.d.) applied, three types of aluminum deposits could be obtained, namely, spongy deposits formed at lower c.d. (below 0.7 mA/cm²), smooth layers deposited at intermediate c.d. (between 2 and 10 mA/cm²), and dendritic or porous deposits obtained at high c.d. (above 15 mA/cm²). However, the smooth aluminum deposits were about five times more voluminous than the theoretical value. The spongy deposits were formed due to difficulties in electronucleation and could be inhibited by application of pulsed currents and/or addition of manganese chloride into the melt.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Technical University of Denmark
Contributors: Li, Q., Hjuler, H. A., Berg, R. W., Bjerrum, N.
Pages: 593-598
Publication date: 1990
Peer-reviewed: Yes

Publication information
Journal: Journal of The Electrochemical Society
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Source: orbit
Source-ID: 248634
Research output: Contribution to journal › Journal article – Annual report year: 1990 › Research › peer-review

Preparation of CuZr₂P₃O₁₂ From Alcoxide Derived Gels: Phase Formation as a Function of Heat Treatment

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Christensen, E., Barner, J. H. V., Engell, J. E., Bjerrum, N.
Pages: 4060-4065
A Novel Inorganic Low Melting Electrolyte for Secondary-Aluminum-Nickel Sulfide Batteries

A new, inorganic low melting electrolyte with the composition LiAlCl4-NaAlCl4-NaAlBr4-KAlCl4 (3:2:3:2) [or equivalently LiAlBr4-NaAlCl4-KAlCl4 (3:5:2)] has been developed. The melting point for this neutral melt is 86°C; the decomposition potential is approximately 2.0 V; the ionic conductivity is measured in the range 97°–401°C and is 0.142 S cm⁻¹ at 100°C, and the density is 2.07 g cm⁻³. The conductivity seems to be an almost linear combination of the conductivities of the four individual halo salts which form the melt. Other examined higher melting mixtures exhibit conductivities deviating less than ±10% from their combination expectations. The low melting electrolyte is employed in the rechargeable battery system Al/electrolyte/Ni₃S₂ at 100°C. The open-circuit voltage of this system is from 0.82 to 1.0 V. Dendrite-free aluminum deposits are obtained. The cycling behavior of the battery system is reported.

Conductivity of Thionyl Chloride-Lithium Tetrachloroaluminate Solutions

The specific conductivity of solutions of LiAlCl4 dissolved in SOCl₂ was determined as a function of composition and temperature. An analytical expression from which the conductivity can be calculated is given as a function of the mole fraction of LiAlCl4 and temperature in the ranges from 0° to 0.37°C and from –20° to +70°C, respectively.
Crystal Structure and Infrared and Raman Spectra of K4(VO)3(SO4)5

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Boghosian, S., Papatheodorou, G., Nielsen, K., Berg, R. W., Bjerrum, N.
Pages: 1847-1853
Publication date: 1989
Peer-reviewed: Yes

Electroless Growth of Aluminum Dendrites in NaCl-AlCl3 Melts.
The spontaneous growth of aluminum dendrites after deposition was observed and examined in sodium chloride-
aluminumchloride melts. The concentration gradient of AlCl3 in the vicinity of the cathode surface resulting from
electrolysisconstitutes a type of concentration cell with aluminum dendrites as electrodes. The short-circuit discharge of
thecell is found to be the driving force for the growth of aluminum dendrites. Such a concentration gradient is proposed to
beone of the causes for dendrite formation in the case of metal deposition.

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry, Technical University of Denmark
Contributors: Li, Q., Hjuler, H., Berg, R. W., Bjerrum, N.
Pages: 2940-2943
Publication date: 1989
Peer-reviewed: Yes
Formation of Crystalline Compounds and Deactivation During SO₂ Oxidation in V₂O₅-M₂S₇O₇ (M = Na, K, Cs) Melts

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Boghosian, S., Fehrmann, R., Bjerrum, N., Papatheodorou, G. N.
Pages: 121-134
Publication date: 1989
Peer-reviewed: Yes

Publication information
Journal: Journal of Catalysis
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On [Na(POCl₃)₄⁺ Complex Ion Formation: Conductivity, Raman and NMR Studies in the System Phosphoryl Chloride-Sodium Tetrachloroaluminate and Related Compounds

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Birkeneder, F., Berg, R. W., Hjuler, H. A., Bjerrum, N.
Pages: 170-184
Publication date: 1989
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Journal: Zeitschrift fuer Anorganische und Allgemeine Chemie
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Original language: English

Raman Spectra of Haloaluminate Melts Containing Oxides

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Gilbert, B. P., Berg, R. W., Bjerrum, N.
Pages: 336-341
Publication date: 1989
Peer-reviewed: Yes

Publication information
Journal: Applied Spectroscopy
Volume: 43
Complex Formation in Pyrosulfate Melts. 3. Density and Conductometric Measurements on the System V2O5-K2S2O7 in the Temperature Range 350-490°C

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Hatem, G., Fehrmann, R., Gaune-Escard, M., Bjerrum, N.
Pages: 195-203
Publication date: 1987
Peer-reviewed: Yes

Publication information
Journal: Journal of Physical Chemistry
Volume: 91
ISSN (Print): 0022-3654
Original language: English
Source: orbit
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Research output: Contribution to journal › Journal article – Annual report year: 1987 › Research › peer-review

Potentiometric Investigation of the Oxide Behavior in NaCl-AlCl3 Melts at 175°C

General information
Publication status: Published
Organisations: Department of Chemistry, Technical University of Denmark
Contributors: Zachariassen, K., Berg, R. W., Bjerrum, N., Barner, J. H. V.
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Publication date: 1987
Peer-reviewed: Yes

Publication information
Journal: Journal of The Electrochemical Society
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Source: orbit
Source-ID: 250703
Research output: Contribution to journal › Journal article – Annual report year: 1987 › Research › peer-review

Complex Formation in Pyrosulfate Melts. 2. Calorimetric Investigations of the System V2O5-K2S2O7, V2O5 . K2S2O7-K2SO4, V2O5 . 2K2S2O7-K2SO4, and V2O5 . 3K2S2O7-K2SO4 at 430°C

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Crystal Structure and Infrared and Raman Spectra of KV(SO$_4$)$_2$

Properties of CsCl/AlCl$_3$ Melts Near Equimolar Composition and the Problem of Corrosive Action of the Melt Towards Container Materials

Raman Spectroscopic Studies of Vapor Complexation in the MCl$_4$-POCl$_3$ and MCl$_4$-AlCl$_3$ (M = Zr, Hf) Binary System
Chloro Complexes in Molten Salts, 10. Potentiometric and Spectrophotometric Study of the System KCl-AlCl3-CuCl at 300°C

General information
Publication status: Published
Organisations: Department of Chemistry, Department of Chemistry, Energy and Materials
Contributors: Barner, J. H. V., Brekke, P. B., Bjerrum, N.
Pages: 2162-2168
Publication date: 1985
Peer-reviewed: Yes

Cryoscopy in the KCl-AlCl3 System. High-Precision Phase Diagram Near Equimolar Composition, with Comments on Oxide Contaminations and Effective Chloride Concentrations in Tetrachloroaluminate Melts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Hjuler, H. A., Bjerrum, N.
Pages: 4506-4511
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Peer-reviewed: Yes

Raman Study of Halogen Exchange Equilibria in Low Melting Mixtures Consisting of Sodium Tetrachloroaluminate and Tetrabromoaluminate

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Kemnitz, E., Hjuler, H. A., Fehrmann, R., Bjerrum, N.
Pages: 457-461
Publication date: 1985
Peer-reviewed: Yes
Secondary Aluminum - Metal Sulphide Batteries with Molten NaAlCl4 Electrolyte

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Hjuler, H., Berg, R. W., Bjerrum, N.
Pages: 1-21
Publication date: 1985

Host publication information
Title of host publication: Secondary Aluminum - Metal Sulphide Batteries with Molten NaAlCl4 Electrolyte : Proceedings of the 14th International Power Sources Symposium
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Source: orbit
Source-ID: 248665

Specific Conductivity of NaCl-AlCl3 and NaCl-AlCl3-Al2S3 Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Hjuler, H. A., Berg, R. W., Zachariassen, K., Bjerrum, N.
Pages: 203-208
Publication date: 1985
Peer-reviewed: Yes

Publication information
Journal: Journal of Chemical and Engineering Data
Volume: 30
ISSN (Print): 0021-9568
Original language: English
Source: orbit
Source-ID: 248667

NbAlCl8. A Molecular Dinuclear Complex in the Solid, Melt and Vapor Phase. Synthesis, Crystal Structure and Raman Spectra

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Pages: 164-171
Publication date: 1984
Peer-reviewed: Yes

Publication information
Journal: Inorganic Chemistry
Volume: 23
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Original language: English
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Phase Diagram of the NaCl-AlCl3 System Near Equimolar Composition, with Determination of the Cryoscopic Constant, the Enthalpy of Melting and Oxid Contaimination
Complexing of Al^{3+} by S^{2-} Ions in Alkali Halide Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Berg, R. W., Bjerrum, N.
Pages: 1442-1443
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Peer-reviewed: Yes

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Research output: Contribution to journal › Journal article – Annual report year: 1983 › Research › peer-review

Density of Molten NaAlCl4. A Reinvestigation

General information
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Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Hjuler, H. A., Bjerrum, N.
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Publication date: 1983
Peer-reviewed: Yes

Publication information
Journal: Journal of Chemical and Engineering Data
Volume: 28
ISSN (Print): 0021-9568
Original language: English
Source: orbit
Complex Formation in Pyrosulfate Melts. 1. Potentiometric, Cryoscopic, and Spectrophotometric Investigations of the Systems K2S2O7-K2SO4 and K2S2O7-K2SO4-V2O5 in the Temperature Range 410-450°C

Lower Oxidation States of Sulfur. 2. Spectrophotometric, Potentiometric, and ESR Study of the Sulfur-Chlorine System in Molten NaCl-AlCl3 (37:63 mol %) at 150 oC

Negative Oxidation States of Chalcogens in Molten Salts. 2. Raman Spectroscopic, Spectrophotometric and Electron Spin Resonance Studies on Chloroaluminate Solutions Containing an S3- Entity
Chloro Complexes in Molten Salts. 8. Potentiometric and Raman Spectroscopic Study of the Systems NaCl-AlCl₃, NaCl-AlCl₃-Na₂O, NaCl-AlCl₃-SeCl₄, and NaCl-AlCl₃-SeCl₄-Na₂O at 175°C

General information
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Barner, J. H. V., Bjerrum, N., Nielsen, O.
Pages: 1712-1718
Publication date: 1981
Peer-reviewed: Yes

Densities of Molten KCl-CuCl₂ Obtained by the Automated Float Method

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Andreasen, H. A., Mahan, A., Bjerrum, N.
Pages: 195-197
Publication date: 1981
Peer-reviewed: Yes

The Chalcogens in Chloroaminate Melts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Bjerrum, N.
Publication date: 1981
Densities of Molten FeCl₃, KCl-FeCl₃ and KCl-AlCl₃

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Pages: 236-239
Publication date: 1980
Peer-reviewed: Yes

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Journal: Journal of Chemical and Engineering Data
Volume: 25
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Original language: English
Source: orbit
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Research output: Contribution to journal » Journal article – Annual report year: 1980 » Research » peer-review

Negative Oxidation States of the Chalcogens in Molten Salts. 1. Raman Spectroscopic Studies on Aluminum Chlorosulfides Formed in Chloride and Chloroaluminate Melts and Some Related Solid and Dissolved Compounds

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Winbush, S. V., Bjerrum, N.
Pages: 2688-2698
Publication date: 1980
Peer-reviewed: Yes

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Journal: Inorganic Chemistry
Volume: 19
ISSN (Print): 0020-1669
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Resonance Raman Spectra of S₃⁻ in Molten Salts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Bjerrum, N., Papatheodorou, G., Winbush, S. V.
Pages: 201-204
Publication date: 1980
Peer-reviewed: Yes

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Research output: Contribution to journal » Journal article – Annual report year: 1980 » Research » peer-review

Chloro Complexes in Molten Salts. 6. Potentiometric and Vapor Pressure Study of the System KCl-AlCl₃ in the Temperature Range 275-350 °C
Chloro Complexes in Molten Salts. 5. Potentiometric and Spectrophotometric Study of Chloro Complexes Formed in KCl-AlCl3-FeCl3 at 300°C

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Andreasen, H. A., Bjerrum, N.
Pages: 3605-3609
Publication date: 1978
Peer-reviewed: Yes

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Journal: Inorganic Chemistry
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ISSN (Print): 0020-1669
Original language: English
Source-ID: 249557

Chloro Complexes in Molten Salts. VII. Potentiometric, Spectrophotometric, and Raman Spectroscopic Study of the System KCl-AlCl3-NbCl5 at 300°C

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Bjerrum, N., Smith, G. P.
Pages: 837-845
Publication date: 1978
Peer-reviewed: Yes

Publication information
Journal: Acta Chemica Scandinavica
Volume: A32
ISSN (Print): 0904-213X
Original language: English
Source-ID: 249554

Electrochemical and Spectroscopic Studies of the Chalcogens in Chloroaluminate Melts

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Bjerrum, N.
Pages: 251-271
Lower Oxidation States of Sulfur. 1. Spectrophotometric Study of the Sulfur-Chlorine System in Molten NaCl-AlCl3 (37-63 mol %) at 150°C

Automated "float" method for determination of densities of molten salts

Copyright (1977) American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics.
**Electrochemistry of Tellurium(IV) in KCl-AlCl₃ Melts**

**General information**
Publication status: Published
Organisations: Microstructures and Interfaces, Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy, Energy and Materials, Department of Chemistry
Contributors: Poulsen, F. W., Bjerrum, N.
Pages: 327-336
Publication date: 1977
Peer-reviewed: Yes

**Publication information**
Journal: Electroanalytical Chemistry: A Series of Advances
Volume: 79
ISSN (Print): 0070-9778
Original language: English
Source: orbit
Source-ID: 249564
Research output: Contribution to journal › Journal article – Annual report year: 1977 › Research › peer-review

**Lower Oxidation States of Selenium. 2. Potentiometric Study Involving Tetravalent Selenium, Tetraselenium(2+), Octaselenium(2+), and Three Other Low Oxidation States of Selenium in Chloroaluminate Melts**

**General information**
Publication status: Published
Organisations: Department of Chemistry, Energy and Materials
Contributors: Fehrmann, R., Bjerrum, N.
Pages: 2089-2094
Publication date: 1977
Peer-reviewed: Yes

**Publication information**
Journal: Inorganic Chemistry
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Original language: English
Source: orbit
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Research output: Contribution to journal › Journal article – Annual report year: 1977 › Research › peer-review

**Low temperature vibrational spectroscopy. I. Hexachlorotellurates**
Far infrared and Raman spectra of six hexachlorotellurate (IV) salts have been obtained at ~100 K for the first time. In the rubidium, cesium, ammonium, and tetramethylammonium salts the Raman active T2g cation lattice translatory mode was found. In the monoclinic K2[TeCl₆] a number of low frequency lattice modes were observed and interpreted in terms of a phase transition near 165 K, similar to transitions in other K2[MX₆] salts. The cubic tetramethylammonium hexachlorotellurate salt undergoes a phase transition of supposed first order at a temperature near 110 K, corresponding to transitions known in analogous uranium and tin compounds. Possible reasons for the transitions are discussed. In the low temperature phases the ν₄ and ν₆ bendings of [TeCl₆]²⁻ have been identified with bands near ~130 and ~110 cm⁻¹. No evidence seemed to favor any stereochemical distortion due to the lone pair of electrons present in hexachlorotellurates. The Journal of Chemical Physics is copyrighted by The American Institute of Physics.

**General information**
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Berg, R. W., Poulsen, F. W., Bjerrum, N.
Pages: 1829-1837
Publication date: 1977
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**Publication information**
Lower Oxidation States of Selenium. I. Spectrophotometric Study of the Selenium-Selenium Tetrachloride System in Molten NaCl-AlCl3 Eutectic Mixture at 150°C

Chloro Complexes in Molten Salts. III. Raman Study of the Chloro Complexes Formed in the Molten KCl-AlCl3-TeCl4 System

Chloro Complexes in Molten Salts. II. Potentiometric and Spectrophotometric Study of Chloro Complexes in KCl-AlCl3-TeCl4 at 300°C
Potentiometric Study of the Systems KCl-AlCl₃ and KCl-AlCl₃-ZnCl₂ at 300°C, Performed with a Chlorine-Chloride Electrode

General information
Publication status: Published
Organisations: Energy and Materials, Department of Chemistry
Contributors: Barner, J. H. V., Bjerrum, N.
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Publication date: 1973
Peer-reviewed: Yes

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Original language: English
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Source-ID: 249571
Research output: Contribution to journal › Journal article – Annual report year: 1973 › Research › peer-review

Lower Oxidation States of Tellurium. III. Ditellurium(2+) in Chloroaluminate Melts

General information
Publication status: Published
Organisations: Department of Chemistry
Contributors: Bjerrum, N.
Pages: 2648-2652
Publication date: 1972
Peer-reviewed: Yes

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Lower Oxidation States of Tellurium. Tellurium(II) in Chloroaluminate Melts

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Contributors: Bjerrum, N.
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Publication information
Projects:

**Fremstilling og karakterisering af materiale og komponenter til mellemliggende emperatur brændselsceller og vandelektrolyse**
Jensen, A. H., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Barner, J. H. V., Supervisor
Christensen, E., Supervisor
Li, Q., Supervisor
Petrushina, I., Examiner
Bouzek, K., Examiner
Steenberg, T., Examiner
Technical University of Denmark
15/08/2011 → 26/11/2014
Award relations: Fremstilling og karakterisering af materiale og komponenter til mellemliggende emperatur brændselsceller og vandelektrolyse
Project: PhD

**Nye typer af elektrokatalysatorer til elektrolyse- og brændselsceller**
Tomás García, A. L., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Petrushina, I., Supervisor
Li, Q., Supervisor
Berg, R. W., Examiner
Skou, E. M., Examiner
Shen, P. K., Examiner
Technical University of Denmark
01/09/2010 → 03/02/2014
Award relations: Nye typer af elektrokatalysatorer til elektrolyse- og brændselsceller
Project: PhD

**Højttemperatur PEM brændselsceller og organiske brændsler**
Vassiliev, A., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Jensen, J. O., Supervisor
Li, Q., Supervisor
Christensen, E., Examiner
Arico, A. S., Examiner
Kær, S. K., Examiner
Technical University of Denmark
01/08/2010 → 30/09/2014
Award relations: Højttemperatur PEM Brændselsceller og organiske brændsler
Project: PhD

**Højttemperatur PEM brændselsceller til energiproduktion og som katalysatorsystem for organiske reaktioner**
Cleemann, L. N., PhD Student, Department of Chemistry
Petrushina, I., Main Supervisor
Bjerrum, N. J., Supervisor
Li, Q., Supervisor
Steenberg, T., Examiner
Bouzek, K., Examiner
Skou, E. M., Examiner
DTU-lønnet stipendie
01/09/2005 → 16/12/2009
Award relations: Højtemperatur PEM brændsels细胞 til energiproduktion og som katalysatorsystem for organiske reaktioner
Project: PhD

Smøremidler og smøremekanismer ved plastisk formgivning af metalliske materialer
Nilsson, M. S., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Christensen, E., Supervisor
Petrushina, I., Supervisor
Gillesberg, B., Examiner
Skou, E. M., Examiner
Steenberg, T., Examiner
Ansat ekstern CAMP
01/02/2001 → 07/07/2005
Award relations: Smøremidler og smøremekanismer ved plastisk formgivning af metalliske materialer
Project: PhD

Udvikling af CVD-processer til fremstilling af tantalbelægninger på rustfrit stål
Eriksen, S., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Larsen, L. E., Examiner
DTU-lønnet stipendie
01/02/1996 → 27/01/2000
Award relations: Udvikling af CVD-processer til fremstilling af tantalbelægninger på rustfrit stål
Project: PhD

Polymer-elektrolyt-brændsels细胞 med driftstemperatur op til 200 c
Bergqvist, R. S., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Li, Q., Supervisor
Hennesø, E., Examiner
Skou, E. M., Examiner
Blandet Finansiering-SU
01/10/1995 → 28/03/2000
Award relations: Polymer-elektrolyt-brændsels细胞 med driftstemperatur op til 200 c
Project: PhD

Højtemperatur korrosion under industrielle
Cappeln, F. V., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Petrushina, I., Supervisor
Skou, E. M., Examiner
Bech-Nielsen, G., Examiner
Karlsson, A., Examiner
Blandet Finansiering-SU
01/05/1995 → 05/02/2002
Award relations: Højtemperatur korrosion under industrielle
Project: PhD

Udvikling af smøremidler til koldflydeprocesser i rustfast stål
Steenberg, T., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Danckert, J., Examiner
Erhvervsforskerordningen
01/04/1994 → 11/02/1998
Award relations: Udvikling af smøremidler til koldflydeprocesser i rustfast stål
Project: PhD

Elektrokatalyse og Katalysatorer til Oxygenreduktion i Polymer Brændselsceller
Zhong, L., PhD Student, Department of Energy Conversion and Storage
Li, Q., Main Supervisor
Teknisk Keramik's egenskaber som funktion af tilsætning af SiO2, MgO, FeO og MnO etc.
Borup, F., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Nordisk finansiering
01/04/1991 → 03/01/1995
Award relations: Teknisk Keramik's egenskaber som funktion af tilsætning af SiO2, MgO, FeO og MnO etc.
Project: PhD

Fremstilling og karakterisering af elektrolytter og elektroder til vandelektrolyse i temperaturområdet 200-400C
Prag, C. B., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Christensen, E., Supervisor
Petrushina, I., Supervisor
Li, Q., Supervisor
Berg, R. W., Examiner
Steenberg, T., Examiner
Sunde, S., Examiner
Technical University of Denmark
15/09/2011 → 11/03/2015
Award relations: Fremstilling og karakterisering af elektrolytter og elektroder til vandelektrolyse i temperaturområdet 200-400C
Project: PhD

Development of High temperature PEM fuel cells
Kannan, A., PhD Student, Department of Energy Conversion and Storage
Jensen, J. O., Main Supervisor
Bjerrum, N. J., Examiner
Andreasen, S. J., Examiner
Zeis, R., Examiner
Offentlig finansiering
15/11/2014 → 17/09/2018
Award relations: Development of High temperature PEM fuel cells
Project: PhD

Development of high temperature stable friction materials
Ramousse, S., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Petrushina, I., Supervisor
Valentin, J., Supervisor
Andersen, B. K., Examiner
Skou, E. M., Examiner
Sørensen, O. T., Supervisor
Hjuler, H., Examiner
Erhvervsforskerordningen
01/01/1999 → 27/05/2002
Award relations: Development of high temperature stable friction materials
Project: PhD

Avancerede overfladebehandlinger
Precht Noyé, P., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Barner, J. H. V., Supervisor
Larsen, L. E., Examiner
Steenberg, T., Examiner
Hjuler, H., Examiner
Forskningsrådsfinansiering
01/04/2000 → 14/10/2003
Award relations: Avancerede overfladebehandlinger
Project: PhD

Omdannelse af methan til methanol
Birch, H., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Gang, X., Supervisor
Andersen, B. K., Examiner
Larsen, L. E., Examiner
Steenberg, T., Examiner
Forskningsrådsstipendium
01/05/1998 → 20/09/2002
Award relations: Omdannelse af methan til methanol
Project: PhD

Kompleks og redoxkemi i saltsmeltebade til overfladebehandlingsprocesser
Andersen, K. B., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Skou, E. M., Examiner
Hjuler, H., Examiner
Forskningsrådsstip.-SU, Eksp
01/01/1993 → 27/02/1997
Award relations: Kompleks og redoxkemi i saltsmeltebade til overfladebehandlingsprocesser
Project: PhD

Gasnitrokarburering
Friehling, P. B., PhD Student, Department of Management Engineering
Thorsen, K. A., Main Supervisor
Somers, M. A. J., Supervisor
Bjerrum, N. J., Examiner
Gundel, P. H., Examiner
Bøttiger, J., Examiner
DTU-Su Stipendium, Eksperiment
01/09/1997 → 09/04/2001
Award relations: Gasnitrokarburering
Project: PhD

Karakterisering af smeltebade til pletteringsprocesser
Gillesberg, B., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Larsen, L. E., Examiner
DTU-Su Stipendium, Eksperiment
01/08/1995 → 18/09/2000
Award relations: Karakterisering af smeltebade til pletteringsprocesser
Project: PhD

Udvikling af lette materaler til brintlægning
Vestbø, A. P., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Barner, J. H. V., Supervisor
Jensen, J. O., Supervisor
Jensen, T. R., Examiner
Noréus, D., Examiner
Jacobsen, T., Examiner
Offentlig finansiering
01/11/2005 → 01/04/2009
Award relations: Udvikling af lette materaler til brintlægning
Pressurized HT PEM Cells for H2/O2 operation
Sandegaard, S., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Cleemann, L. N., Supervisor
Jensen, J. O., Supervisor
Petrushina, I., Examiner
Steenberg, T., Examiner
Schmidt, T. J., Examiner
Institut, samfinansiering
01/08/2012 → 30/09/2015
Award relations: Pressurized HT PEM Cells for H2/O2 operation
Project: PhD

Inorganic Proton Conducting Materials
Anfimova, T., PhD Student, Department of Energy Conversion and Storage
Li, Q., Main Supervisor
Bjerrum, N. J., Supervisor
Bonanos, N., Examiner
Norby, T., Examiner
Jensen, T. R., Examiner
Technical University of Denmark
15/04/2011 → 24/09/2014
Award relations: Inorganic Proton Conducting Materials
Project: PhD

Kinetic studies and Computational Fluid Dynamics (CFD) simulations to aid in the development of Tantalum coated extreme corrosion resistance welded plate heat exchangers (ECWP)
Mugabi, J. A., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Christensen, E., Supervisor
Petrushina, I., Supervisor
Li, Q., Examiner
Papatheodorou, G., Examiner
Skou, E. M., Examiner
Eriksen, S., Supervisor
Technical University of Denmark
01/10/2011 → 17/12/2014
Award relations: Kinetic studies and Computational Fluid Dynamics (CFD) simulations to aid in the development of Tantalum coated extreme corrosion resistance welded plate heat exchangers (ECWP)
Project: PhD

Development of improved electrodes in high temperature PEM fuel cells
Permyakova, A. A., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Jensen, J. O., Supervisor
Li, Q., Supervisor
Christensen, E., Examiner
Bajo, J. L., Examiner
Arenz, M., Examiner
DTU, Samfinansiering
15/03/2010 → 11/12/2013
Award relations: Development of improved electrodes in high temperature PEM fuel cells
Project: PhD

Fremstilling og synteseanvendelse af elektrolytisk fremstillet hydrogen
Hansen, M. K., PhD Student, Department of Energy Conversion and Storage
Bjerrum, N. J., Main Supervisor
Christensen, E., Supervisor
Jensen, J. O., Supervisor
Petrushina, I., Examiner
New Polymeric Electrolytes for application in water electrolysis

Aili, D., PhD Student, Department of Chemistry
Bjerrum, N. J., Main Supervisor
Barner, J. H. V., Supervisor
Christensen, E., Supervisor
Li, Q., Supervisor
Berg, R. W., Examiner
Bleha, M., Examiner
Steenberg, T., Examiner
Technical University of Denmark
01/03/2009 → 23/05/2012
Award relations: Fremstilling og synteseanvendelse af elektrolytisk fremstillet hydrogen
Project: PhD

SUCAP: Sustainable Carbon Power

SUCAP eller ("Grøn Kulkraft") handler om at fremstille ikke-fossilt kulstof til kombineret energilagring og CO2 fjernelse. Den centrale idé i SUCAP projektet er at konvertere kombinationen af elektrisk vedvarende energi og CO2 til kombinationen af kul og oxygen, altså til et lager af potentielt energi. Processen er absolut mulig rent kemisk, men ikke udviklet eller prøvet, idet det altså er muligt at udvikle et lager af potentielt energi. SUCAP handler om et projekt med som synergetic afslutning af CO2 til kul, d.v.s. at konvertere CO2 til energi. Projektet har som opgave at udvikle metoder og demonstrere gennemførelse af processen i praksis, samt at vurdere økonomien. Hvis effektiviteten kan blive rimelig, kan projektet få meget vidtrækkende betydning for samfundets energiforsyning.
Berg, R. W., Project Participant, Department of Chemistry
Bjerrum, N. J., Project Applicant, Department of Energy Conversion and Storage
01/01/2014 → 31/08/2018
Keywords: carbon dioxide, carbon capture, electricity-load-leveling, energy, environment
Project: Research

Noble Free: Noble Metals Free Intermediate Temperature Supported Liquid Phase Electrolyzer

The strategic development of the NobleFree project is noble metal free intermediate-temperature (200-400 C) fuel cells and water electrolyser with the same characteristics as of the Nafion®, PBI and Aquivion™ systems. This goal will be achieved by use of alkaline metals dihydrogen phosphates as proton-conducting supported liquid phase electrolytes (SLPE). These electrolytes will be liquid immobilized on ceramic nano fibers, whiskers and powders. It has been discovered recently, that nickel, high-nickel alloys and austenitic stainless steels containing small amounts of Ti have high corrosion resistance in the molten alkali metals dihydrogen phosphates in the above mentioned temperature range. The NobleFree will start with the parallel development of electrolytes and nickel-based catalysts. The final stage of the project will be design and test of noble metal free intermediate temperature water electrolyser. Possibilities of use SLPE system as a fuel cell will be also studied.
Nikiforov, A. V., Project Participant, Department of Energy Conversion and Storage, Proton conductors, Energy and Materials
High-efficiency, low-cost electrode surfaces for next generation alkaline electrolysis
Nikiforov, A. V., Project Participant, Department of Energy Conversion and Storage, Proton conductors, Energy and Materials
Jensen, J. O., Project Participant, Department of Energy Conversion and Storage, Proton conductors, Department of Chemistry
Bjerrum, N. J., Project Participant, Department of Energy Conversion and Storage, Proton conductors, Energy and Materials

Keywords: Alkaline Electrolysis, Water splitting, Electrodes, Sustainable Energy
Project: Research

MEDLYS: Medium Temperature Water Electrolysis

Hydrogen has the potential to provide a reliable, secure and clean source of power. Water offers a practical way of hydrogen production in association with renewable energy sources. The main challenges for water electrolysers are high cost, low efficiency and insufficient lifetime. The strategy of MEDLYS to address these issues is to develop novel materials and technologies for a medium temperature steam electrolyser operating at 200-400°C. The temperature range is optimal for 1) improving thermodynamics and kinetics of the process, 2) potentially replacing noble metal based catalysts with cost-effective alternatives, 3) allowing for a wide selection of construction materials from metals, ceramics and thermal plastics for conducting, insulating or sealing purposes and 4) maintaining long-term durability. MEDLYS will start with development of fundamental materials including inorganic/composite proton conducting electrolyte, alternative catalysts and other construction (electrode substrate, current collector, and bipolar plate) materials. Based on the materials, electrolyser components will be manufactured and a lab-scale cell will be constructed for evaluation and concept-proof test. The proposal is based on the results from ongoing activities within DSF HyCycle Center by most of the consortium partners, who have expertise from materials science and technological know-how and strong intention to further exploit the achievements after the project. The fulfilment of MEDLYS objectives is believed to bring breakthroughs in the hydrogen production technology, which, in turn, would promote the renewable energy technologies on a national as well as an European and global level.

Christensen, E., Project Participant, Department of Energy Conversion and Storage, Proton conductors
Bjerrum, N. J., Project Coordinator, Department of Energy Conversion and Storage, Proton conductors, Energy and Materials
Barner, J. H. V., Project Participant, Department of Chemistry
Li, Q., Project Participant, Department of Energy Conversion and Storage, Proton conductors, Energy and Materials
Chorkendorff, I., Project Participant, Department of Physics, Experimental Surface and Nanomaterials Physics
Petrushina, I., Project Participant, Department of Energy Conversion and Storage, Proton conductors

External Project ID: DSF: 10-093906
01/03/2011 → 28/02/2015
Collaborators: Technical University of Munich, Danish Power Systems ApS, University of Southern Denmark, Tantaline A/S

Project: Research

PROCON: Intermediate Temperature Proton Conducting Systems (PROCON)

Bjerrum, N. J., Project Manager, Department of Chemistry, Energy and Materials
Li, Q., Project Participant, Department of Chemistry, Energy and Materials
Petrushina, I., Project Participant, Department of Chemistry, Energy and Materials
Jensen, J. O., Project Participant, Department of Chemistry, Energy and Materials
Christensen, E., Project Participant, Department of Chemistry, Energy and Materials
Cleemann, L. N., Project Participant, Department of Chemistry, Energy and Materials

Forsk. Andre statslige danske - Grundforskn.fonden: DKK15,000,000.00
01/06/2010 → 31/05/2013
Award relations: Intermediate Temperature Proton Conducting Systems (PROCON)

Project: Research

Materialeproblemer i affaldskedler
Bjerrum, N. J., Project Participant, Department of Chemistry
Cappeln, F. V., Project Participant, Department of Chemistry
Larsen, O. H., Project Participant, Elsam A/S
Tiedje, N., Project Participant
Jensen, J. P., Project Participant, Energi E2 A/S
Matthiesen, H. D., Project Participant, Babcock & Wilcox Vølund
Iversen, S. B., Project Participant, FLS Miljø A/S
Frederiksen, J., Project Participant, International Mineral Development & Exploration, Inc
Project ID: PSO no. 4104
Forskningsprojekter - Erhvervsministeriet: DKK1,200,000.00
01/01/2002 → 31/12/2006
Award relations: Materialeproblemer i affaldskedler
Project: Research

Udvikling af mere effektive og billigere MEA'er til PEM brændselssceller
Bjerrum, N. J., Project Manager, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry
Yde-Andersen, S., Project Participant, EWII Fuel Cells A/S
Steenberg, T., Project Participant, Danish Power Systems ApS
Plackett, D., Project Participant, Risø National Laboratory for Sustainable Energy, Polymer Department
Forskningsprojekter - Andre ministerier og styrelser: DKK2,075,000.00
03/02/2005 → 31/01/2008
Award relations: Udvikling af mere effektive og billigere MEA'er til PEM brændselssceller
Project: Research

Metal hydride storage tank for hydrogen vehicle
The aim of the project is to develop and produce a metal hydride based hydrogen storage tank for demonstration purposes. The tank will be used (1) in a hydrogen car with combustion engine reconstructed by "Nordvestjysk Folkecenter for Vedvarende Energi" and (2) in a car with fuel cells from IRD A/S in cooperation with Fiat. Bjerrum, N. J., Project Manager, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry
Hennesø, E., Project Participant, Department of Chemistry
01/01/1999 → 30/06/2000
Collaborators: EWII Fuel Cells A/S
Project: Research

Lubrication Mechanisms and Lubricants for Cold Forging and Sheetforming of Stainless Steel
As an alternative to machining, bulk and sheet forming of stainless steel has large potential in Danish industry producing pumps, equipment for dairy and other victual products etc. This concerns especially the two groups of forming processes "cold forging" and "deep drawing". Due to the high flow stress and heavy strain hardening, however, the tribological conditions are very severe. New tribologic tests are developed, to make up a series of tests ranging from laboratory tests to full scale production tests. New lubricants are evaluated with respect to their environmental safety.
The new type of lubricants for sheet forming of stainless steel developed during the previous MUP2-project (annual reports 1996-97) have been further improved, and tested on a variety of different types of steel and other metals as well as of different geometries of specimens. This work has been carried out in close collaboration with the other project partners. Furthermore, an electrolytic process for applying coatings of zinc-calcium-phosphate on stainless steel previously developed, has been further improved. These coatings are used in combination with sodium stearate as lubricants for cold forging of stainless steel. Work concerning problems of upscaling this coating process has been carried out, including methods for process control etc. The possibility of preparing other types of coatings in a similar way (metal oxides and hydroxides) has also been investigated.
Christensen, E., Project Manager, Department of Chemistry
Bjerrum, N. J., Project Participant, Department of Chemistry
Petrushina, I., Project Participant, Department of Chemistry
Steenberg, T., Project Participant, Department of Chemistry
Bergqvist, R. S., Project Participant, Department of Chemistry
Bay, N. O., Project Participant, Department of Manufacturing Engineering
Eriksen, M., Project Participant, Department of Manufacturing Engineering
Bach, J. I., Project Participant, Department of Manufacturing Engineering
Kofod, N., Project Participant, Department of Manufacturing Engineering
Andreasen, J. L., Project Participant, Department of Manufacturing Engineering
01/01/1998 → 31/12/1998
Collaborators: Danfoss AS, Houghton Denmark A/S, Danish Technological Institute, Esti Chem A/S
New Metal Hydrides for Energy Storage

Jensen, J. O., Project Participant, Department of Chemistry
Bjerrum, N. J., Project Manager, Department of Chemistry
Hauback, B. C., Project Manager, Institute for Energy Technology
Noréus, D., Project Participant, Stockholm University
Fjellvåg, H., Project Participant, University of Oslo
Noréus, D., Project Participant, Stockholm University
Milcius, D., Project Participant, Lithuanian Energy Institute in Lithuania, Surface Engineering Group,
Lampinen, M. J., Project Participant, Helsinki University of Technology

Project ID: 62-02
Forsk. Andre offentlige og private - Nordiske: DKK500,000.00
01/01/2003 → 31/12/2006
Collaborators: Stockholm University, Institute for Energy Technology, University of Oslo, Helsinki University of Technology, Lithuanian Energy Institute, Lithuanian Energy Institute in Lithuania, Surface Engineering Group,
Award relations: New Metal Hydrides for Energy Storage

High Performance Coating Materials for Application in Corrosive and Abrasive Environments

The main object of this project is to develop processes for electrolytical deposition of corrosion resistant coatings of niobium and tantalum from alkali fluoride melts (FLINAK). The aim is to protect components used in chemical industry against corrosion. The work is concentrated partly towards coating of objects of steel with a high complexity of geometry, as well as basic scientific studies of the electrochemistry and complex formation in the molten electrolytes. A number of tantalum coated steel objects have been produced for field tests in Danish industry. The project is carried out in close cooperation with Danfoss A/S.

Bjerrum, N. J., Project Manager, Department of Chemistry
Andersen, B. K., Project Participant, Department of Chemistry
Berg, R. W., Project Participant, Department of Chemistry
Barner, J. H. V., Project Participant, Department of Chemistry
Gillesberg, B., Project Participant, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry
Polyakova, L., Project Participant, unknown organisation
Polyakov, E., Project Participant, unknown organisation
01/01/1992 → …
Collaborators: unknown organisation

Complex and Redox Chemistry in Molten Halides

Chloride, fluoride and mixed chloride-fluoride melts are currently investigated by Raman and IR spectroscopy and by electrochemical methods like cyclic voltammetry and square wave voltammetry. The scope of the project is to clarify the complex and oxidation reactions taking place in melts, that can be applied as molten salt baths for plating with corrosion and abrasion resistant layers.

Barner, J. H. V., Project Manager, Department of Chemistry
Berg, R. W., Project Participant, Department of Chemistry
Bjerrum, N. J., Project Participant, Department of Chemistry
Gillesberg, B., Project Participant, Department of Chemistry
Polyakov, E., Project Participant, unknown organisation
Polyakova, L., Project Participant, unknown organisation
Lantelme, F., Project Participant, unknown organisation
Picard, G., Project Participant, unknown organisation
01/01/1993 → …
Collaborators: unknown organisation

Anode Materials for Metal Hydride Batteries

The aim is to develop new hydrogen storage alloys. The alloys are to be used as active material in the negative electrode of nickel metal hydride batteries (NiMH). State-of-the-art for NiMH is intermetallic compounds based on rare earth elements. These are developed from LaNi5. CaNi5 has the same structure and comparable hydrogen storage properties. If suitable electrode materials can be developed based on CaNi5, there is a potential for cheaper materials with a higher capacity. Intermetallics based on CaNi5 with partial substitutions are prepared and tested during the project. The hydrogen storage alloys are prepared from the elements by mechanical alloying in a planetary ball mill. After milling for several hours nanocrystalline intermetallics or amorphous alloys are formed. The alloys are characterized by X-ray powder diffraction before and after annealing in inert atmosphere. The hydrogen storage capacity is measured by gas absorption...
and the electrochemical properties are tested in half cells.

Bjerrum, N. J., Project Manager, Department of Chemistry
Berg, R. W., Project Participant, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry
Hjuler, H., Project Participant, unknown organisation
Hennesø, E., Project Participant, unknown organisation
08/02/1993 → 30/04/1997
Collaborators: unknown organisation
Project: Research

New Technologies for Water Electrolysis

"Midler til forberedelse af ansøgninger til EU-forskningsmidler
Bjerrum, N. J., Project Manager, Department of Chemistry
Project ID: 40359
Forskningsprojekter - Andre ministerier og styrelser: DKK300,000.00
01/12/2006 → 30/06/2007
Award relations: New Technologies for Water Electrolysis
Project: Research

Environmentally Safe Lubricants for Sheet Forming and Cold Forging of Stainless Steel
Carried out under the "MUP2" Programme.
As an alternative to machining, bulk and sheet forming ("cold forging" and "deep drawing") of stainless steel has large potential in Danish industry. Due to the high flow stress and heavy strain hardening, however, the tribological conditions are very severe. A further problem is the large tendency of oxides on stainless steel to break down during plastic deformation of material causing direct metal-to-metal contact between workpiece and tool surface. The result of this is pick-up of workpiece material on the tool surface, and subsequent scoring of the workpiece surface when it passes such assemblies of pick-up. The purpose of the project is to develop new, inorganic lubricants for cold forging and methods for the necessary coating processes on stainless steel, and to develop alternatives to the commercially applied paraffin oils, which are undesirable from an environmental point of view. To achieve these goals basic research is carried out concerning reactions of the lubricants on the steel surface, phase transitions in the coatings under extreme pressure and high temperatures, as well as investigations of the various coating processes. New tribologic tests are developed to make up a series of tests ranging from laboratory tests to full scale production tests. All new lubricants are evaluated with respect to their environmental safety. A new type of lubricant for sheet forming of stainless steel has now been developed to the production test level. Furthermore, a new process for applying coatings of zinc-calcium phosphate on stainless steel based on the work carried out in an industrial Ph.D. project (Thomas Steenberg) has been further developed to the level of production test. These coatings are used in combination with sodium stearate as lubricants for cold forging.
Bjerrum, N. J., Project Manager, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry
Petrushina, I., Project Participant, Department of Chemistry
Steenberg, T., Project Participant, Department of Chemistry
Bay, N. O., Project Participant, Department of Manufacturing Engineering
Wibom, O., Project Participant, Department of Manufacturing Engineering
Andreasen, J. L., Project Participant, Department of Manufacturing Engineering
01/07/1994 → 31/12/1997
Collaborators: Danfoss AS, Houghton Denmark A/S, Grundfos DK AS, Danish Technological Institute, Esti Chem A/S
Project: Research

Molten Carbonate Fuel Cells (MCFC)
One of the major problems for operating molten carbonate fuel cells is the corrosion of metal oxide electrodes. In this connection the dissolution of various oxides of transition metals in molten Li-K carbonates has been studied. Electrochemical behavior of several metal electrodes (Au, Ag, Cu, Fe, Al, Ti, Cr etc.) has been studied. A novel method for corrosion protection of metals in molten alkali carbonates is also developed by deposition of an AIN-TIN layer.
Bjerrum, N. J., Project Manager, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry
Ukendt: DKK1,900,000.00
01/01/1993 → 31/12/1998
Collaborators: Ansaldo STS, Foundation for Research and Technology-Hellas
Award relations: Molten Carbonate Fuel Cells (MCFC)
Project: Research

Phosphoric Acid Fuel Cells (PAFC)
The research activity in this area is mainly concentrated on the technology of the PAFC stack. Manufacturing of Gas diffusion electrodes and related techniques are further improved in order to enhance the catalytic efficiency for oxygen
reduction. Chemical and electrochemical techniques are also under development for minimizing the poisoning effect of fuel impurities on the anodic catalysts.

**Electrochemical Promotion of Catalytic Reactions**

The project is concerned with the study of the effect of electrochemical disturbances on the activity and selectivity of catalytic systems. The project builds upon the network, experience and scientific results obtained by Department of Chemistry (DTU) in the field of electrochemistry, fuel cells and catalysis. With regard to this project, recent discoveries concerning the effect of non-Faradaic electrochemical promotion of liquid-phase catalytic reactions (SO2 oxidation) are of special interest.

The project consists of two main tasks:
1. Electrochemical promotion of the catalytic conversion of the polluting emissions from combustion engines.
2. Electrochemical promotion of the catalytic oxidation of methane to methanol.

(1. ICAT project).

**Industrial punching and ironing - lubrication mechanisms and environmental aspects (ISOPS)**

"Center Contract" Danish Ministry of Research.

**Reliability improvements for co-combustion plants**

Program under The European Coal and Steel Community (EU).

**Production and distribution of power and heat**

**HotMEA: Danish high temperature PEMFC components, MEA and stack**

Bjerrum, N. J., Project Manager, Department of Chemistry

Lundsgaard, J., Project Participant, EWII Fuel Cells A/S

Themsen, J., Project Participant, Ballard Power Systems Europe A/S

Albæk, P., Project Participant, Ballard Power Systems Europe A/S
Advanced Surface Treatments
The project deals with surface modifications of steel and titanium based materials to improve corrosion and abrasion resistance. The scope is to provide the fundamental and technical data necessary to develop new CVD (chemical vapour deposition) and electrochemical based processes.
The elements to be used in surface coatings are mainly titanium, niobium, zirconium, boron, carbon and nitrogen - either in the pure form or in combination such as alloys or borides, nitrides and carbides. These materials show in general high corrosion resistance and a good biocompatibility. The borides, carbides and nitrides are materials with large hardness.
Our approach to the formation of the mentioned surfaces are for the main part entirely new and unexplored. In the choice of reaction media we will try to minimize possible environmental and health hazards.

D. E. Ministry of Research
Bjerrum, N. J., Project Manager, Department of Chemistry
Barner, J. H. V., Project Participant, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry
Petrushina, I., Project Participant, Department of Chemistry
Gillesberg, B., Project Participant, Department of Chemistry
Eriksen, S., Project Participant, Department of Chemistry
Precht Noyé, P., Project Participant, Department of Chemistry

Chemical Vapor Deposition (CVD)
The primary objective of the CVD-research is tantalum coating of stainless steel, carbon steel, nickel, copper, titanium and aluminum by CVD. Tantalum is deposited from TaCl5 by reduction with hydrogen at 625-1000 C. The TaCl5 is generated directly from Ta and Cl2 at 400-600 C prior to mixing with H2 and heating to the deposition temperature. Niobium and tungsten coatings are deposited by similar processes.
Catalytically active platinum layers has been prepared by metalorganic-CVD. Platinum is deposited from platinum bis penta-2,4-dion in hydrogen at 300 C and 0,1 mbar.
Copper deposition on nickelbased alloys from copper bis 1,1,1,5,5,5-hexafluoropenta-2,4-dion is a new CVD activity and subject of a PMP (3 students).
Bjerrum, N. J., Project Manager, Department of Chemistry
Eriksen, S., Project Participant, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry

Autobrane: Automotive High Temperature Fuel Cell Membranes
The automotive application of PEM fuel cells is facing some crucial problems:
- the relatively low operating temperatures limiting heat rejection
- too small an operating temperature range and
- high humidification needs

New types of electrolyte membranes and catalysts offer a solution; their systematic development and testing is the main focus of the effort; along with that work on MEA, entire cells and small scale stacks is foreseen to finally validate the results at a representative level of power

The project combines and exploits the European expertise in the field of advanced polymer membranes in a focused clustered and network type activity. Collaboration with institutes from non EU member states, in particular China, Russia and India, is addressed as well.

A steering group with representatives of seven automobile OEMs shall coordinate the project and iteratively focus and guide the developers by specifications and assessment of results
Erdle, E., Contact Person, Daimler AG
Zandiri, S., Project Participant, Fiat
Brachmann, T., Project Participant, Honda R&D Europe (D) GmbH
Wieser, C., Project Participant, Opel AG
Cornet, N., Project Participant, Renault
De Colvenaer, B., Project Participant, Toyota Motor Europe
Hübner, G., Project Participant, Volkswagen AG
Sinigersky, V., Project Participant, Bulgarian Academy of Sciences
Jones, D., Project Participant, CNRS
Fridell, E., Project Participant, Chalmers University of Technology
Antonucci, V., Project Participant, Consiglio Nazionale delle Ricerche
Gülzow, E., Project Participant, Deutches Zentrum Für Luft- und Raumfahrt, Institut für Technische Thermodynamik (TT),
Wakker, A., Project Participant, Energy research Centre of the Netherlands - ECN
Gautier, L., Project Participant, European Institute for Energy Research
Banhardt, V., Project Participant, Freudenberg FCCT oHG, Application Engineering,
Bauer, B., Project Participant, Gesellschaft für Funktionelle Membranen und Anlagentechnologie mbH, Fumatech GmbH,
Hayden, B., Project Participant, Ilika Plc
Hards, G., Project Participant, Johnson Matthey Plc
Lundblad, A. O., Project Participant, KTH - Royal Institute of Technology
Klapper, M., Project Participant, Max-Planck-Gesellschaft zur Foerderung der Wissenschaften e.V., Max Planck Institute for Polymer Research,
Toro, A., Project Participant, Nuvera Fuel Cells Europe Srl, Stack Department,
Henschel, C., Project Participant, PEMEAS GmbH, Market Development,
Ghielmi, A., Project Participant, Solvay Solexis S.p.A., Solvay Solexis R&T Center,
Bjerrum, N. J., Project Participant, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry
Corti, F., Project Participant, TIMCAL SA, Technology Department,
Zuber, R., Project Participant, Umicore AG & Co KG
Alberti, G., Project Participant, Universita Degli Studi Di Perugia
Tenhu, H., Project Participant, University of Helsinki
Jannasch, P., Project Participant, Lund University

Award relations: Automotive High Temperature Fuel Cell Membranes
Project: Research

Dry, Intrinsic proton conducting membranes for fuel cells
Bjerrum, N. J., Project Manager, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry
Begstrup, M., Project Participant, The Danish University for Pharmaceutical Sciences, Department of Medicinal Chemistry,
Planckett, D. V., Project Participant, Danish Polymer Center
Steenberg, T., Project Participant, Danish Power Systems ApS

Forskningsrådene - STVF: DKK1,258,131.00
01/01/2006 → 31/12/2008

Collaborators: Danish Power Systems ApS, University of Copenhagen, Danish Polymer Center, The Danish University for Pharmaceutical Sciences, Department of Medicinal Chemistry,

Award relations: Dry, intrinsic proton conducting membranes for fuel cells
Project: Research

Novel Electrochemically Activated Catalysts and Processes
Bjerrum, N. J., Project Manager, Department of Chemistry
Petrunchina, I., Project Participant, Department of Chemistry

Project ID: 40244

Forskningsrådene - STVF: DKK222,000.00
01/01/2004 → 31/12/2006

Award relations: Novel Electrochemically Activated Catalysts and Processes
Project: Research
ISOPS, Industriel stansning og pladeformgivning – smøremekanismer, smøremidler og miljøaspekter

Punching and stamping of stainless steel is characterised as tribologically difficult due to galling caused by the brittle oxides and the large affinity of the base material to pick-up on the tool surface resulting in scoring of subsequently passing work piece surface. Until recently, the only lubricants able to impede galling in severe deep drawing, stretch forming and ironing operations were chlorinated paraffin oils, which are expected to be abandoned in near future due to environmental problems.

In a national Danish research programme, 1994-99, two new lubricant systems have been developed as substitutes to chlorinated paraffin oils. Testing of these environmentally harmless lubricants under controlled laboratory conditions has shown very promising results and so has initial industrial tests at Danfoss, Grundfos and Volvo among others. In the present research programme "Industrial punching/blanking and sheet metal forming – lubricants, mechanisms of lubrication and environmental aspects" running from 2000-2003 the development and testing of lubrication systems will be further studied in a co-operative project between Institut for Kemi, DTU, Institut for Produktion, DTU (in the following named IPT), Danfoss, Grundfos, RM Rich. Müller, Esti Chem and Houghton Danmark.

Objectives
The objective of the present project is to develop a general methodology for determination of the limits of lubrication in sheet metal forming of stainless steel. Furthermore development and testing of tailor-made surface topographies improving the resistance to lubricant film breakdown will be studied.

Bay, N. O., Project Manager, Department of Management Engineering
Olsson, D. D., Project Participant, Department of Management Engineering
Andreasen, J. L., Project Participant, Department of Management Engineering
Bjerrum, N. J., Project Participant, Department of Chemistry
Person, U., Project Participant, Esti Chem A/S
Person, U., Project Participant, Houghton Denmark
Person, U., Project Participant, RMIG

Forskningsrådene - STVF: DKK1,250,000.00
01/10/2000 → 01/12/2003
Collaborators: Avesta Sheffield AB, Houghton Denmark A/S, RMIG, Houghton Denmark, Esti Chem A/S, RMIG A/S
Award relations: ISOPS, Industriel stansning og pladeformgivning – smøremekanismer, smøremidler og miljøaspekter
Project: Research

Højtemperaturen PEM brændselscelle

Bjerrum, N. J., Project Manager, Department of Chemistry
Henriksen, N., Project Participant, Elsam A/S
Hennese, E., Project Participant, Danish Power Systems ApS
Yde-Andersen, S., Project Participant, EWII Fuel Cells A/S

Project ID: 4760
Forskningsrådene - Andre: DKK1,850,000.00
01/01/2004 → 30/09/2006
Award relations: Højtemperaturen PEM brændselscelle
Project: Research

Udvikling af 2 kW naturgasreformere for høj- og lavtemperatur PEM-brændselsceller

Wit, J. D., Project Manager, Danish Gas Technology Centre A/S
Bjerrum, N. J., Contact Person, Department of Chemistry
Yde-Andersen, S., Project Participant, IRD Fuel Cell AS
Balslev, P., Project Participant, Danfoss AS
Steenberg, T., Project Participant, Danish Power Systems ApS
Pedersen, A. H., Project Participant, DONG Energy AS
Kær, S. K., Project Participant, Aalborg University

Project ID: 33030-0021
Forskningsprojekter - Miljø- og Energiforvaltning: DKK930,000.00
01/01/2004 → 30/09/2006
Award relations: Udvikling af 2 kW naturgasreformere for høj- og lavtemperatur PEM-brændselscelle
Project: Research

Synthesis, characterization and applications of polymer membranes for high temperature fuel cells

The project deals with novel materials for an advanced polymer membrane fuel cell system, which produces electricity and heat from natural gas, biomass or other environmentally friendly fuels. The fuel cell system operates at about 200°C with a
high CO-tolerance (at least 30,000 ppm). This high CO tolerance makes it possible for the fuel cell system to use reformate hydrogen obtained directly from reforming of various types of fuel. The system can therefore be used for both mobile and stationary applications with a high energy efficiency and considerably reduced emissions, compared to the present technology. As the key requisite for this technology, temperature-resisting polymers will be synthesized, membranes of the polymers will be fabricated and functionalised for creating proton conductivity. Electrochemical and fuel cell tests and other physical chemical characterizations will be carried out. Correlations between the materials structures and performances will be established. Evaluation of the materials and fabrication processes will be made.

Bjerrum, N. J., Project Manager, Department of Chemistry
Begtrup, M., Project Manager, Danish University for Pharmaceutical Sciences, Department of Medicinal Chemistry,
Project ID: 2058-03-0005
Forskningsrådene - STVF: DKK1,000,000.00
01/01/2004 → 31/12/2006
Collaborators: Danish University for Pharmaceutical Sciences, Department of Medicinal Chemistry, , University of Copenhagen
Award relations: Synthesis, characterization and applications of polymer membranes for high temperature fuel cells
Project: Research

**AMFC: Advanced Methanol Fuel Cell Systems**
The project aims at developing materials and technologies for an advanced methanol fuel cell system for vehicle propulsion. The system is an integration of a methanol reformer, a catalytic burner, and a fuel cell stack operational at temperatures around 200°C.

Ekdunge, P., Project Manager, Volvo Car Corporation
Bjerrum, N. J., Contact Person, Department of Chemistry
Tunold, R., Project Participant, Norwegian University of Science and Technology
Kløv, K., Project Participant, Statoil ASA

Project ID: ENK5-CT-2000-00323
Forsk. EU - Rammeprogram: DKK6,800,000.00
01/02/2001 → 31/08/2005
Collaborators: Norwegian University of Science and Technology, Statoil ASA, Volvo Car Corporation
Award relations: Advanced Methanol Fuel Cell Systems
Project: Research

**High Temperature Polymer Methanol Fuel Cell,**
Kløv, K., Project Participant, Statoil ASA
Bjerrum, N. J., Project Manager, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry
Tunold, R., Project Participant, Norwegian University of Science and Technology
Ekdunge, P., Project Participant, Gruppechef Per Ekduenge, Volvo Teknisk Utveckling AB,

Project ID: P00030
Forsk. Andre offentlige og private - Nordiske: DKK512,500.00
01/01/2001 → 31/12/2002
Collaborators: Statoil ASA, Gruppechef Per Ekduenge, Volvo Teknisk Utveckling AB, , Volvo Car Corporation, Norwegian University of Science and Technology
Award relations: High Temperature Polymer Methanol Fuel Cell,
Project: Research

**FURIM: Further Improvement and System Integration of High Temperature Polymer Electrolyte Membrane Fuel Cells**
The project is devoted to further development of the PEMFC technology based on temperature-resistant polymer membranes for operation above 100°C. The strategic developments of the FURIM are in three steps: (1) improvement of high temperature polymer membranes and related materials; (2) development of technological units including fuel cell stack, hydrocarbon reformer, afterburner and power management system; and (3) integration of the HT-PEMFC stack with these compatible subunits. The advanced features of the integrated power system include high system efficiency, high power density (small size and light weight of the overall system), simple construction and operation, effective cost, high reliability, less maintenance, and better transient response capacities, which are desirable for both automobile and stationary applications.

Bjerrum, N. J., Project Manager, Department of Chemistry
Ekdunge, P., Project Participant, Volvo Technology Corporation
Borresen, B., Project Participant, Norwegian University of Science and Technology
Scott, K., Project Participant, University of Newcastle upon Tyne
Henriksen, N., Project Participant, Elsam A/S
Hennesø, E., Project Participant, Danish Power Systems ApS
Savinell, R., Project Participant, Case Western Reserve University
Kerres, J., Project Participant, University of Stuttgart
High Temperature Corrosion

A large number of important engineering systems operating at high temperatures (480-1100°C) involve contact of metallic or ceramic materials with combustion product gases or other oxidizing gases containing inorganic impurities, e.g. gas turbines, steam generators, incinerators, petrochemical process vessels. As the gases are cooled, fused salt films may condense on the hardware to generate highly corrosive conditions analogous in some aspects to aqueous atmospheric corrosion.

Some other engineering systems, such as the molten carbonate fuel cell, heat treatment baths, high-temperature homogeneous catalysis etc. use molten salts to accelerate the electrochemical and chemical reactions. When materials come into contact with corrosive molten salt films one can also expect high rates of the corrosion reactions but in this case the acceleration is undesirable and makes corrosion more severe than in aqueous solutions. However the availability of high quality fossil fuels becomes limited, and technologies of solid waste utilization and other efficient energy conversion processes are under development. The damage of hot corrosion is likely to increase. The most important features of hot corrosion are:

1. Generally molten salts are ionic conductors so that the corrosion attack must be electrochemical in nature.
2. Oxyanion molten salts (silicates, sulphates, carbonates, phosphates etc.) exhibit an acid-base behavior. Acidity of the electrolyte often defines the mechanism of the corrosion process.
3. The main products of the reaction between metal and molten salt layer are oxides. Solubility of these oxides in the melt defines the corrosion resistance.

Thermochemistry in Molten Salts

The main purpose of this project is to obtain relevant thermochemical information on molten salt systems - especially those which are of importance in other projects dealt with in the Materials Science Group at Department of Chemistry. Most of the work is carried out in a high temperature heat-flux-calorimeter (max. 550°C) constructed at AMT and in our workshops. Currently molten salt mixtures containing aluminium and alkali halogenides are investigated in the temperature range 200 to 350°C.

Electrochemistry in Molten Salts

A noticeable part of the important electrochemical processes proceeds at high temperatures using molten salt electrolytes. Electrochemistry of molten salts started at the beginning of the nineteenth century, when H. Davy extracted potassium and sodium from molten hydroxides by electrolysis in 1807. At the end of the nineteenth century C. M. Hall and P. L. T. Hérout invented the electrolytic route to aluminium production, and this led to the establishment of the largest industry of metal extraction from molten salts. Compared to aqueous solutions and organic electrolytes, the advantages of molten salts are the following:

1. The electrical conductivity is higher, i.e. about an order of magnitude higher than that of aqueous solutions and several orders higher than that of organic electrolytes.
2. The electrode reactions are faster at high temperatures.
3. The absence of water in the molten salt and therefore no hydrogen reduction. As a result metals with more negative potentials than hydrogen can be reduced.

Electrolytic production of metals from molten salts, with the Hall-Hérout process as the most important industrial application, is currently a major part of modern electrochemistry. In 1995 for example, the total world production was about 6.3 thousand metric tons of lithium, 339 thousand metric tons of magnesium, and 19.4 million metric tons of aluminium. It is clear that in order to use and to develop the high-temperature electrochemical technologies the knowledge in modern electrochemistry of molten salts is important.

It was shown in the BRITE/Euram II Project (Contract no. BRE2.CT93.0447) that electrochemical investigation of the
Molten Salt Catalysis

First publications on molten salt catalysis appeared more than 100 years ago and now processes with molten salt catalysts (molten metal halides and oxides and their mixtures: ZnCl2, AlCl3, CuCl2, V2O5, MoO3 etc.) are widely used in the industrial production of isoparaffins, chlorination of hydrocarbons, gasification of coal etc. It was also proved that the catalytic SO2 oxidation during the sulfuric acid production takes place in a film consisting of V2O5 in molten alkali pyrosulfates.

Molten salt catalysis is the usual type of homogeneous catalytic reaction. However molten salt catalysts have the peculiar properties which make them sometimes the only possibility to synthesize definite organic or inorganic compounds due to:
1. High working temperatures.
2. Absence of water.
3. High concentration of catalyst.
4. Wide acid-base range.
5. High thermal and electric conductivity.

Study on the mechanism of the catalytic SO2 oxidation was the main aim of BRITE/Euram II Project Contract no. BRE2.CT93.0447. In this investigation the V2O5 - M2S2O3 (M is alkali metal) melt was used as a model of the catalyst for the sulphuric acid production. It was shown that electrochemical techniques can be a powerful tool in the study of the mechanism of a catalytic reaction.

Polymer Electrolyte Fuel Cell

The groups research in this area is focused on the investigation and development of low platinum loading gas diffusion electrodes (GDE) for the polymer electrolyte fuel cell (PEFC).

Tests are being conducted on a single fixed test cell. Power densities of more than 0.5 W/cm² are achieved when running the cell on pure hydrogen and oxygen at 80 C and ambient pressure. Operational parameters such as gas humidification, pressure, temperature and composition of fuel and oxidant gases are also investigated.

Development of air metal hydride battery (AMHBAT)

The aim of the project is to develop a rechargeable air hydride battery to be used in electric vehicles (EV). The operating principle of an air metal hydride battery is rather simple: Water is split into hydrogen and oxygen as the battery is charged. Oxygen is released to the atmosphere and hydrogen is stored in the negative electrode which is made of a hydrogen storage alloy similar to those used in nickel metal hydride batteries. On discharge the process is reversed, and stored hydrogen recombines with atmospheric oxygen to form water. The air hydride battery has been studied since 1988 at Helsinki University of Technology (HUT) and the state of the art is a prototype batteries (24 V, 360 W) made by HUT and the Finnish company Hydrocell.

The project involves 5 European universities and 6 industries. It is Supported by the European Community (JOULE, fourth framework programme).

Electrochemical and Spectroscopic Investigation of Electrochemical Cells and Catalysts

The project is concerned with a study of the different non-aqueous chemical processes using electrochemical (cyclic voltammetry, square-wave voltammetry, chronoamperometry etc.) and spectroscopic (Raman, IR, ESR, NMR etc.)
techniques. All the studied processes involve electrochemical steps or electrochemical techniques were used for their study.

The project involves investigation of following electrochemical reaction or systems:

1. Electroplating with refractory metals (niobium, tantalum) from molten salts.
2. Phosphoric acid, molten carbonate and solid oxide fuel cells.
3. Development of the active materials for nickel-metal hydride batteries.

Bjerrum, N. J., Project Manager, Department of Chemistry
Fehmann, R., Project Participant, Department of Chemistry
Barner, J. H. V., Project Participant, Department of Chemistry
Berg, R. W., Project Participant, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry
Nielsen, K., Project Participant, Department of Chemistry
Petrushina, I., Project Participant, Department of Chemistry
Eriksen, K. M., Project Participant, Department of Chemistry
Gang, X., Project Participant, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry

01/01/1996 → 31/12/2002

Project: Research

Development of a Method for On-line Measurements of High Temperature Corrosion

The aim of the project is to develop a method for on-line measurements of high temperature corrosion. It is the idea to use the method in order to keep corrosion under surveillance under various types of operation in existing power plants. For this purpose an electrochemical noise probe will be designed and tested at Masnedø Power Station near Vordingborg – a biomass fired plant constructed in 1996 which only uses straw as fuel.

Bjerrum, N. J., Project Manager, Department of Chemistry
Cappeln, F. V., Project Participant, Department of Chemistry

01/04/1999 → 31/03/2002

Collaborators: Elsam A/S, Elkraft Power Co Ltd.
Project: Research

Advanced Solid Polymer Fuel Cells for Operation at Temperatures up to 200oC (ASPEC)

As a clean and efficient technology fuel cells are expected to provide a practical form of power generation. Among these solid polymer fuel cells (SPFC) using e.g. perfluorosulfonic acid polymer membrane (nafion,µ) have been receiving more and more attention due to their promise as a power generator for both stationary and transportation applications. The operational temperature is limited to be below 100 oC at atmospheric pressure since the presence of water is necessary. The low temperature results in a low catalytic activity at the electrodes (and hence slow kinetics) and strong effect of fuel impurity poisoning. As a consequence neither methanol nor hydrogen from reforming of hydrocarbons can be used. The requirement of high purity hydrogen as the fuel not only increases operation cost but also limits the application of the SPFC.

To overcome these problems the present project aims to develop materials and technologies for an advanced high temperature solid polymer fuel cell (HTSPFC) stack operating at 150 ¡V 200oC with hydrogen from methane or methanol steam reforming (containing 2-3 % CO) as fuel. This will avoid problems associated with hydrogen storage and make the new technology promising in stationary on-site power generation plants and especially for transportation applications.

(JOULE programme (EU))

Bjerrum, N. J., Project Manager, Department of Chemistry
Li, Q., Project Participant, Department of Chemistry

01/02/1998 → 31/07/2000

Collaborators: Ansaldo STS, University of Patras
Project: Research

Lubricants for Cold Forging of Stainless Steel

One of the major problems related to cold forging of stainless steel is to secure sufficient lubrication during the process. The severe conditions during the process (i.e. high normal pressures and large surface expansion) usually requires a two component lubricant system consisting of a porous carrier coating lubricated with a suitable lubricant.

This project deals with the development of two new lubricant systems for cold forging of stainless steel. The lubricant systems are based on zinc phosphate and iron(III) chloride respectively. The zinc phosphate coating serves as a porous “carrier coating” for the actual lubricant (i.e. sodium stearate or MoS2). Iron(III) chloride can be used alone or in combination with MoS2 or graphite. The work has been focusing on application methods, characterisation and tribological tests.

An electrochemical method for depositing zinc/calcium phosphate coatings on stainless steel from an aqueous nitric acid solution has been developed. The method involves hydrogen evolution at the surface of the specimen and the deposition occurs due to decreasing solubility of the metal phosphates at increasing pH.

The lubrication mechanism of iron(III) chloride is believed to involve the reaction between iron(III) chloride and the stainless
steel surface to form iron(II) chloride. Results from backward can extrusion tests confirm that this reaction contributes significantly to the lubrication properties.

Backward can extrusion tests of zinc/calcium phosphate (lubricated with sodium stearate) and iron(II) chloride show that a height/diameter ratio of more than two can be obtained. A height/diameter ration of 1.2 can be obtained with the current State of The Art lubricant system (Iron oxalate combined with MoS2).

Bjerrum, N. J., Project Manager, Department of Chemistry
Christensen, E., Project Participant, Department of Chemistry
Berg, R. W., Project Participant, Department of Chemistry
Andersen, B. K., Project Participant, Department of Chemistry
Jensen, J. O., Project Participant, Department of Chemistry
Bergqvist, R. S., Project Participant, Department of Chemistry
01/01/1994 → 31/12/2001

Project: Research

**Conversion of Methane**
The purpose of this project is to develop a direct conversion process to convert methane (from natural gas) to, for example, methanol which can easily be transported and which is also a more flexible and valuable raw chemical. The project aims at developing a process which is selective and effective enough so that as little methane as possible will be re-circulated in the process. Several types of catalysts have been found in connection to the project, and very high methanol yields have been achieved by using them.

Bjerrum, N. J., Project Manager, Department of Chemistry
Gang, X., Project Participant, Department of Chemistry
Birch, H., Project Participant, Department of Chemistry
01/01/1995 → 31/12/2002

Project: Research