Challenges and Possibilities of EIS on PEMEC

Electrochemical impedance spectroscopy (EIS) has been proven a very strong electrochemical characterization tool in electrochemical research in general and in the areas of fuel cell and battery research in particular. However, this is not the case for polymer electrolyte membrane electrolysis cells (PEMEC), for which relatively few reports on the application of systematic EIS studies are available. Asking experienced researchers in the field about why, the answer has often been that these cells reveals too much electrical noise to obtain EIS with acceptable quality due to O₂ and H₂ bubble formation. Our view of the ideal structure of a PEMEC is that there ought not to be any effect of gas bubbles on the EIS as the current paths should not be disturbed by bubbles. However, we also see noise in our spectra, but the level of noise varies very much from one cell type to another. We have studied noise on three types of PEMEC and two type of alkaline electrolysis cell (AEC) for comparison. A characteristic feature of the studied PEMEC is that there is no or very little noise seen in the EIS in the frequency range above ca. 500 Hz and again not much noise below 5 Hz. Our hypothesis is that this phenomenon is related to bubbles that are adhering to active sites of the electrocatalyst. When the catalyst layer is subjected to alternating current (AC) during the EIS then, in the PEMEC case, the O₂ pressure and volume of the bubbles growing on the catalyst layer will oscillate with the frequency of the AC. The volume change will naturally change with the frequency. The longer the wave period (the lower the frequency) is, the bigger is the change in the amount of O₂ production during an AC period. In other words, a vibration of the O₂ bubble size and internal pressure must be induced by the AC current. Thus, we imagine that at some low frequency, the bubbles adhering to the catalytic layer get more unstable and detach with an uneven rate from the catalyst surface. This causes the noise observed. Presumably, the structure and the properties of the interface of the catalyst to the liquid aqueous phase as well as the operation parameter will affect the frequency range and the size of noise in the EIS.

Long-term operation of a solid oxide cell stack for coelectrolysis of steam and CO₂

High temperature electrolysis based on solid oxide electrolysis cells (SOECs) is a promising technology for production of synthetic fuels. The SOEC units can be used for co-electrolysis of steam and CO2 to produce synthesis gas (syngas, CO+H₂), which can be further processed to a variety of synthetic fuels such as methane, methanol or DME. Previously we have reported electrolysis operation of solid oxide cell stacks for periods up to about 1000 hours. In this work, operation of a Haldor Topsoe 8-cell stack (stack design of 2014) in co-electrolysis mode for 6000 hours is reported. The stack consists of Ni/YSZ electrode supported SOEC cells with a footprint of 12X12 cm². The co-electrolysis operation was carried out by supplying a mixture of 45 % CO₂ + 45 % H₂O + 10 % H₂ to the stack operating with a fixed conversion of 39 % for steam and CO₂. The stack was operated at different conditions. Initial operation at 700 °C and -0.25 A/cm² lasted for only 120 hours due to severe degradation of the bottom cell. Regaining the stack performance was realized by increasing the operation temperature to 750 °C. After reactivation, the stack showed negligible degradation at 750 °C and -0.25 A/cm² and about 1.4 %/1000 h performance degradation at 750 °C and -0.5 A/cm². This study demonstrates feasibility of long-term co-electrolysis operation via SOEC stacks and of careful temperature variation as a tool to regain the stack performance.
Modelling of gas diffusion limitations in Ni/YSZ electrode material in CO\textsubscript{2} and co-electrolysis

Carbon formation during CO\textsubscript{2} and co-electrolysis (combined electrolysis of H\textsubscript{2}O and CO\textsubscript{2}) has been observed in recent studies, under operating conditions where carbon formation, based on the bulk gas composition, should be thermodynamically unfavorable. The carbon can principally be formed by the Boudouard reaction (2CO \rightarrow CO\textsubscript{2} + C(s)) or the CO reduction reaction (CO + H\textsubscript{2} \rightarrow H\textsubscript{2}O + C(s)), and will disintegrate the cell structure as it grows. It is therefore of great importance to be able to predict when the carbon is formed, and subsequently take actions to prevent formation. The literature offers suggestions that the carbon formation is caused by diffusion limitations within the Ni/YSZ electrode, but this has not been verified.

To do so, the diffusion has been modelled with the dusty gas model and the effect of the electrode tortuosity, porosity, temperature T, electrode thickness d\textsubscript{c}, and current density i, has been investigated. It is shown that diffusion limitations in reactant transport may lead to significant increases in equilibrium temperatures for the two carbon forming reactions. For given electrode properties (e, t, and d\textsubscript{c}) increasing current density leads to increasing equilibrium temperatures. The model can be used to calculate limitations on operating conditions (T, i) that ensure no carbon formation.

Quantitative review of degradation and lifetime of solid oxide cells and stacks

A comprehensive review of degradation and lifetime for solid oxide cells and stacks has been conducted. Based on more than 50 parameters from 150 publications and 1 000 000 hours of accumulated testing, this paper presents a quantitative analysis of the current international status of degradation and lifetime in the field. The data is used to visualize specific trends regarding choice of materials, operating conditions and degradation rates. The average degradation rate reported is decreasing and is quickly approaching official targets. The database is published online for open-access and a continued updating by the community is encouraged. Furthermore, the commonly reported test parameters and degradation indicators are discussed. The difficulty in standardizing testing due to variations in cell and stack design, materials and intended purpose of the system is acknowledged. A standardization of reporting of long-term single-cell- and stack-tests is proposed.
Relation between shape of Ni-particles and Ni migration in Ni-YSZ electrodes – a hypothesis

This is an attempt to explain a phenomenon of total depletion of Ni next to the electrolyte in Ni-YSZ cermet electrodes in solid oxide electrolysis cells during electrolysis at high current density/overpotential. Intuitively, we would think that Ni would always migrate down the steam partial pressure (pH2O) gradient as previously observed [1], but in the present cases Ni seems to migrate up the pH2O gradient. However, it is also observed that there is a preceding phase in this Ni-YSZ electrode degradation, namely that the Ni-particles closest to the YSZ electrolyte loose contact to each other. This means that the active three phase boundary (TPB) moves away from the electrolyte and causes a significant increase in the ohmic resistance as is also observed in electrochemical impedance spectra.

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Relaxation of stresses during reduction of anode supported SOFCs

To assess the reliability of solid oxide fuel cell (SOFC) stacks during operation, the stress field in the stack must be known. During operation the stress field will depend on time as creep processes relax stresses. This work reports further details on a newly discovered creep phenomenon, accelerated creep, taking place during the reduction of a Ni-YSZ anode. This relaxes stresses at a much higher rate (~×104) than creep during operation. Thus, the phenomenon of accelerated creep during reduction has to be considered both in the production of stacks and in the analysis of the stress field in a stack based on anode supported SOFCs. Accelerated creep has previously been studied in experiments with simultaneous loading and reduction. The hypothesis for the phenomenon centers around a significant softening of the Ni phase, which amongst other should lead to a significant relaxation of internal stresses in the Ni(O)-YSZ microstructure. The internal residual stresses can be anticipated due the different thermal contractions of the two phases from the sintering temperature to the reduction temperature. It was thus concluded that with the recorded high creep rates, the stresses in a cell at the time of reduction should decrease significantly over minutes. In this work these internal stresses are measured in-situ before and after the reduction by use of X-ray diffraction. This is done by determining the elastic micro-strains (correlating to the stresses), which are assessed from the widening of the Bragg peaks. This enables us to determine the stresses in the different phases locally inside the microstructure of the composite Ni(O)-YSZ anode. Furthermore, the residual stresses have been modeled during cool-down from the reduction temperature. The stresses have been assessed by use of a combination of a 3D microstructural reconstruction by FIB-SEM, a microstructural finite element model and analytical homogenization considerations. A significant decrease of stresses is observed through the reduction as predicted, which partly confirms the hypothesis for the accelerated creep. Also, a significant relaxation of stresses to lower temperatures (~300°C) was also found. This was confirmed by the models, but is however not consistent with previous recorded coefficients of thermal expansion.

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Accelerated creep of Ni-YSZ anodes during reduction

To evaluate the reliability of solid oxide fuel cell (SOFC) stacks during operation the stress field must be known at all times. This is influenced by external loads, the operating conditions, the particular design of the stack components and their mechanical properties and finally by the thermomechanical history of the stack (e.g. sintering temperature, time at temperature etc.). During operation the stress state will depend on time as stresses are relaxed by creep processes. Creep has mainly been studied at operating conditions, where the Ni-YSZ anode is in the reduced state and YSZ is the main load-carrying component. In this work we report on a new creep-reduction phenomenon observed to take place during the reduction process itself, where stresses are relaxed at a rate much faster (~×10^4) than during operation where the anode is in fully reduced state. Furthermore, samples exposed to a very small tensile stress (0.004 MPa) were observed to expand during reduction, which is in contrast with reports in literature [Ref]. The “accelerated” creep has a tremendous impact on the stress field in an operating SOFC stack. Creep experiments, where carried out on NiO-YSZ anode support structures loaded in three point bending or uniaxial tension and the deformations recorded during the reduction process. The fast creep is observed only during the reduction, but due to the extremely high rate this will effectively relax all the residual compressive stresses in the electrolyte at the reduction temperature. Therefore this phenomenon has to be considered both in the production of stacks and in the simulation of the stress field in an SOFC stack.

Advanced impedance modeling of solid oxide electrochemical cells

Impedance spectroscopy is a powerful technique for detailed study of the electrochemical and transport processes that take place in fuel cells and electrolysis cells, including solid oxide cells (SOCs). Meaningful analysis of impedance measurements is nontrivial, however, because a large number of modeling parameters are fit to the many processes which often overlap in the same frequency ranges. Also, commonly used equivalent circuit (EC) models only provide zero-dimensional (0-D) approximations of the processes of the two electrodes, electrolyte and gas transport. Employing improved analytical techniques to provide good guesses for the modeling parameters, like transforming the impedance data to the distribution of relaxation times (DRT), together with experimental parameter sensitivity studies, is the state-of-the-art approach to achieve good EC model fits.

Here we present new impedance modeling methods which advantageously minimize the number of modeling parameters and the parameters used have direct physicochemical meaning. This is accomplished by (i) employing an improved cell model where the representative 0-D resistive-capacitive type EC elements are replaced by analytical 1-D porous electrode and 2-D gas transport models which have fewer unknown parameters for the same number of processes, (ii) use of a new model fitting algorithm, “multi-fitting”, in which multiple impedance spectra are fit simultaneously with parameters linked based on the variation of measurement conditions, (iii) constraining the parameter values during fitting to ranges of physically reasonable values.

Using these methods, the number of fitting parameters for four impedance spectra measured with isolated changes to the fuel and oxidant gas compositions, has been reduced from 80 to 21-34 depending on the model. The obtained results include structural parameters like porosity and tortuosity; or if those characteristics are known, use of even fewer fitting parameters is possible. The methods have been implemented in a software package written by one of the authors, which also implements many previously used impedance analysis methods and integrates the analysis process in a modular workflow – data validation (Kramers-Kronig), clean-up, visualization (DRT and others), modeling (nonlinear least-squares fitting), and final plotting for publication.
Assessment of full ceramic solid oxide fuel cells based on modified strontium titanates

Today’s solid oxide fuel cells based on composite Ni-cermet anodes have been developed up to reasonable levels of performance and durability. However, especially for small combined heat and power supply systems, known failure mechanisms e.g. re-oxidation, sulfur tolerance and coking have stimulated the development for full ceramic anodes based on strontium titanates. Furthermore, the Ni-cermet is primarily a hydrogen oxidation electrode and efficiency losses might occur when operating on carbon containing fuels.

In the European project SCOTAS-SOFC full ceramic cells comprising CGO/Ni infiltrated SrTiO3 anodes, and LSM/YSZ cathodes have been developed and tested as single 5 x 5 cm2 cells and up 100 cm2 circular cells. The initial performance exceeded 0.4 W/cm2 at 850 °C and redox tolerance has been proven. The cell concept provides flexibility with respect to the used electro-catalysts and various infiltrated metals including Ni and Ru have been studied. Stable power output has been observed for Ru and Ni-CGO as infiltrate. While redox tolerance is maintained, both types of cells degrade rapidly under exposure to sulfur. An initial assembly of a 60 cell stack in a one kW Hexis Galileo system indicates the necessity for further stack design adaptation in order to account for the lower electronic conductivity compared to Ni-cermet based cells.

Degradation of Solid Oxide Electrolysis Cells Operated at High Current Densities

In this work the durability of solid oxide cells for co-electrolysis of steam and carbon dioxide (45 % H2O + 45 % CO2 + 10 % H2) at high current densities was investigated. The tested cells are Ni-YSZ electrode supported, with a YSZ electrolyte and either a LSM-YSZ or LSCF-CGO oxygen electrode. A current density of -1.5 and -2.0 A/cm2 was applied to the cell and the gas conversion was 45 % and 60 %, respectively. The cells were operated for a period of up to 700 hours. The electrochemical analysis revealed significant performance degradation for the ohmic process, oxygen ion interfacial transfer process and the reaction process at the Ni-YSZ triple-phase boundaries. The performance degradation is mainly ascribed to the microstructural changes in the Ni-YSZ electrode close to the YSZ electrolyte, including percolation loss of Ni and the contact loss of Ni and YSZ electrolyte. The type of the oxygen electrode showed an influence to the ohmic degradation: the better performing oxygen electrode corresponded to a lower Rs increase. However, the oxygen electrode itself was found to be relative stable both with respect to the electrochemical performance and microstructure.
Durable solid oxide electrolysis cells for hydrogen production

Solid oxide cell (SOC) for electrolysis application has attracted great interest in recent years due to its high power-to-gas efficiency and capability of co-electrolysis of H2O and CO2 for syngas (H2 + CO) production. The demonstration of durable solid oxide electrolysis cell operation for fuel production is required for promoting commercialization of the SOEC technology. In this work, we report a recent 4400 hours test of a state-of-the-art Ni-YSZ electrode supported SOEC cell. The cell consists of a Ni-YSZ (YSZ: yttria stabilized zirconia) support and active fuel electrode, an YSZ electrolyte layer, a CGO (Gd doped ceria) inter-diffusion barrier layer and a LSCF-CGO (LSCF: lanthanum ferrite doped with strontium and cobalt) oxygen electrode layer. The electrolysis test was carried out at 800 °C under 1 A/cm2 with 90 % H2O + 10 % H2 supplied to Ni-YSZ electrode compartment. The results show that except for the first 250 hours fast initial degradation, for the rest of the testing period, the cell showed rather stable performance with a moderate degradation rate of around 25 mV/1000 h. The electrochemical impedance spectra show that both serial resistance and polarization resistance of the cell increased during the durability test. Further analyses of the cell impedance show that both the LSCFCGO electrode and Ni-YSZ electrode degraded and the degradation was dominated by that of the Ni-YSZ electrode. Post-mortem analysis on the Ni-YSZ electrode revealed loss of percolation between Ni-Ni grains and changing of porosity inside the active layer. The degree of these microstructural changes becomes less and less severe along the hydrogen-steam flow path. The present test results show that this type of cell can be used for early demonstration electrolysis at 1A/cm2. Future work should be focus on reducing the high initial degradation rate and improving the long term durability.

Fuel flow distribution in SOFC stacks revealed by impedance spectroscopy

As SOFC technology is moving closer to a commercial break through, methods to measure the “state-of-health” of operating stacks are becoming of increasing interest. This requires application of advanced methods for detailed electrical and electrochemical characterization during operation. An operating stack is subject to compositional gradients in the gaseous reactant streams, and temperature gradients across each cell and across the stack, which complicates detailed analysis.

An experimental stack with low ohmic resistance from Topsoe Fuel Cell A/S was characterized using Electrochemical Impedance Spectroscopy (EIS). The stack measurement geometry was optimized for EIS by careful selection of the placement of current feeds and voltage probes in order to minimize measurement errors. It was demonstrated that with the improved placement of current feeds and voltage probes it is possible to separate the loss contributions in an ohmic and a polarization part and that the low frequency response is useful in detecting mass transfer limitations. This methodology can be used to detect possible minor changes in the supply of gas to the individual cells, which is important when going to high fuel utilizations. The fuel flow distribution provides important information about the operating limits of the stack when high electrical efficiency is required.
Impedance Spectra of Activating/Passivating Solid Oxide Electrodes

The aim of this paper is to show that the inductive arcs seen in electrochemical impedance spectra of solid oxide cells (SOCs) are real electrochemical features that in several cases can be qualitatively explained by passivation/activation processes.

Several degradation processes of Solid Oxide Fuel Cells (SOFC) and Electrolyser Cells (SOEC) exist. Not all of them are irreversible, especially not over short periods. A reversible degradation is termed “passivation” and the reverse is then “activation”. These processes may exhibit themselves in the Electrochemical Impedance Spectra (EIS) as inductive arcs at low frequencies, often below 1 Hz.

The phenomenon has been observed and reported in the literature far back in time, for a large variety of electrodes and in many different circumstances. Examples of such EIS of SOC electrodes are shown and discussed. EIS of both technological and model electrodes are presented. The inductive arcs in the EIS of the porous technological electrode are usually less pronounced compared to model electrodes. Inductive arcs in EIS of both H2 and O2 electrodes in SOCs are treated here and for both cases the inductive arcs are explained by i-V curves that are not reflecting really stable electrode performance. This is in line with frequent observations of oscillating current density at electrode potentials in the vicinity of the ranges in which the inductive arcs are observed.

Micromechanical Modeling of Solid Oxide Fuel Cell Anode Supports based on Three-dimensional Reconstructions

The efficiency and lifetime of solid oxide fuel cells (SOFCs) is compromised by mechanical failure of cells in the system. Improving the mechanical reliability is a major step in ensuring feasibility of the technology. To quantify the stress in a cell, mechanical properties of the different layers need to be accurately known. Since the mechanical properties are heavily dependent on the microstructures of the materials, it is highly advantageous to understand the impact of microstructures and to be able to determine effective mechanical properties for cell or stack scale analyses. The purpose of this work is to provide such a link. State-of-the-art SOFCs are supported by a porous layer of Ni-3YSZ which has a complex microstructure and a drastic difference in behaviors between their phases. This work investigates the microscopic stress distribution and macroscopic creep rate of porous Ni-3YSZ in the operating temperature through numerical micromechanical modeling. Three-dimensional microstructures of Ni-3YSZ anode supports are reconstructed from a two-dimensional image stack obtained via focused ion beam tomography. Time-dependent stress distributions in the microscopic scale are computed by the finite element method. The macroscopic creep response of the porous anode support is determined based on homogenization theory. It is shown that micromechanical modeling provides an effective tool to study the effect of microstructures on the macroscopic properties.
Ni/YSZ microstructure optimization for long-term stability of solid oxide electrolysis cells

In the last decade there has been a renewed and increased interest in electrolysis using solid oxide cells (SOC). So far the vast majority of results reported on long-term durability of solid oxide electrolysis cells (SOEC) have been obtained using SOC produced and optimized for fuel cell operation; i.e. solid oxide fuel cells (SOFC). However, previous long-term tests have shown that the stability behavior of the Ni/yttria-stabilized-zirconia (Ni/YSZ) fuel electrode may fall out quite differently depending on whether the cell is operated in fuel cell or electrolysis mode at otherwise similar test conditions. Initial work has shown significant microstructural changes of the Ni/YSZ electrode close to the electrolyte interface after long-term steam electrolysis test at -1 A/cm² at 800 C. The results indicate that it will be advantageous to optimize the electrode structure with the aim of keeping the Ni particles in their required positions in the porous Ni/YSZ cermet close to the electrolyte. In this work we report cell tests and microstructures from reference and long-term tested SOEC with varied initial Ni/YSZ ratio with the aim of investigating the effect of changed Ni/YSZ ratio on long-term stability during steam electrolysis.

Overview of SOFC/SOEC development at DTU Energy Conversion

According to a broad political agreement in Denmark, the Danish energy system should become independent on fossil fuels like oil, coal and natural gas by the year 2050. This aim requires expansion of electricity production from renewable sources, in particular wind mills. In order to balance the fluctuating power production and to cope with the discrepancies between demand and supply of power, solid oxide fuel cells and electrolysis are considered key technologies. DTU Energy Conversion has a strong record in SOFC/SOEC research, with a close collaboration with industry, in particular with Danish Topsoe Fuel Cell A/S. Recent achievements will be presented ranging from development of new cell generations, manufacturability, up to testing under realistic operating conditions including degradation studies and high pressure testing. A strong focus will be on development of methodologies, e.g. in micro structural analysis and electrochemistry, in order to understand fundamental processes in detail and thus being able to improve SOFC/SOEC based on this knowledge.
Performance characterization of solid oxide cells under high pressure

Solid oxide electrolysis cells (SOECs) offer a great potential for large scale conversion of renewable electrical energy into chemical energy via electrolysis of H2O and CO2 to produce syngas (H2 + CO). The produced syngas can be further catalytically converted into various gaseous or liquid hydrocarbon fuels, which is normally performed at high pressure to achieve a high yield. Operation of SOECs at elevated pressure will therefore facilitate integration with the downstream fuel synthesis and is furthermore advantageous as it increases the cell performance. In this work, recent pressurised test results of a planar Ni-YSZ (YSZ: Yttria stabilized Zirconia) supported solid oxide cell are presented. The test was performed at 800 °C at pressures up to 15 bar. A comparison of the electrochemical performance of the cell at 1 and 3 bar shows a significant and equal performance gain at higher pressure in both fuel cell mode and electrolysis mode. In electrolysis mode at low current density, the performance improvement was counteracted by the increase in open circuit voltage, but it has to be born in mind that the pressurised gas contains higher molar free energy. Operating at high current density is in particular more beneficial when operating the SOEC at increased pressure.

Residual stresses in a co-sintered SOC half-cell during post-sintering cooling

Due to the thermal expansion mismatch between the layers of a Solid Oxide Cell, residual stresses (thermal stresses) develop during the cooling after sintering. Residual stresses can induce cell curvature for asymmetric cells but more importantly they also result in more fragile cells. Depending on the loading conditions, the additional stress needed to break the cells can indeed be smaller due to the initial thermo-mechanical stress state. The residual stresses can for a bilayer cell be approximated by estimating the temperature at which elastic stresses start to build up during the cooling, i.e. the reference temperature (Tref) or the strain difference based on the curvature. This approximation gives good results for bilayers with a defined cooling temperature profile, where the curvature of the bilayer defines a unique balance between the two unknown residual stress states in the two layers. This methodology is however not valid for more layers, as several configurations of residual stresses in the layers can result in the same curvature. Therefore the development of residual stresses of co-sintered multilayer cells during the cooling after sintering is here studied by a finite element model simulation taking into account the elastic response and creep of each layer. The model is validated by measuring the curvature and residual stresses of multi-layer cells.
Thermodynamic Evaluation of LSCF Cathode Stability and Tolerance towards Gas Impurities

Strontium and iron co-doped lanthanum cobaltites (La$_{1-x}$Sr$_x$Co$_{1+y}$Fe$_y$O$_{3-δ}$, LSCF) show good oxygen ion and electronic conductivity and fast oxygen surface exchange kinetics at temperatures between 600 and 800 °C, and is considered today one of the most promising class of cathode materials for intermediate-temperature solid oxide fuel cells. Despite its technological importance, the phase stability of the LSCF perovskite has not yet been fully mapped out and may be critical for the use of the materials during long-term operation. For cells with LSCF or LSCF/CGO (CGO: gadolinia doped ceria) cathodes, partial decomposition of the perovskite phase has been reported as a possible cause of high degradation rates. In addition, the LSCF perovskite is prone to react with gas species, such as CO$_2$ and water vapor, which are present in atmospheric air, or species evaporated from stack components (interconnects and glass seals), such as chromium- or boron-containing gas species. In this paper, a thermodynamic database for the multicomponent La-Sr-Co-Fe-O system is presented which was established employing the CALPHAD (CALculation of PHAse Diagrams) methodology. The phase stability of LSCF itself is then discussed as a function of composition, temperature and oxygen partial pressure. The results show that the LSCF perovskite phase will decompose at high Sr or Co content, at elevated temperature, or at reduced oxygen partial pressure. The LSCF reactivity towards gas impurities is further analyzed under realistic SOFC operating conditions.

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Pressurized H$_x$C$_y$O$_z$ Cells at ca. 250 °C: Potential and Challenges

The increasing need for easy and affordable storage of intermittent renewable energy has encouraged us to explore the possibilities of pressurized electrolysis and fuel cells operating in the temperature range of 200 – 300 °C and pressure from a few bar up to 50 bar and above. Most electrochemical rate limiting processes are strongly thermal activated. Also, increased pressure may increase the electrode reaction rates. High pressure means increase energy density in gaseous products. Furthermore, as hydrocarbons, alcohols or ethers in common denoted H$_x$C$_y$O$_z$ - are very convenient fuels, we have focus on cells that may have a potential of forming or using H$_x$C$_y$O$_z$ in electrolysis or fuel cell mode, respectively. Examples of H$_x$C$_y$O$_z$ are hydrogen with (x,y,z) = (2,0,0), carbon monoxide with (x,y,z) = (0,1,1), methane with (x,y,z) = (4,1,0), gasoline with approximately (x,y,z) = (18,8,0), methanol with (x,y,z) = (4,1,1), and dimethyl ether (DME) with (x,y,z) = (6,2,1). The temperature about 200 – 300 °C is of particular interest because if the direct electrochemical reduction products from electrolysis of H$_2$O and CO$_2$ mixtures are H$_2$ and CO (syngas) then this temperature together with increased pressure makes it potentially possible to convert the syngas into H$_x$C$_y$O$_z$ inside the cathode compartment using suitable catalysts, because such conditions are very similar to the commercial catalysis technology used by chemical industry.

A brief review of some literature behind this strategic thinking is given, followed by examples of results from our own laboratory. So far the concept of high temperature and pressure electrolysis has proven successful on small scale using button cell with KOH(aq.) electrolyte immobilized in a porous ceramic layer. Also cells using immobilized K$_2$CO$_3$(aq.), CsH$_2$PO$_4$ solid acid, and BaZr$_{1-u}$Ce$_u$Y$_v$O$_{3-δ}$ proton conducting electrolytes have been constructed and tested. Reduction of CO$_2$ seems significantly more difficult than reduction of H$_2$O. This and many other challenges appear from our work.

The apparent challenges and the potential benefits that make it worthwhile to overcome the challenges are discussed and some main arguments in favor of continuing this strategy are presented.

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Advances in Metal Supported Cells in the METSOFC EU Consortium

Employing a mechanically robust metal support as the structural element in SOFC has been the objective of various development efforts. The EU-sponsored project "METSOFC", completed at the end of 2011, resulted in a number of advancements towards implementing this strategy. These include robust metal supported cells (MSCs) having low ASR at low temperature, incorporation into small stacks of powers approaching ½kW, and stack tolerance to various operation cycles. DTU Energy Conversion's (formerly Risø DTU) research into planar MSCs has produced an advanced cell design with high performance. The novel approach has yielded robust, defect-free cells fabricated by a unique and well-tailored co-sintering process. At low operation temperatures (650°C), these cells have shown remarkable ASRs: 0.35 Ωcm² in cell tests (16 cm² active area) and under 0.3 Ωcm² in button cells (0.5 cm² active area). Further success was attained with even larger cell areas of 12 cm squares, which facilitated integration into stacks at Topsoe Fuel Cell. Development of MSC stacks showed that the MSCs could achieve similar or better performance, compared to SoA anode supported ceramic cells. The best stacked MSCs had power densities approaching 275 mW/cm² (at 680°C and 0.8V). Furthermore, extended testing at AVL determined extra stack performance and reliability characteristics, including behavior towards sulfur and simulated diesel reformate, and tolerance to thermal cycles and load cycles. These and other key outcomes of the METSOFC consortium are covered, along with associated work supported by the Danish National Advanced Technology Foundation.

Break-down of Losses in High Performing Metal-Supported Solid Oxide Fuel Cells

Metal supported SOFC designs offer competitive advantages such as reduced material costs and improved mechanical robustness. On the other hand, disadvantages might arise due to possible corrosion of the porous metal parts during processing and operation at high fuel utilization. In this paper we present the results of performance and stability improvements for a metal supported cell developed within the European project METSOFC and the Danish National Advanced Technology Foundation. The cells consist of a porous metal backbone, a metal / zirconia cermet anode and a 10ScYSZ electrolyte, cofired in hydrogen. The electrochemically active parts were applied by infiltrating CGO-Ni precursor solution into the porous metal and anode backbone and screenprinting (La,Sr)(Co,Fe)O3-based cathodes. To prevent a solid state reaction between cathode and zirconia electrolyte, CGO buffer layers were applied in between cathode and electrolyte. The detailed electrochemical characterization by means of impedance spectroscopy and a subsequent data analysis by the distribution of relaxation times enabled us to separate the different loss contributions in the cell. Based on an appropriate equivalent circuit model, the ohmic and polarization losses related to the gas diffusion in the metal support, the electrooxidation in the anode functional layer and the oxygen reduction in the mixed ionic electronic conducting cathode were determined. An additional process with a rather high relaxation frequency could be attributed to the formation of insulating interlayers at the cathode/electrolyte-interface. Based on these results, selective measures to improve performance and stability, such as (i) an improved PVD-deposited CGO buffer layer, (ii) LSC-CGO based in-situ sintered cathodes and (iii) reduced corrosion of the metal support were adopted and validated.
Infiltrated SrTiO₃:FeCr-based anodes for metal-supported SOFC

The concept of using highly electronically conducting backbones with subsequent infiltration of electrocatalytic active materials, has recently been used to develop an alternative SOFC design based on a ferritic stainless steel support. The metal-supported SOFC is comprised of porous and highly electronically conducting layers, into which electrocatalytically active materials are infiltrated after sintering.

This paper presents the first results on single cell testing of 25 cm² cells with 16 cm² active area of a metal-supported SOFC were the anode backbone consists of a composite of Nbdoped SrTiO₃ (STN) and FeCr. Electrochemical characterization and post test SEM analysis have been used to get an insight into the possible degradation mechanisms of this novel electrode infiltrated with Gd-doped CeO₂ and Ni. Accelerated oxidation/corrosion experiments have been conducted to evaluate the microstructural changes occurring in the anode layer during testing. The results indicate that the STN component in the anode seems to have a positive effect on the corrosion stability of the FeCr-particles in the anode layer.

Durability of SOFCs using sulphur containing fuels

The concept of using highly electronically conducting backbones with subsequent infiltration of electrocatalytic active materials, has recently been used to develop an alternative SOFC design based on a ferritic stainless steel support. The metal-supported SOFC is comprised of porous and highly electronically conducting layers, into which electrocatalytically active materials are infiltrated after sintering.

This paper presents the first results on single cell testing of 25 cm² cells with 16 cm² active area of a metal-supported SOFC were the anode backbone consists of a composite of Nbdoped SrTiO₃ (STN) and FeCr. Electrochemical characterization and post test SEM analysis have been used to get an insight into the possible degradation mechanisms of this novel electrode infiltrated with Gd-doped CeO₂ and Ni. Accelerated oxidation/corrosion experiments have been conducted to evaluate the microstructural changes occurring in the anode layer during testing. The results indicate that the STN component in the anode seems to have a positive effect on the corrosion stability of the FeCr-particles in the anode layer.

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La$_{0.99}$Co$_{0.4}$Ni$_{0.6}$O$_3$-δ/Ce$_{0.8}$Gd$_{0.2}$O$_{1.95}$ as composite cathode for SOFCs

**General information**
Publication status: Published
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Contributors: Hjalmarsson, P., Mogensen, M. B.
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Ni based solid oxide cell electrodes

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Organisations: Electrochemistry, Fuel Cells and Solid State Chemistry Division, Risø National Laboratory for Sustainable Energy
Contributors: Mogensen, M. B., Holtappels, P.
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Status of development and manufacture of Solid Oxide Fuel Cells at Topsoe Fuel Cell A/S and Risø DTU

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Modelling of the polarization resistance from surface exchange and diffusion coefficient data

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Søgaard, M., Hendriksen, P., Jacobsen, T., Mogensen, M. B.
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Oxidation states of Mn, Cr, and Co in mixed spinels studied by XANES

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Hagen, A., Østby, J.
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Performance and stability of barium strontium cobaltite composite cathodes for SOFC

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Wang, W., Jensen, S. H., Mogensen, M. B.
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The effect of minor alloying elements in ferritic steels for interconnects in SOFCs

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Schuisky, M., Rosberg, A., Mikkelsen, L., Hendriksen, P., Christiansen, N., Larsen, J.
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The H2/H2O/Ni/zirconia point electrode: Effects of impurities on the zirconia surface

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Høgh, J., Hansen, K., Chorkendorff, I., Jacobsen, T., Mogensen, M. B.
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Break down of losses in thin electrolyte SOFCs

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Barfod, R., Hagen, A., Ramousse, S., Hendriksen, P., Mogensen, M. B.
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Electrode activation and passivation of solid oxide fuel cell electrodes

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Oxidation behaviour of iron-chromium steels for solid oxide fuel cell interconnect

General information
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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Pedersen, T., Linderoth, S., Laatsch, J.
Pages: 897-907
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Proceedings. Vol. 1-3

General information
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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Mogensen, M. B.
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Properties and performance of SOFCs produced on a pre-pilot plant scale

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Contributors: Hagen, A., Menon, M., Ramousse, S., Larsen, P., Barfod, R., Hendriksen, P.
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Solid oxide fuel cell performance under severe operating conditions

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Koch, S., Hendriksen, P., Mogensen, M. B., Dekker, N., Rietveld, B., Haart, B. D., Tietz, F.
Pages: 299-308
Publication date: 2004

Status and recent advances in SOFC development at Haldor Topsøe/Risø

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Christiansen, N., Kristensen, S., Holm-Larsen, H., Larsen, P., Mogensen, M. B., Hendriksen, P., Linderoth, S.
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Testing of Ni-plated ferritic steel interconnect in SOFC stacks

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Dinesen, A., Nielsen, K., Poulsen, F., Mikkelsen, L., Hendriksen, P.
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Publication date: 2004
Proton conductivity of phosphoric acid doped polybenzimidazole and its composites with inorganic protonic conductors

Polymer electrolytes have received considerable attention, especially for polymer electrolyte membrane fuel cells (PEMFCs) operating at temperatures above 100°C. Phosphoric acid doped polybenzimidazole (PBI) and PBI composite membranes have been prepared in the present work. The PBI composites contain inorganic protonic 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 blending 15 wt.% of ZrP in a PBI membrane at 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 up to 110°C.

General information
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Organisations: Department of Chemistry
Contributors: Li, Q.
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Defect chemistry modelling of complex SOFC materials

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Poulsen, F., Søgård, M.
Pages: 687-694
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Place of publication: Oberrohrdorf (CH)
Publisher: European Fuel Cell Forum
Editor: Huijsmans, J.
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Development of thin-electrolyte solid oxide fuel cells

General information
Publication status: Published
Electrochemical evaluation of functionally graded SOFC cathodes

Evaluation of ferrite stainless steels as interconnects in SOFC stacks

LSCF-CGO composite cathodes for intermediate temperature solid oxide fuel cells (IT-SOFCs)
Manufacture and properties of NiO-YSZ anode supports and current collectors

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Ni-YSZ and Ni-CGO anodes for integrated planar solid oxide fuel cells: Performance comparison

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Lapena-Rey, N., Hart, N., Collins, R., Brandon, N., Bonanos, N.
Pages: 883-892
Publication date: 2002

Status of SOFC development at Haldor Topsøe / Risø

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Christiansen, N., Kristensen, S., Holm-Larsen, H., Larsen, P., Mogensen, M. B., Hendriksen, P., Linderoth, S.
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Publication date: 2002
Strategies for testing of solid oxide fuel cells and electrodes

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Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Mogensen, M. B., Hendriksen, P., Kammer Hansen, K.
Pages: 893-902
Publication date: 2002

Test and performance analysis of SOFC stack units

General information
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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Nielsen, K., Linderoth, S., Kindl, B., Bilde-Sørensen, J., Larsen, P.
Pages: 729-736
Publication date: 2002

Fabrication of thin anode-supported SOFCs

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Juhl Jørgensen, M., Larsen, P., Primdahl, S., Bagger, C.
Pages: 203-210
Publication date: 2000
Improved cathode performance using graded structures

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Cassidy, M., Brandon, N., Day, M., Bagger, C.
Pages: 637-646
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Place of publication: Oberrohrdorf (CH)
Publisher: European Fuel Cell Forum
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Improving durability of SOFC stacks (IDUSOFC)

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Linderoth, S., Mogensen, M. B.
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Low-cost fabrication and improved performance of SOFC stack components

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Linderoth, S.
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Optimisation of perovskite titanates and niobates as anode materials for SOFCs

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Organisations: Risø National Laboratory for Sustainable Energy
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Research

Electrochemical performance and structure of composite (La$_{0.85}$Sr$_{0.15}$)$_{0.9}$MnO$_{3-y}$/YSZ cathodes

General information
Publication status: Published
Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Holtappels, P., Juhl Jørgensen, M., Primdahl, S., Mogensen, M. B., Bagger, C.
Pages: 311-320
Publication date: 1998

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Research

In plane conductivity of improved Ni-cermet anodes

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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Kindermann, L., Poulsen, F., Bagger, C.
Pages: 133-143
Publication date: 1998

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Research

Non-destructive evaluation of electrodes for solid oxide fuel cells
Oxidation studies of Cr and Cr-rich alloys: Influence of atmosphere and yttria-dispersion

Performance of fuel cells with a ceria-based anode

Properties of multiple-doped lanthanum chromites
Synthesis and properties of La-Sr-Mn-Fe-O based perovskites

General information
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Organisations: Risø National Laboratory for Sustainable Energy
Contributors: Kindermann, L., Poulsen, F., Larsen, P., Nickel, H., Hilpert, K.
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