Development of Hydrogen Electrodes for Alkaline Water Electrolysis - DTU Orbit

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The share of renewable energy worldwide is expected to increase by 38% in the period between 2011 and 2035. Consequently, the share of energy from fluctuating energy sources, such as wind, sun and hydro, will escalate and new alternatives for energy conversion, energy storage and load management will be needed. Producing hydrogen via water electrolysis using surplus, low cost, power from renewables offers the possibility of increased production capacity and load management with no greenhouse emissions. Hydrogen is a valuable energy carrier, which is able to contribute to various forms of energy, such as, production of electricity via fuel cells, fuel for internal combustion engines or gas turbines, or as a raw material for the production of synthetic fuels via Sabatier or Fischer - Tropsch process. In some situations it may be suitable to simply inject hydrogen into the existing natural gas based infrastructure. Alkaline water electrolysis (AWE) is the current standard (stat of the art) for industrial large-scale water electrolysis systems. One of the main criteria for industrial AWE is efficient and durable electrodes. The aim of the present PhD study was to develop electrode materials for hydrogen production in order to improve the efficiency and durability, and decrease the costs associated with industrial AWE. The primary effort was reserved to the hydrogen electrodes. Additionally, a new test setup for efficiency and durability measurements was to be designed and constructed. During the present PhD study, new hydrogen electrodes with large electrocatalytic active surface area were developed. The electrodes were produced by physical vapour deposition (PVD) of about 20 μm of aluminium onto a nickel substrate followed by thermo-chemical diffusion and selective aluminium leaching. The obtained electrode surfaces were found to be highly porous; both at micro- and nano-scale, and surface roughness factors of up to 2300 times that of polished nickel were measured. The electrocatalytic surfaces were characterized to have unique adhesion to the substrate, which is a critical criterion for industrial applications. High Resolution Scanning Electron Microscope (HR-SEM) images reveal highly skeletal structure with pores down to a few nanometres. Half-cell potentiodynamic polarisation curves, recorded at 25°C, 200 mA/cm², show the electrodes to have 385 mV lower hydrogen overpotential and 50 mV lower oxygen overpotential, when compared to polished nickel. Durability test was carried out in an industrial sized bipolar, non-zero gap AWE stack where the developed electrodes were applied both as anode and cathode. The stack was operated with 30 wt.% KOH electrolyte at a maximum temperature of 80°C and a pressure of 22 bar. The duration of the test was about 2 years where the stack was operated for approximately 9000 hours. Comparison of data captured from the first month of operation to data captured after the durability testing period indicates no significant deactivation/deterioration in performance of the electrodes during the whole operation period. The stack efficiency was measured to be 81% (HHV), after the test period, at 200 mA/cm² and 80°C. It is noted that the electrolysis test stack was in the development stage and some losses were expected in the stack itself due to stray currents. Durability measurements were also carried out in a non-zero gap, single cell electrolysis setup with 50 wt.% KOH electrolyte at 120°C and 200 mA/cm² for 1600 hours. The developed electrodes were applied both as cathode and anode. The cell efficiency was measured to be 88% (HHV) during the first two hours of operation. After about 100 hours, the efficiency had decreased to 84% and was thereafter constant throughout the remaining test period. The reason for the efficiency drop is proposed to be degradation of the electrodes, caused by gas-erosion corrosion, together with formation of nickel hydrides in electrode metal lattice. The material degradation was considerably more severe at the anode compared to the cathode. The durability single-cell measurements indicate no deactivation of electrodes after shut-downs. Microstructure investigations on the PVD Al-Ni diffusion couples at 610°C indicate the diffusion mechanism to be dominated by grain boundary diffusion of nickel-rich phases into the aluminium-rich PVD structure. The first intermetallic phase formed is determined to be AlNi3. The phase is observed as small particles in the columnar grain boundaries of the aluminium structure, after only a few minutes of heat treatment. Due to the high mobility of aluminium at the annealing temperature, finding nickel and nickel-rich species to be the most mobile during the heat treatment is highly unexpected and is in contrast with what is stated in the current scientific literature. Together with the AlNi and Al3Ni2, the Al2Ni3 phase can be observed in the aluminium residue, and Al3Ni2 and Al3Ni3 are observed after 10-30 minutes of heat treatment. Over 30 minutes of heat treatment results in depletion of the aluminium and formation of highly porous γ-Al2O3 phase at the top surface. After 2 hours, of heat treatment only Al3Ni2 and thin layers of AlNi and Al3Ni are observed in the diffusion zone, with no traces of the AlNi3 phase. Heat treatments performed for longer than 2 hour result in gradual thickening of the AlNi, Al3Ni and γ-Al2O3 diffusion layers and grain growth in the Al2Ni3 phase. The diffusion mechanism can be the key to good properties of the developed PVD Al/Ni electrodes. Electrodes produced with shorter time of diffusion, 10-30 minutes, are found to be more prone to alkaline aluminium leaching and only 4-5 wt.% of alumimium residue is found in the leached skeletal nickel structure. For the electrodes heat treated for 24 hours, up to 15 wt.% aluminium residue is observed in the skeletal nickel structure. However, leaching of the PVD Al-Ni structure, after short periods of diffusion, results in formation of cracks perpendicular to the Ni substrate. The cracks reduce/affect the mechanical strength of the treated coatings. Electrodes heat treated for short times are found not to be stable under OER. However, selective aluminium leaching of electrodes heat treated for 24 hours results in dense, crack free and more mechanically stable/stronger structure. Electrochemical characterisation on the effect of surface area of the developed electrodes, indicate that the electrocatalytic activity increases in proportion to the porous layer up to the width of the 20 μm investigated. With the aim of reducing the production costs associated with the electrode manufacturing, four process techniques and combinations of these were screened. These were; (1) hot dip aluminium of nickel followed by thermo-chemical diffusion, (2) direct thermo-chemical diffusion of aluminium and nickel sheets, (3) aluminium ionic liquid electroplating on a nickel plate followed by thermo-chemical diffusion and (4) physical vapour deposition of aluminium onto electroplated sulfamate nickel substrate followed by thermo-chemical diffusion. Due to the high affinity of aluminium towards hydrogen and oxygen, producing oxide free AlNi alloy coatings in an inexpensive and simple manner was found to be challenging. Only the direct diffusion between aluminium and nickel sheets in argon atmosphere and the PVD Al onto electroplated sulfamate nickel were found to give promising coatings.