High Temperature and Pressure Alkaline Electrolysis

The production of energy from renewable sources has the possibility to fulfill the worldwide energy demand. Electricity generation from wind energy converters and photovoltaic systems will be implemented within the European Union to a large extent. The fluctuation of the wind speed and solar radiation raises the necessity to store the produced energy.

Hydrogen production by water electrolysis is one of the most promising ways to do so. Alkaline electrolyzers have proven to operate reliably for decades on a large scale (up to 160 MW), but in order to become commercially attractive and compete against conventional technologies for hydrogen production, such as natural gas reforming, the production and investment costs have to be reduced. A reduction of the investment costs may be achieved by increasing the operational pressure and temperature of the electrolyzer, as this will result in: 1) production of pressurized hydrogen and oxygen, 2) improved electrical efficiencies and 3) increased current density, i.e. increased hydrogen production rate for a given electrolyser cell area. This thesis describes an exploratory technical study mainly in order to examine the possibility to produce hydrogen and oxygen with a new type of alkaline electrolysis cell at high temperatures and pressures. To perform measurements under high pressure and at elevated temperatures it was necessary to build a measurement system around an autoclave which could stand high temperatures up to 250 °C and pressures up to 200 bar as well as extremely caustic environments. Based on a literature study to identify resistant materials for these conditions, Inconel 600 was selected among the metals which are available for autoclave construction. An initial single atmosphere high temperature and pressure measurement setup was build comprising this autoclave. A second high temperature and pressure measurement setup was build based on experiences from the first setup in order to perform automatized measurements.

The conductivity of aqueous KOH at elevated temperatures and high concentrations was investigated using the van der Pauw method in combination with electrochemical impedance spectroscopy (EIS). Conductivity values as high as 2.7 S cm⁻¹ for 35 wt%, 2.9 S cm⁻¹ for 45 wt%, and 2.8 S cm⁻¹ for 55 wt% concentrated aqueous solutions were measured at 200 °C. The conductivity of immobilized KOH was determined by the same method in the same temperature and concentration range. Conductivity values as high as 0.67 S cm⁻¹ for 35 wt%, 0.84 S cm⁻¹ for 45 wt%, and 0.73 S cm⁻¹ for 55 wt% concentrated immobilized aqueous solutions were determined at 200 °C. A new type of an alkaline electrolysis cell was developed in order to operate at high temperatures and pressures. Aqueous potassium hydroxide immobilized electrolyte in porous SrTiO₃ was used in those cells. Electrolysis cells with metal foam based gas diffusion electrodes and the immobilized electrolyte were successfully demonstrated at temperatures up to 250 °C and 40 bar. Different electro-catalysts were tested in order to reduce the oxygen and hydrogen overpotentials. Current densities of 1.1 A cm⁻² and 2.3 A cm⁻² have been measured at a cell voltage of 1.5 V and 1.75 V, respectively, without using expensive noble metal catalysts. Electrical efficiencies of almost 99 % at 1.1 A cm⁻² and 85 % at 2.3 A cm⁻² combined with relatively small production costs may lead to both reduced investment and operating costs for hydrogen and oxygen production. One of the produced electrolysis cells was operated for 350 h. Based on the successful results a patent application covering this novel cell was filed. Assuming that the developed cells will be scaled up and successfully tested for some thousand hours, they may offer an important role in future energy storage scenarios.