Proton conducting polymeric materials for hydrogen based electrochemical energy conversion technologies

Proton transport is one of the most fundamental phenomena in nature and it also plays key role in proton exchange membrane (PEM) fuel cells and water electrolyzers. Conventionally, a well hydrated membrane of perfluorosulfonic acid (PFSA) such as Nafion® (DuPont) is used as proton conductor and electrolyte separator in both PEM fuel cells and water electrolyzers. The proton conductivity mechanism of Nafion® is strongly dependent on the presence of water within the membrane nanostructure, which limits the operating temperature to about 80 °C unless the system is pressurized in order to keep the membrane well hydrated. However, some of the main issues of the conventional PFSA based PEM fuel cells and water electrolyzers are directly or indirectly related to their relatively low operating temperature. An elevated operating temperature results in better electrode kinetics in general and improved impurity tolerance of the catalysts, especially for the fuel cell anode. From a system engineering point of view it also allows for simplified cooling and water management and better possibilities for heat recovery. Furthermore, a higher operating temperature is strongly beneficial when the cell is operated in electrolysis mode since it results in a decreased thermodynamic energy requirement for the water splitting reaction. The aiming for an elevated operating temperature has thus resulted in an increasing demand for novel anhydrous proton conducting polymeric materials for both PEM fuel cells and water electrolyzers. This thesis gives an overview of the principles and the current state-of-the-art technology of the hydrogen based electrochemical energy conversion technologies, with special emphasis on the PEM based water electrolyzers and fuel cells (Chapter 1).

The fundamental thermodynamics of water electrolyzers and fuel cells is also explained. A detailed literature review is given that covers proton conducting polymeric materials and composite membrane concepts as well as the mechanisms of proton conduction in these types of structures. The experimental part of this thesis has focused on the development and characterization of polymer based proton conducting membranes for operation at temperatures above 100 °C. The most frequently recurring experimental methods and techniques are described in Chapter 2. For PEM steam and liquid water electrolysis at temperatures up to 130 °C (Chapter 3 and 4), the presented approaches in this work mainly include chemical modification of the conventional PFSA materials with phosphoric acid or inorganic proton conducting particles such as zirconium phosphate (ZrP) or boron phosphate (BP). A novel methodology for the preparation of homogeneous Nafion®/poly[2,2’-(m-phenylene)-5,5’-bibenzimidazole] (PBI) polymer blends was also developed. The miscibility behavior between Nafion® and PBI was investigated using different Nafion® counter cations. It was demonstrated that NH4⁺ could be used as compatibilizer in the Nafion®/PBI system to give homogenous solution cast blend membranes covering the whole composition range. The strong intermolecular coulumb interactions gave the polymer blends improved mechanical characteristics. However, it allowed for very limited volume swelling in phosphoric acid and therefore a very low acid uptake, which resulted in poor proton conductivity in the 10-5-10-3 S cm⁻¹ range at 130 °C. The pristine phosphoric acid doped Nafion® and PBI membranes, on the other hand, exhibited proton conductivity in the 10-2 S cm⁻¹ range at 130 °C, which was superior compared with that of the ZrP or BP composite materials based on Nafion®. Steam electrolysis tests were thus conducted using membrane electrode assemblies (MEAs) based on pristine phosphoric acid doped Nafion® and PBI. The PBI based MEAs suffered from severe durability limitations due to membrane degradation, which was most likely connected to the acid catalyzed hydrolysis of the polymer. The phosphoric acid doped Nafion® based MEAs, on the other hand, exhibited better durability but showed rather high ohmic resistance. The moderate steam electrolysis performance was most likely connected to the poor dimensional stability of Nafion® under the experimental conditions.

The mechanical properties of the recast Nafion® membranes at elevated temperature could be slightly improved by annealing the membrane in order to increase its degree of crystallinity. Short side chain (SSC) PFSA membranes such as Aquivion™ (Solvey Solexis), on the other hand, are generally characterized by a considerably higher degree of crystallinity than Nafion®. The melting point of the large crystalline regions is also considerably higher than that of Nafion®, which allows for better mechanical characteristics at elevated operating temperatures. The low equivalent weight of Aquivion™ also leads to high phosphoric acid uptake, which improves the proton conductivity. The steam electrolysis performance of the Aquivion™ based MEA was thus superior compared with that of the corresponding Nafion® based MEA. The importance of the dimensional behavior of the electrolyte material was further demonstrated by reinforcing recast Nafion® with a highly porous polytetrafluoroethylene (PTFE) material. During liquid water electrolysis tests at 120-130 °C (3 bar back pressure), the PTFE reinforced Nafion® based MEA reached as high current density as 2500 mA cm⁻² at 1.95 V. The conductivity of the reinforced membrane was also demonstrated to be superior over time compared with the commercially available melt extruded Nafion® 117 membrane. Phosphoric acid doped PBI has emerged as one of the most promising electrolyte materials for high temperature PEM fuel cells operating at temperatures up to about 200 °C during the last 1-2 decades. High phosphoric acid content is the key to achieve high proton conductivity of the membrane, which is of critical importance in order to minimize the ohmic voltage losses in the high current density range. However, the mechanical strength of PBI membranes is strongly correlated to its phosphoric acid content due to the strong plasticizing effect of the dopant. Consequently, the doping level of the membrane has to be a compromise between sufficient mechanical strength for the MEA preparation and maximized proton conductivity. In this work, PBI membranes were crosslinked, either by posttreatment with divinylsulfone or by thermal curing, in order to improve their mechanical characteristics at high acid doping levels (Chapter 5 and 6). In addition to the improved mechanical characteristics of the crosslinked membranes, they also exhibited improved radical-oxidative stability which naturally should improve their long term durability. The feasibility of the crosslinked membranes was demonstrated in fuel cell tests at temperatures up to 180 °C. The MEA based on the cured PBI demonstrated an average voltage decay rate as low as 43 μV h⁻¹ during 1800 h of continuous fuel cell operation at 600 mA cm⁻² at 160 °C. Under these conditions, the average cell voltage decay rate of the MEA based on the non-cured reference membrane (308 μV h⁻¹) was more than 700% higher compared with that of the MEA based on the cured PBI membrane. The results confirmed that the long term durability of phosphoric acid doped PBI based high temperature PEM fuel cells is highly dependent on the membrane characteristics, especially during...
operation at high current loads. The thesis is completed by summing up on the results and conclusions (Chapter 7). Further research should be devoted to ex situ accelerated membrane degradation tests in combination with in situ tests and post mortem analysis in order to unravel and completely understand the membrane degradation mechanisms in the operating electrochemical cells. This knowledge is the key to an intelligent design and synthesis of new, high-performing proton conducting polymer materials with improved long term durability for PEM water electrolyzers as well as PEM fuel cells.

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