CHARACTERIZATION OF PROTON CONDUCTING PHOSPHOSILICATE MEMBRANES FOR H_2/O_2 FUEL CELLS

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Introduction

The steeply increasing cost of crude oil and consequently the price of petrol force the main car producers to develop an alternative engines and fuels for their vehicles. One of the promising possibilities is a car powered by affordable hydrogen fuel cells. For such fuel cells the membranes are a critical component. They must tolerate a wide range of operating conditions including low humidity and intermediate temperatures up to 130°C for transportation applications. The low operating temperatures of currently available proton conducting polymer membranes and their humidity requirements add complexity to the fuel cell system that impacts its cost and durability. Therefore, the recent research has been focused on the development of improved membranes with better performance at lower cost [1, 2]. One of the promising candidates for the improved membranes is a material based on hybrid inorganic-organic phosphosilicate polymers (HPS membrane). Generally, silicate compounds possess high temperature stability and chemical durability. Polysiloxans (silicons), by substituting O atoms with organic groups, "soften" the silicate network, providing it a rubber-like elasticity. Bonds –Si-O-Si- have high bonding energy about 454 kJ/mol (compared to 349 kJ/mol of –C-C- bonds) and form a heat resistant back bone for the HPS membrane. Additionally, they have a high polarity that stabilizes the organic groups on Si atoms. Siloxanes are stable in a wide range of temperatures, from -90 to 250°C. In this temperature range, they posses a good electronic resistivity and high chemical durability, and they are biologically inert. Their fabrication process based on polymerization, filler additions, and vulcanization can, to a large extend, modify and control the properties of silicon rubbers [3, 4]. Therefore, this durable elastic material is ideal for forming a backbone of HPS membranes.

Experimental and Results

The preparation of the hybrid inorganic-organic phosphosilicate membranes was based on acid(A)-base(B) reaction, A-OH + B-Cl $\rightarrow$ A-O-B + HCl, in liquid or molten orthophosphoric acid (H_3PO_4) at temperatures up to 250°C. The organic components and heteroatoms are incorporated into the phosphosilicate polymer structure by using dialkyldichlorsilanes and liquid or low-melting chlorides as starting materials.

We obtained a transparent elastic material of amorphous character as was verified by X-ray diffraction.

The sufficient proton conductivity is one of key properties important for the useful application of a membrane in a fuel cell. We used electrochemical impedance spectroscopy to determine the proton conductivity of prepared membranes and its dependence on temperature at low relative humidity. Fig. 1 illustrates a typical impedance spectrum of our membranes with the inserted equivalent circuit used for data analysis and calculation of the conductivity. Fig. 2 shows conductivities as a function of temperature at low humidity of three membranes prepared by different procedures.

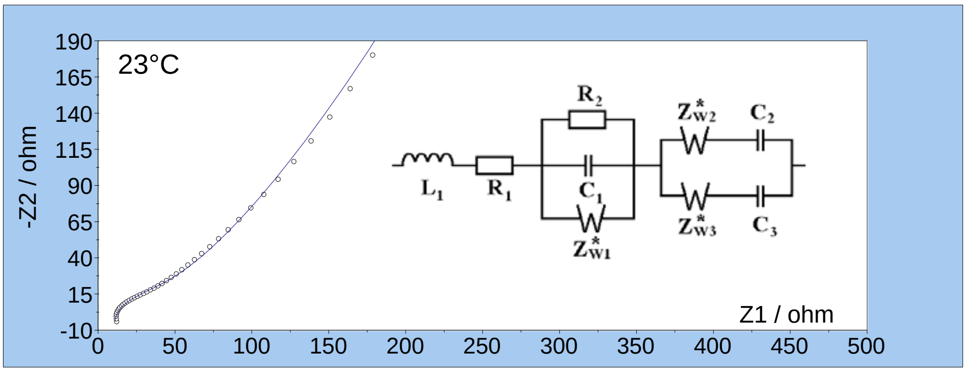

***Fig. 1** High-frequency part of the measured impedance spectrum fitted with the shown equivalent circuit.*

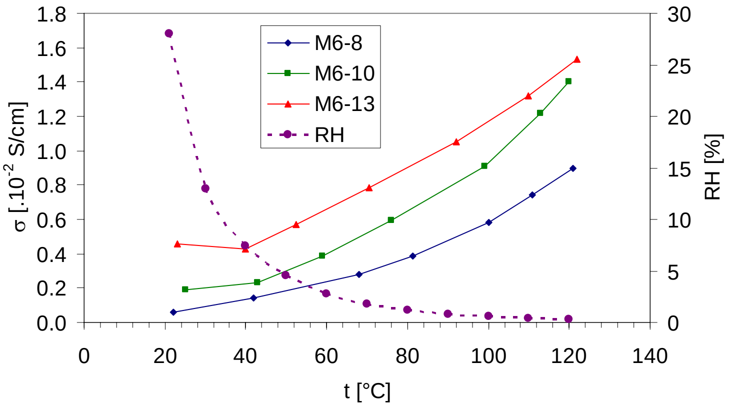

***Fig. 2** Temperature dependence of conductivity for different HPS membranes*

We tested the performance of our membranes in a H_2/O_2 fuel cell using standard E-TEK electrodes Pt/C under low humidity conditions where the reactant gas streams were not humidified. The results are plotted in Fig. 3.

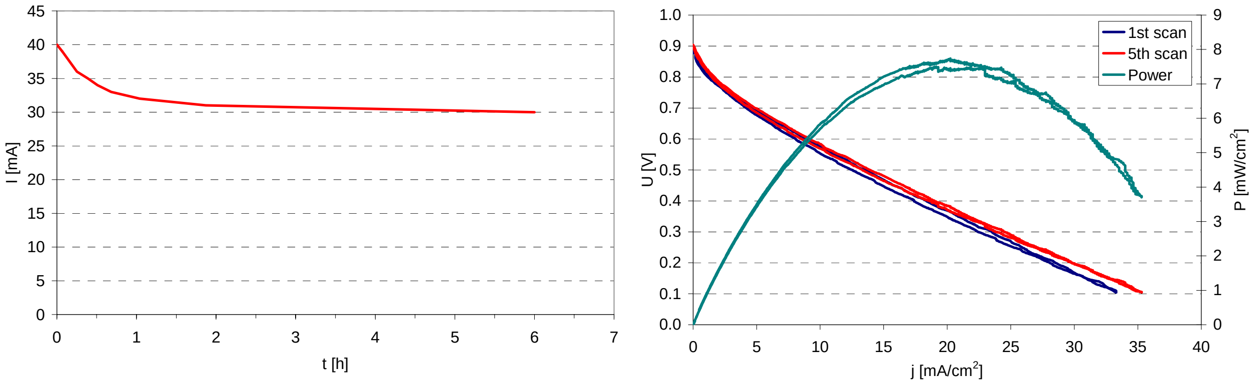

Fig. 3 *Polarization curve of HPS-based fuel cell (left). Time dependence of current generated by the fuel cell (right). In both experiments the standard ELAT E-TEK electrodes Pt/C were used at 60°C, and dry atmosphere (H_2 and O_2 were not humidified).*

Discussion and Conclusions

The low humidity atmosphere influenced the conductivity much less comparing to the current generation polymer proton exchange membranes, which makes this material promising for the proposed applications. The structure of our membrane with plenty of –OH groups probably results in increased probability of successful direct hopping of protons at higher temperatures. This can probably fully compensate the loss of free H_2O molecules which transport protons at low temperature, thus we did not observed a drop of conductivity. Our preliminary testing in a laboratory fuel cell confirmed that our membranes can operate at very low humidity conditions.

Acknowledgements

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