Test of non-fluorinated PSU-PBI blend membranes for middle temperature DMFC

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Introduction & Motivation

Fuel cells are usually classified into working temperature categories. High temperature fuel cells (HTFC), such as the Solid Oxide Fuel Cell (SOFC) or the Molten Carbonate Fuel Cell (MCFC) are working in a temperature range of 600-950°C that allows a sufficient conductivity of the electrolyte. State of the art HTFCs have already shown high cell efficiency up to 60%. Low temperature fuel cells (LTFC) are mostly equipped with a polymer membrane such as Nafion whose conductivity depends on the presence of water molecules. Therefore, their working temperatures are usually limited to 80-100°C. With exception of MCFC that is specially designed for stationary electricity plans, both, high and low temperature fuel cells are planned to be used in a foreseeable future as energy converter for stationary and automotive applications. In the case of the middle temperature PEMFC, however, more robust systems and especially, more stable polymer membranes than pure PBI-based ones, which are still sensitive to water presence and phosphoric acid leaching that are able to work at 100-150°C are needed. This project aims together with nine german institutes at the development of a middle-temperature PEMFC. In this subproject, PSU-PBI blend membranes with excess acid have been prepared by IVCT University Stuttgart and tested in our 5 cm² laboratory DMFC. This work aims at investigate the influence of the membrane pretreatment in HCl or H_2SO_4 on the electrochemical activity of the MEA in the DMFC.

MEA preparation and experiment description

The Pt catalyst loading of the cathode and anode was fixed at 1.6 & 2 mg/cm², respectively. The Pt/Vulcan catalyst was mixed in water/isopropanol solution with 10%wt Nafion and 20%wt PTFE and sprayed with PRISM 450 either on Freudenberg-CH2315CX190 for the cathode or on Toray-TGP-H-60 for the anode. Both electrodes were coated with 1mg cm^{-2} Nafion suspension before hot pressing at 130°C and 7 bar with the blend ionomer membrane to form an MEA. The excess acid blend ionomer membranes ((SACO64-(SPSU)-PBIOO) was pretreated either in 10%wt HCl (MEA-3) and 0.5 N H_2SO_4 (MEA-4). In the DMFC, following media and parameters were used:
Anode: 2M methanol, 10 ml/min - Cathode: air/oxygen, 300 ml/min
To reduce the methanol crossover from the anode to the cathode, the pressure on the anode was 0.1 bar smaller than that on the cathode.

Results

The influence of cell temperatur and backing pressure on current-voltage curves of MEA-3 and MEA-4 with (left) oxygen and (right) can been seen in fig. 1 to 3.

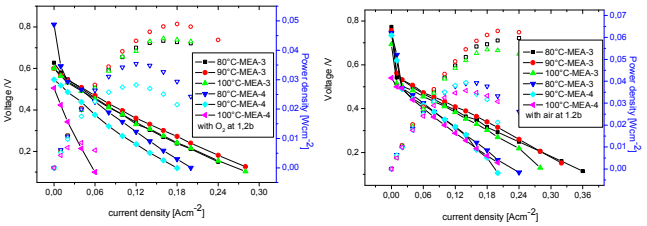

Fig.1: Current voltage curves of MEA-3 und MEA-4 at different temperatures (80-100°C) with oxygen and air on the cathode at a pressure of 1,2 bar.

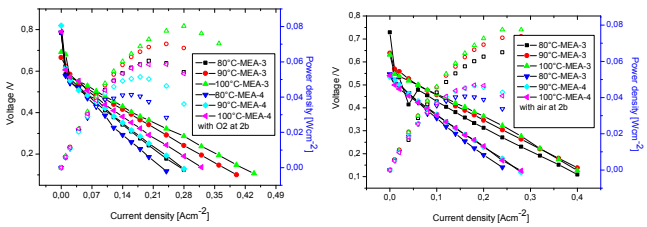

Fig.2: Current voltage curves of MEA-3 und MEA-4 at different temperatures 80-100°C with oxygen and air on the cathode at a pressure of 2 bar.

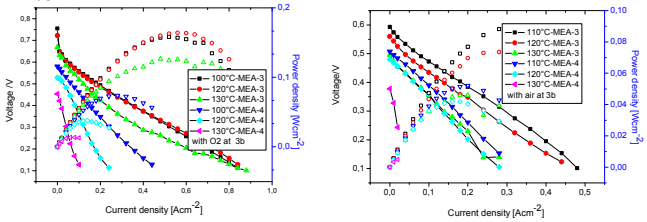

Fig.3: Current voltage curves of MEA-3 und MEA-4 at different temperatures (100-130°C) with oxygen and air on the cathode at a pressure of 3 bar.

Table 1: Summary of power density values of MEA-3/4 at different temperatures and pressures

	O_2 at 1.2 bar	Air at 1,2 bar	O_2 at 2 bar	Air at 2 bar	O_2 at 3 bar	Air at 3 bar
MEA-3	50 mW cm^{-2} at 90 °C	65 mW cm^{-2} at 90 °C	80 mW cm^{-2} at 100°C	80 mW cm^{-2} at 100 °C	150 mW cm^{-2} at 120°C	90 mW cm^{-2} at 110°C
MEA-4	25 mW cm^{-2} at 90 °C	39 mW cm^{-2} at 90 °C	50 mW cm^{-2} at 100°C	45 mW cm^{-2} at 100 °C	90 mW cm^{-2} at 100 °C	50 mW cm^{-2} at 110°C

The maximum power densities measured with MEA-3 & -4 and shown in Fig. 1 to 3 are summarized in Table1. These are obviously depending on the temperature, the nature and pressure of the working gas as well as on the different pretreatments of the membrane. In all experiments, better performances were observed with the MEA fabricated with the HCl-treated membrane. At a pressure of 1.2 bar at 90°C, MEA-3 exhibits a ca. 25 mW cm^{-2} higher power density than MEA-4 in oxygen and air. In air, the highest power density was measured with MEA-3 at 3 bar and amounts to 90 mW cm^{-2}.

Table 2 shows a summary of the ohmic resistance of MEA-3/4 obtained from electrochemical impedance measurements (EIS) (@ 100 mA cm^{-2}) at different temperatures using oxygen or air as cathode gas. As expected, the ohmic resistance of the MEAs decreases with increasing temperature. Surprisingly, twofold higher impedances values were measured at MEA-3 than at MEA-4.

Table 2: Ohmic resistance of MEA-3 and MEA-4.

	80°C	**90°C**	**100°C**
MEA-3/air	600 mΩ	420 mΩ	350 mΩ
MEA-3/O_2	540 mΩ	410 mΩ	220 mΩ
MEA-4/air	198 mΩ	178 mΩ	180 mΩ
MEA-4/O_2	260 mΩ	240 mΩ	160 mΩ

After the experiments in DMFC, the components of MEAs have been systematically investigated (see Fig.4). In all cases, a detachment of the electrodes from the membrane was observed. This is an indication of an incompatibility of the Nafion binder with the acid-base blend membrane. Additionally, a rupture of the membrane along the electrode edges can be observed in the photography (Fig. 4) that is obviously due to an insufficient mechanical and/or chemical stability at higher temperature than 80°C. In order to evaluate their chemical stability separately, the acid-base membranes were immersed in 10 M Methanol in a stainless steel reactor at 150°C & 5 bar. After 4 days, the membranes were partially dissolved.

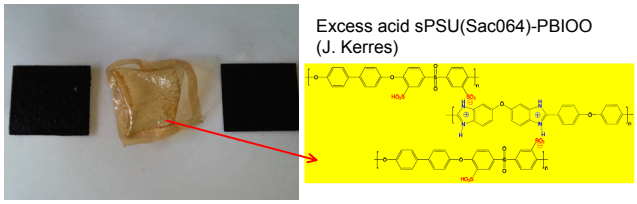

Fig. 4: MEA-4 after 3 weeks of experiment in DMFC at 80-130°C

Conclusion

- Despite higher ohmic resistance, the MEA with the acid-base blend membrane treated in HCl shows a higher activity than the MEA with the membrane treated in H_2SO_4. At 3 bar and 110°C, a maximal power density of ca. 90 mW/cm² was reached.
- The performances of both MEA increase in the temperature range of 80-110°C.
- At temperatures higher than 110°C, the cell performance decreases with increasing temperature. This is probably due to the rupture of the inter-ionic bonding of the PSU and PBIOO polymers in the membrane structure and/or strong swelling of the membrane in the presence of methanol.

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