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HT-PEM - Efficient and renewable energy

Energy Dispersive X-ray Analysis Used to Quantify the Phosphoric Acid Doping Level in Polybenzimidazole Based Fuel Cells.

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Introduction

In high temperature polymer electrolyte membrane (HT-PEM) fuel cells, the membrane is made of polybenzimidazole (PBI). The necessary proton conductivity of the membrane is ensured by doping it with phosphoric acid (PA). The amount of PA contained in the membrane is described by the doping level (*DL*), which is the number of PA molecules per repeating unit of PBI. It is important for the HT-PEM fuel cell performance that the doping level is high from the beginning and that it will remain high during the lifetime of the cell. Therefore, it is desirable to have a method, which can quantify the membrane's doping level - for example as a *post mortem* analysis after a durability test in order to monitor a possible loss of PA over time.

Method

We have used energy dispersive X-ray spectroscopy (EDS) to establish the amount of PA in the membrane electrode assembly (MEA) structure. Elemental analysis of the membrane's content of phosphorus and oxygen from the PA relative to the carbon and nitrogen content from the PBI yields indications about the doping level. Samples were prepared by making a cross-section cut through the MEA structure. Argon ion milling was used to gently do a final polishing of the cross-sectional surface, before the sample entered the scanning electron microscope (SEM). The EDS spectra were acquired from a 10 x 10 µm² area in the center of the 30-60 µm thick membranes and analyzed with the INCA software from Oxford Instruments, see Fig. 1.

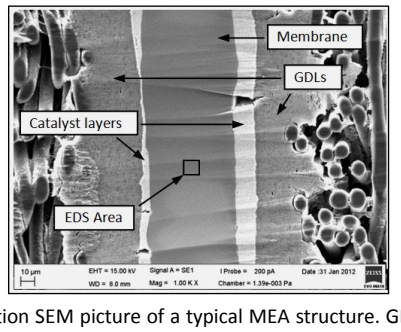

Figure.1. Cross-section SEM picture of a typical MEA structure. GDL represents the gas diffusion layer. The SEM acceleration voltage was in the range 8-18 kV.

The membrane's molecular composition is assumed to have the following form:

$$\mathrm{P\ (wt\ \%)} = \frac{DL \cdot M(\mathrm{P})}{M(\mathrm{PBI}) + DL \cdot M(\mathrm{PA})} \qquad \mathrm{O\ (wt\ \%)} = \frac{DL \cdot M(\mathrm{O_4})}{M(\mathrm{PBI}) + DL \cdot M(\mathrm{PA})}$$

$$\mathrm{C\ (wt\ \%)} = \frac{M(\mathrm{C_{20}})}{M(\mathrm{PBI}) + DL \cdot M(\mathrm{PA})} \qquad \mathrm{N\ (wt\ \%)} = \frac{M(\mathrm{N_4})}{M(\mathrm{PBI}) + DL \cdot M(\mathrm{PA})}$$

where the molar masses are: $M(\mathrm{PA}) = M(\mathrm{H_3PO_4}) \approx M(\mathrm{PO_4}) \approx 95.0$ g/mol. $M(\mathrm{PBI}) = M(\mathrm{C_{20}N_4H_{12}}) \approx M(\mathrm{C_{20}N_4}) \approx 296.2$ g/mol. The hydrogen contribution is neglected, since EDS is not sensitive to this element. The difference between this model and the actual measured EDS-values is described by the following root-mean-square error function:

$$\varepsilon_{RMS} = \sqrt{\frac{\varepsilon_{\mathrm{P}}^2 + \varepsilon_{\mathrm{O}}^2 + \varepsilon_{\mathrm{C}}^2 + \varepsilon_{\mathrm{N}}^2}{4}}$$

where ε = wt % (model) – wt % (EDS). The doping level is now defined as the value of *DL*, which minimizes ε_{RMS}. This is equivalent to the traditional least-squares method.

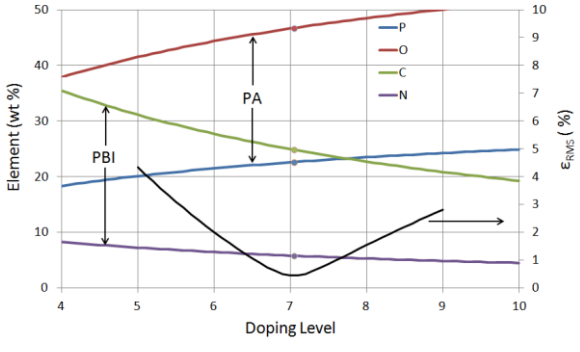

Figure 2. The coloured curves show the modeled atomic weight distribution of the four elements as a function of the doping level. An example of the error function, ε_{RMS}, is also shown. In this case, ε_{RMS} is minimum for *DL* ≈ 7.0-7.1. On average, ε_{RMS} < 1 %.

Results

Doping levels in the range 5-8 with an uncertainty of ± 0.5 were measured. This uncertainty is based on the observation, that the calculated doping levels depend somehow on the SEM acceleration voltage. In Fig. 3, doping level measurements are combined with durability data for three different MEAs.

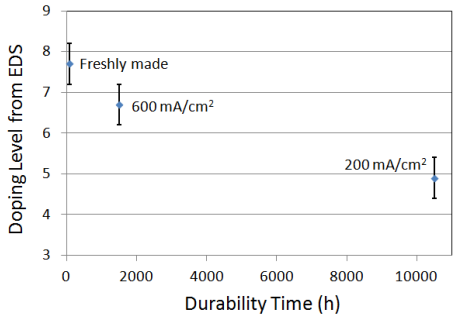

Figure 3. Doping level measurements combined with durability data. All cells were operated at 160 °C and fueled with air and H_2. The cell area was 10 cm². The legends state the current density used during the durability study.

Conclusion

A method, based on EDS measurements, to quantify the phosphoric acid doping level of HT-PEM fuel cell membranes is suggested. From the EDS measurements of the membrane's elementary constituents, P, O, N, and C, it can be seen that phosphoric acid is lost over time as expected. Even after ≈ 10,000 hours of operation, the doping level is ≈ 5, which indicates that the durability issue only in part is related to the loss of phosphoric acid in the membrane.

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