

## The Proton Conductivity of DMFC Catalyst Layers

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Sufficient proton conductivity of the catalyst layers of the direct methanol fuel cell (DMFC) is important, because it enables an extension of the reaction zone from the membrane surface into the bulk of the catalyst layer. However, proton conductivity is difficult to determine, because pseudo capacitances in the interface of the noble metal catalyst and the ionomer phase inside the catalyst layer enable the flow of an electronic current.

Different methods were proposed in the literature to avoid this problem. For example, the proton conductivity was estimated from the well-known specific conductivity of the Nafion membrane in combination with an approximated volume fraction of the Nafion phase within the catalyst layer [1-3]. This method is simple, but it tends to overestimate proton conductivity, because it does not consider the microstructure, e.g. the tortuosity of the Nafion phase. Other methods include the replacement of the electronically conducting catalyst by silica [4] or the introduction of an 'inactive catalyst layer' sandwiched between two Nafion membranes [5]. The latter methods require the use of modified catalyst layers or membrane electrode assemblies different from those used in fuel cells under practical operating conditions.

We recently introduced a new method for the determination of the specific proton conductivity in PEMFC and DMFC electrodes [6]. This method is based on the condition, that the high frequency part of the impedance spectra of a composite material is dominated by ionic transport and double layer charging. In this case, a straight line at a 45°-angle is observed in the high-frequency limit. According to Eikerling and Kornyshev [7], the slope of the high frequency linear part yields the ratio of proton conductivity,  $R_p$ , and pseudo double layer capacitance,  $C_{pdl}$ , following

$$Z = \sqrt{\frac{R_p}{C_{pdl}}} \omega^{-1/2} \frac{\sqrt{2}}{2} (1-i),$$
$$|Z| = \sqrt{\frac{R_p}{C_{pdl}}} \omega^{-1/2} \Rightarrow K = \sqrt{\frac{R_p}{C_{pdl}}}$$

with  $Z$ , the complex impedance and  $\omega$ , the frequency of the harmonic signal. If the pseudo double layer capacitance is known, e.g. from the capacitive current in cyclic voltammograms, the proton conductivity can be calculated. The advantage of the new method is, that the proton conductivity can be easily determined by means of common electrochemical *in-situ* techniques without any modification of the MEA. Under certain conditions, this method is also applicable for determining the ion conductivity of other electro-active layers with a composite structure including ionic and electronic conducting phases. These conditions are:

- In the high-frequency limit of the impedance spectra, the electrode response has to be dominated by double layer charging and ion transport.

- The electro-active layer has to be represented by an RC-transmission line equivalent circuit, without branching or fractality of the network.
- The ion conductivity must not be too high. Otherwise, e.g. at high volume fractions of the ionomer in the catalyst layer and/or high specific conductivity of the ionomer, the linear regime will be barely perceptible and the method will not be applicable. This is even more problematic, if high-frequency inductances or other disturbances originating from the measuring set-up mask or falsify the high-frequency impedance signal.

In the present work, the proton conductivity of DMFC catalyst layers was determined as a function of their composition, i.e. the Nafion and catalyst fractions and the content of hydrophobic agents. The catalysts were supported on carbon with a composition of 60 wt% Pt/Ru (anode, Johnson Matthey HiSpec 10000) or 60 wt% Pt (cathode, Johnson Matthey HiSpec 9100) and 40 wt% C.

The specific proton conductivities obtained are in the range of some mS/cm up to several ten mS/cm, depending on the composition. Regarding the variation of the Nafion content, it turns out, that the specific proton conductivities are a factor of 2-3 smaller than data reported by Boyer et al. [5]. However, the data of Boyer were obtained by a different method, a different catalyst composition (40 wt.% Pt, 60 wt.% C) and possibly a different carbon support. Following Boyer et al., the unexpectedly high conductivities observed by these authors at low Nafion fractions can be explained by an additional proton conductivity caused by the transport of protons along anion impurities on the carbon surface. Therefore, not only the microstructure and composition of the catalyst layer, but also the nature of the carbon surface including impurities and functional groups influences the proton conductivity of the catalyst layers.

## References

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