Influence of Platinum Precipitation on Properties and Degradation of Nafion[®] Membranes

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A limiting factor for the lifetime of proton exchange membrane fuel cells (PEMFCs) is the degradation of the electrolyte membrane. One of the major causes of degradation is the chemical decomposition of the ionomer due to radicals.¹ The radicals can be formed at platinum (Pt) particles originating from the cathode and precipitated in the membrane during cell operation. It is assumed that the size and distribution of the Pt particles are influencing degradation.²

Most studies on this topic have focused on examining Pt deposit as they are present after degradation tests. But in-situ depositing of Pt in the ionomer is a dynamic process due to the continuous Pt dissolution and subsequent transport as well as particle growth, resulting in changing Pt particle characteristics. Therefore, to better understand the influence of particle parameters, experiments with defined Pt precipitation are required.

In this study, the role of concentration and distribution of Pt precipitation in the membrane on ionomer degradation was investigated. Nafion[®] membranes were impregnated with different mass fraction of Pt via ion-exchange.³ The Pt-membranes were coated with electrodes, which exhibit a high Pt stability and prevent additional deposition of Pt in the ionomer during the subsequent degradation test of 140 h at open-circuit voltage.

Thus, for the first time, various membrane electrode assemblies (MEA) with known Pt concentration were compared by electrochemical in-situ measurements such as polarization curve, impedance spectroscopy and cyclic voltammetry. Ionomer degradation was further measured by means of fluoride emission rate (FER). Additionally, SEM/EDX was used to analyse Pt particle distribution in the membrane cross sections. For comparison of Pt precipitated artificially and during operation, a MEA with electrodes exhibiting a higher Pt solubility was also tested.

The Pt impregnated membranes exhibited homogeneously distributed Pt particles throughout the membrane as can be seen in Fig. 1. They showed a strong dependence of cell performance on gas humidification and a significantly increased membrane thickness, which indicates a change of morphology.

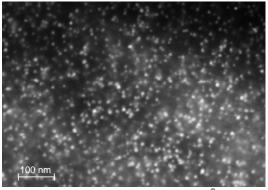


Fig. 1: SEM image of a Pt impregnated Nafion® membrane.

The accelerated ageing test clearly showed that degradation is enhanced by Pt concentration, as the loss of open-circuit voltage and exponential increase of FER (Fig. 2) demonstrate. An impact on the hydrogen crossover through the membrane was not found.

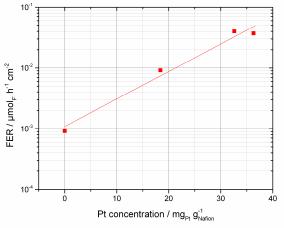


Fig. 2: FER of membranes with different Pt concentration. FER increases exponentially with Pt mass fraction.

The distribution of Pt precipitation forming during operation differs considerably from the artificially deposited Pt. The former are larger, farther apart, less numerous and concentrate in a Pt band within the membrane. These different particle characteristics appear to be the cause for the relatively high FER of this MEA.

References

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