The Effect of Relative Humidity on Chemical Degradation of Styrene Based Radiation Grafted Membranes in the PEFC

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Operating the polymer electrolyte fuel cell at low relative humidity (RH) is particularly targeted for transportation applications, since the pre-humidification of the reactant gases increases system complexity, part count, thermal rejection requirements and freeze risks [1]. To date, however, commonly used polymer electrolyte materials, such as Nafion®, still can hardly be used in the fuel cell under low RH conditions. One of the reasons is the faster chemical degradation of membranes compared to that under high RH conditions.

The chemical degradation of perfluoroalkylsulfonic acid (PFSA) membranes, measured by fluoride emission rate (FER), is accelerated with decreasing RH [2,3], which can promote membrane thinning and formation of pinholes. It has been reported that cell failure due to significant reactant gas crossover occurs after shorter lifetimes as the operating conditions become direr [4]. The faster decay of open circuit voltage (OCV) of the membrane electrode assembly (MEA) is also observed under sub-saturated conditions during the OCV hold test [5]. However, the discussion regarding the effect of RH on styrene based radiation grafted membranes is still rare. This kind of membrane is a potentially cost-effective alternative to PFSA membrane, such as Nafion® [6], and the optimized membranes exhibit superior durability under dynamic operating conditions in comparison with state-of-the-art Nafion® XL-100 [7].

In this contribution, aspects of chemical degradation of styrene-based membranes prepared by radiation grafting are discussed in detail in the context of exploring the effect of RH. Various durability test protocols are employed, including accelerated stress tests under OCV conditions, steady operating conditions at constant current density, a range of humidification levels of reactant gases, and imbalanced humidification at anode and cathode. Online measurement of OCV decay and high frequency resistance (HFR) is used to monitor the "state-of-health" of the membrane. Hydrogen permeation rate measured by an electrochemical method is used to evaluate the gas barrier properties of pristine membranes and assess membrane mechanical integrity during testing. Post-test analysis based on Fourier transform infrared spectroscopy (FTIR) is carried out after the durability tests to qualitatively and quantitatively analyze the degradation of tested membranes. Furthermore, the chemical aging trends of different ionomer classes as a function of RH are elucidated from the point of view of C-S bond stability and individual chemical degradation mechanisms.

Influence of RH on membrane chemical degradation

We have tested a set of uncrosslinked styrene grafted and sulfonated membranes on the basis of 25 μm thick poly(ethylene-*co*-tetrafluoroethylene) (ETFE) film in single cells with a cell temperature of 80 °C under OCV conditions as a function of RH [8]. Post-test analysis shows that, in contrast to PFSA membranes, the degree of chemical degradation of the radiation grafted membranes decreases with decreasing RH, and follows the trend of the reactant crossover rate through the membrane at different RH (**Figure 1**), which is believed to be a main driver for the formation of radical species in the fuel cell. The OCV decay follows the same trend of chemical degradation of membranes with decreasing RH.

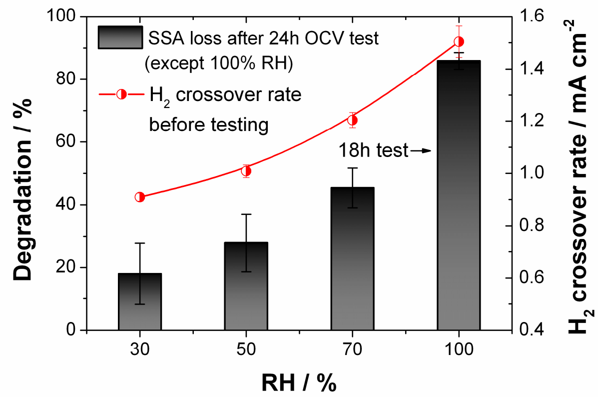

Figure 1. Degree of membrane degradation (left axis) after the OCV tests at various RH, measured by the loss in the grafted SSA units. H_2 crossover rates (right axis, expressed as current density) at different RH measured at 80 °C and 2.5 bar_a backpressure for pristine styrene grafted and sulfonated membranes [8].

Long-term test

Although the styrene radiation grafted membranes show reduced chemical degradation with decreasing RH in the short-term OCV tests (**Figure 1**), their lifetime under sub-saturated conditions is still unknown. Our result shows that, after 110 h OCV test at 50% RH, the tested membrane can provide comparable performance to that of the pristine membrane, while the same membrane shows a dramatic loss in performance after 18 h OCV test at 100% RH. Gradual loss of membrane integrity is not detected during testing at 50% RH via hydrogen crossover current density. It suggests the lifetime of the styrene radiation grafted membranes at OCV can be substantially increased under sub-saturated conditions.

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