Radiation Effects on the Performance of Proton Exchange Membranes in Electrochemical Cells

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Proton exchange membranes (PEMs) are widely used in PEM electrolysis cells, PEM fuel cells and hydrogen purification processes. The practically used and mostly studied PEMs are polyperfluorosulfonic acid (PFSA) membranes such as Nafion[1]. Nafion membranes are popular in electrochemical cells because of their high proton conductivity, good chemical stability and mechanical strength [1].

Besides the applications for hydrogen-related processes, the Nafion-based electrochemical cells have also been studied for use in the electrolytic processing of radioactive liquids involving tritium. Heavy water upgrading [2] and light water detritiation [3] are two typical examples which require the exposure of the Nafion membrane to tritium. Tritium has a half life of 12.3 years and emits beta-radiation while decaying into helium-3. The performance and durability of Nafion membranes is of great concern in the presence of radiation. It has been reported that Nafion membranes are prone to degradation under ionizing radiation, especially at high dose levels [3, 4]. However, there is still a lack of good understanding of the radiation effects on Nafion membranes, particularly in a tritium environment.

In this study, the Nafion 112 membranes (40 mm x 60 mm) were exposed to 57.5 Ci/L tritiated heavy water at room temperature for a total dose of about 200 kGy. The reference Nafion 112 membranes were immersed in de-ionised water for the same amount of time. The exposed membrane was thoroughly decontaminated before carrying out post-exposure tests. There was no discoloration or defect observed in all Nafion membrane samples by visual inspection. The SEM analysis of both exposed and reference membranes did not reveal any holes, dents or cracks. The tritiated water used for exposure was also clear. Chemical analysis of the tritiated water samples found a fluoride concentration of 24 mg/kg, corresponding to 3.8 mg fluoride per gram of dry Nafion. The sulfate in the same water sample was measured to be 12 mg/kg, corresponding to 1.9 mg of sulfate per gram of dry Nafion. The presence of fluoride and sulfate in the water sample was indicative of the Nafion degradation in a tritium environment.

Both the tritium exposed and reference Nafion 112 membranes were used to prepare membrane electrode assemblies (MEAs) and tested in a fuel cell at 75°C and various humidity levels. The mass activity at a cell voltage of 0.8 V decreased 20-30% after the Nafion 112 membrane was exposed to 200 kGy. However, the internal resistance of these MEAs in Figure 1 only shows very minimal differences between the irradiated and reference Nafion membranes, indicating that the ionic conductivity of the membranes was not responsible for the observed decrease in the mass activity. The decrease in mass activity may be due to the damage on the carbon backbone of the Nafion, thus promoting the gas crossover through the membrane. This assumption is consistent with the fluoride and sulfate analysis results.

The exposed membrane was also tested in a water electrolysis cell at 70°C. Figure 2 shows that the exposed Nafion 112 membrane leads to marginally higher cell voltages than the reference Nafion membrane. In summary, the beta-radiation at 200 kGy may damage the carbon backbone more than the sulfonic group under experimental conditions. However, the Nafion degradation was very gentle at the dose level studied.

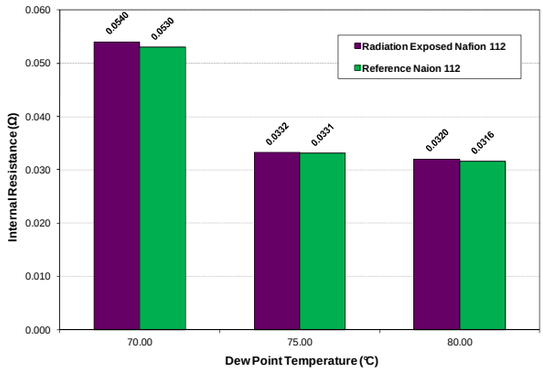

Figure 1. Internal Resistance of an exposed Nafion 112 membrane at various humidity levels.

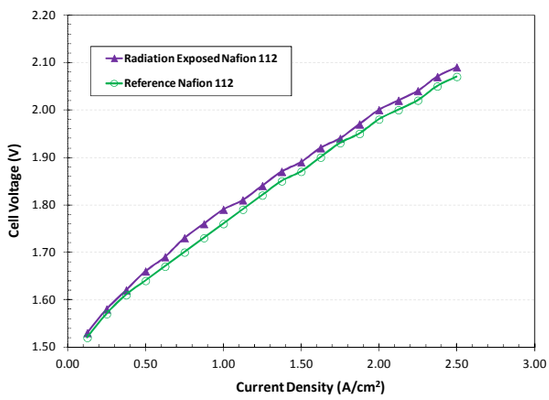

Figure 2. Performance comparison of an exposed Nafion 112 membrane (triangle) and a reference Nafion 112 membrane (circle) in a PEM water electrolysis cell at 70°C.

References

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[2] H. Boniface, S. Suppiah, K. Krishnaswamy, L. Rodrigo, J. Robinson, P. Kwon, *Fusion Science and Technology*, **60**, 1347 (2011).
[3] R. Michling, I. Cristescu, L. Dorr, T. Fanghanel, S. Welte, W. Wurster, *Fusion Science and Technology*, **54**, 475 (2008).
[4] Y. Iwai, A. Hiroki, M. Tamada, K. Isobe, T. Yamanishi, *Radiation Physics and Chemistry*, **79**, 46 (2010).

[1] NAFION® is a registered Trademark of E.I. du Pont de Nemours Company for their PFSA-based products.