

Oxygen Reduction Kinetics in Solid Polymer Electrolytes Under Controlled Relative Humidity

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Introduction

Previous studies have shown positive correlations between increases in either temperature or pressure with improved oxygen reduction reaction (ORR) kinetics in perfluorinated membrane moieties[1,2]. More recently, efforts have been made to substantiate the effect of relative humidity (RH) on the same kinetics, with overall improvement of oxygen mass transport resulting from high levels of hydration (>60% RH for Nafion® studied) [3,4,5].

In the present work, the dependence on time is investigated with respect to environmental hydration conditions. Specifically, the length of time required for ORR kinetics to reach steady state is studied. Furthermore, the possibility of a reversible trend i.e. water generation during measurement is also probed, in order to shed light on interfacial processes occurring during experimentation.

Experimental

An in house designed and fabricated electrochemical cell (Fig 1) was custom made to fit inside an Espec SH-241 environmental chamber, used in all experiments. The cell facilitates simultaneous determination of up to three samples, with separate electrodes for each sample. A 50 µm Pt microdisk electrode fitted with a compression spring is pressed against the membrane of interest, which is exposed only to the controlled air/water vapor environment. A Pt mesh counter electrode, and dynamic hydrogen electrode as reference, are similarly secured against the membrane.

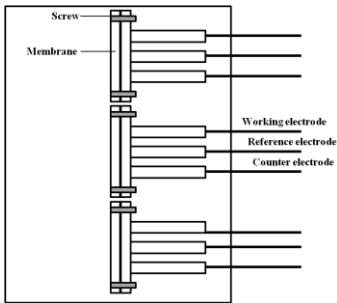


Fig. 1 3-sample electrochemical cell

ORR kinetic variables are determined from potential step coulometry, taken by a PAR 283 hooked up to a PC through GPIB cable. After cell equilibration, the potential is held at 1.1 V for 10 s, then brought to 0.4 V for 5 s. Within this time, the current response is linear via Cottrellian behavior.

Results and Discussion

From the cyclic voltammogram shown in Figure 2, taken at 70% RH, 50 °C for Nafion® 117, a high level of certainty is ascertained that the system has reached steady state after 5 days equilibration, since subsequent CV scans are identical.

Figures 3 and 4 show the result of potential step coulometry, where each point is an individual coulometric step outlined in the previous section, with two minutes

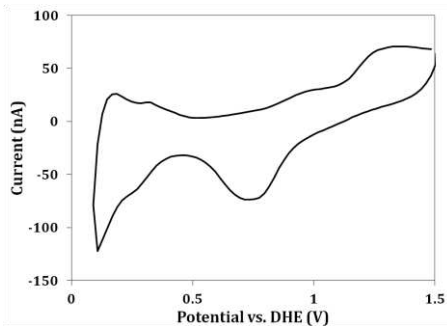


Fig. 2 Nafion® 117 at 70% RH, 50 C, 100 mV/s

rest time between each point at open circuit potential. In between sets of data, the system is allowed to rest for 30 minutes at open circuit. Towards the end of experimentation, it appears that a steady state is realized and some reversibility is attained.

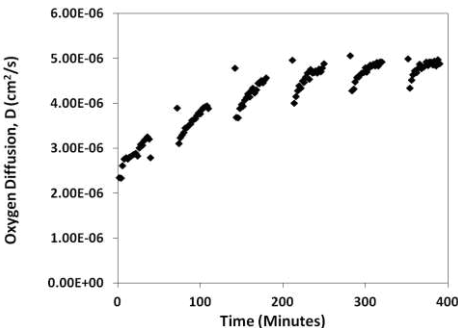


Fig. 3 Oxygen diffusion over repeated measurement at steady state

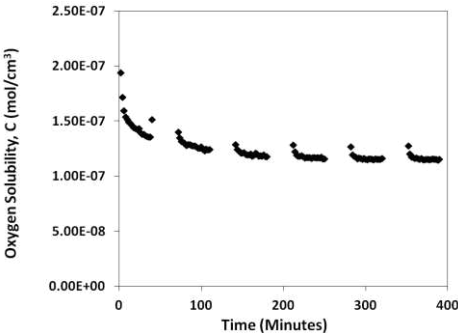


Fig. 4 Oxygen solubility over repeated measurement at steady state

The shift over time observed in Nafion® 117 samples as presently tested may be attributed to water formation during each measurement (pico molar quantities) diffusing through the interface. Surface restructuring may be to blame, where current experiments aim to verify the effect through various means.

Acknowledgements

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References

1. V. Basura, P. Beattie, S. Holdcroft. J Electroanal. Chem., **458**, 1, (1998).
2. P. Beattie, V. Basura, S. Holdcroft. J Electroanal. Chem., **468**, 2, (1999).
3. Y. Takamura, E. Nakashima, H. Yamada, A. Tasakam, M. Inaba, ECS Trans., **16**, 881, (2008).
4. J. Chlistunoff, F. Uribe, B. Pivovar, ECS Trans., **6**, 137 (2006).
5. J. Chlistunoff, F. Uribe, B. Pivovar, ECS Trans., **8**, 37 (2007).