

Durability at the Polymer Electrolyte-Electrocatalyst Interface Containing Non Fluorinated Ionomers Designed for Elevated Temperature Operation

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Introduction:

Cheaper alternatives to the current state of the art perfluorinated sulfonic acid (such as Nafion®) polymer electrolytes with non fluorinated thermoplastics capable of elevated temperature operation are currently the subject of a lot of research and development. Besides low cost, these new proton-conducting polymers must satisfy several criteria simultaneously such as high proton conductivity ($>0.1\text{S/cm}$), thermal and mechanical stability in the presence of moisture to temperatures up to 150°C and chemical stability to acids and free radicals *etc.* The aggressive environment in a PEMFC can initiate different modes of degradation mechanisms and aging processes that result in either chemical or morphological alteration. The free radical initialized membrane degradation is particularly interesting since a common feature of these new hydrocarbon based polymer materials is that the building block consists of sulfonic acid substituted aromatic rings, which are possibly sensitive to radical attack.

Up to now, the studies of the degradation of non-fluorinated membranes during the long-term fuel cell operations are mainly limited to the polystyrene and polystyrene-grafted sulfonic acid membranes. Two mechanisms were postulated. 1. Oxygen diffusing through the membrane to the anode with concomitant formation of HOO^\bullet radicals at the surface of the catalyst resulting in susceptibility of attack of the tertiary hydrogen at the α -carbon of the polymer^{1,2}; 2. Oxygen reduction at the cathode proceeding through a peroxide intermediate H_2O_2 , reacting with trace metal ions primarily in the carbon support at the reaction layer interface to form HOO^\bullet and HO^\bullet radicals, resulting in membrane degradation during the cathode reaction³.

The objective of this presentation is to show various aspects of the durability and degradation phenomena of several new promising alternative non fluorinated polymer electrolytes such as sulfonated poly (arylene-ether-sulfone) (SPES) and sulfonated polyether ether ketones (SPEEK) and identify the possible site of degradation in PEMFC environment.

Experimental

An Accelerated Membrane Durability Test method has been designed for this investigation. The idea is evaluating membrane durability by short-term fuel cell test under real operating conditions. The source of peroxide radical is generated *In-situ* electrochemically.

The degradation of the polymer is characterized by means of IR, SEM and EDAX techniques besides monitoring variations of proton conductivity.

Results and Discussions

Our prior research evaluating the performance of Pt based supported catalysts using RRDE method has shown that varying amounts of hydrogen peroxide

intermediate could be generated during the oxygen reduction process based on the choice of electrocatalyst (Pt and Pt alloys) as well as water activity at the interface.⁴ The effect of choice of electrocatalysts is shown in Fig 1, where the peroxide yield is compared between a supported Pt/C and a PtCo/C electrocatalysts measured in 1 M Trifluorosulfonic acid (TFMSA). These peroxide intermediates have the potential to attack not only the polymer electrolyte membrane but also the ionomer component within the active layer, with concomitant decrease in cell performance. Such a degradation of an SPES (40% sulfonated) is shown below as changes in the IR spectra (Fig. 2).

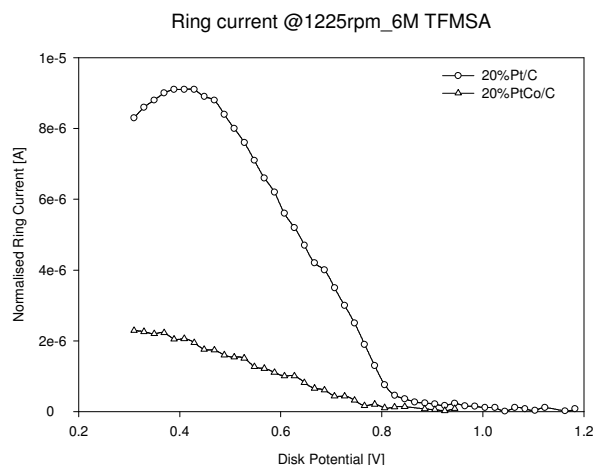


Figure 1. Disk potential vs Ring current for various Pt based catalyst in 6M TFMSA

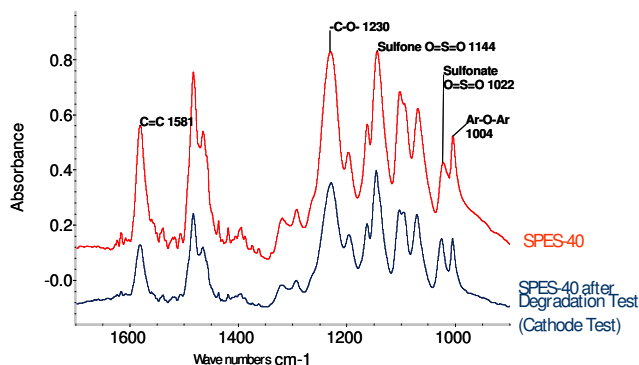


Figure 2. FTIR spectra of SPES-40 before and after the H_2O_2 Degradation Test

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References

1. F. N. Buchi, B. Gupta, Haas and G. G. Scherer, *Electrochim. Acta*, 1995, **40**, 345.
2. G. G. Scherer, *Ber. Bunsen-Ges. Phys.Chem.*, 1990, **94**, 1008.
3. Q. Guo, P. N. Pintauro, H. Tang and S. O' Connor, *J. Membr. Sci.* 1999, 154, 175.
4. V. Srinivasamurthy and S. Mukerjee. ECS Paris Meeting, May, 2003