Electronic Supplementary Information (ESI)

Detailed experimental procedures for the fabrication of composite Nafion® membranes, MEA preparation, fuel cell performance testing and durability testing

Panagiotis Trogadas, Javier Parrondo and Vijay Ramani*

Department of Chemical and Biological Engineering
Illinois Institute of Technology
Chicago, IL 60616 USA

Email: ramani@iit.edu; Tel: +1 312 567 3064

Characterization techniques

X-ray diffraction [(XRD); Rigaku Miniflex diffractometer] studies were conducted to confirm the presence of platinum on CeO_2 as well as to estimate the crystallite size of the additives studied. Diffractograms were recorded from 20° to 80° 2θ with a step of 2 min/degree.

Transmission electron microscopy (TEM) was used to determine the particle size and size distribution of supported Pt on CeO_2 nanoparticles. The supported metal and metal oxide nanoparticles were dispersed in ethanol; the dispersed particles were deposited onto carbon-coated copper grids and dried at room temperature. TEM micrographs were obtained using a JEOL JEM 3010 microscope at an acceleration voltage of 300kV.

Fabrication of composite Nafion® membranes and MEAs

Composite membrane precursor mixtures were prepared by addition of CeO_2 supported Pt and MnO_2 particles to 5wt% Nafion® (1100 EW) dispersion, maintaining the loading of additive constant at 3 wt%. Membranes were prepared by casting the mixture on a 7.5 cm x 7.5 cm glass plate, followed by overnight drying at 60°C for solvent evaporation. The membranes were then peeled off from the glass plate and the edges were cut and discarded. Recast Nafion® membranes were prepared for comparison. The membranes were washed in deionized water, dried, and hot-pressed at 120-130°C and 2.75 MPa for 5 min. Membranes of 25±2 μm were prepared in this work.

The membranes were prepared by casting controlled amount of polymer solution with the aim of getting membranes of approximately 25 μm in thickness. The thickness of the prepared membranes was measured using a digital micrometer (averaged across 10 points for each sample) and only the membranes with a thickness close to 25 μm were used in the experiments (the std. error in thickness was < 2 microns). The thickness of every membrane used in the experiments was also measured before preparing the MEAs. The measured value for the thickness was used in the calculation of the membrane conductivity. This, in conjunction with the fact that the membranes were all of the same thickness confirm that the membrane thickness did not introduce any error in the estimation of membrane conductivity. The error bars (standard error) shown in Fig 3 represent the variation of conductivity calculated for at least 4 different samples.

Membrane electrode assemblies (MEAs) with an active area of 5 cm^2 were prepared by applying Pt/C electrocatalyst at the anode and cathode. The electrodes were applied by spraying a well-mixed slurry comprising Pt/C, solubilized Nafion® and methanol on to the PEM surface using an airbrush. The overall loading of platinum on each electrode was estimated gravimetrically and was maintained at 0.4 ± 0.05 $mg\text{-}cm^{-2}$. Nafion loading in the electrodes was fixed at 30 wt%. The resultant MEAs were hot-pressed one more time to ensure proper adhesion of the electrode layers to the PEM. The MEAs were assembled in a standard test fixture from Fuel Cell Technologies Inc. prior to testing. Multiple membrane and MEA samples were prepared to aid replicate measurements.

MEA testing - Performance and durability

Linear sweep voltammetry (LSV) was the first experiment performed on each fuel cell to check for hydrogen crossover and electronic shorting in the MEA. Only cells demonstrating low hydrogen crossover (1-2 $mAcm^{-2}$) and no shorting were chosen for further testing. The performance of the cell was evaluated for 2 consecutive days by obtaining polarization curves at a temperature of 80°C and an inlet relative humidity (RH) of 75% (corresponding to a saturator dew point of 73°C). Air was used as oxidant and hydrogen was used as fuel. Stoichiometric ratios of 2 with minimum flows of 0.2 SLPM[1] were employed at each side during the experiment. The tests were performed at 1 atm absolute pressure.

To monitor the PEM degradation rate, the MEAs were tested at open circuit at 90^{o}C and 30% RH (corresponding to a saturator dew point of 60°C). For the accelerated degradation test, O_2 was used as the oxidant at the cathode and H_2 was used as the fuel at the anode. The flow rate for both gases was 0.2 SLPM. The test was run for 24 hours for each MEA and the effluent water in the anode and cathode streams were independently condensed in cold-traps. The fluoride ion concentrations in the condensate water were measured using a fluoride ion selective electrode (Denver instruments) that was freshly calibrated before each measurement. This data, in conjunction with the condensation rate of water, was used to calculate the fluoride emission rate (FER) from the MEA and hence quantify the rate of PEM degradation. Each experiment was repeated at least 3 times to quantify the experimental error.

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[1] SLPM. Standard liter per minute (standard conditions: 1 atm and 273.15K)

Additional Discussion Items:

The additional 0.3 order of magnitude reduction in FER upon addition of Pt to the ceria (over and above the 1.5 orders of magnitude observed upon addition of just ceria) is significant. Work performed in industry has shown clearly that the initial FER correlates directly to stack life, with a strong correlation coefficient. Since the onset of degradation is a process with a long induction period, any added reduction in initial FER can translate into 100s of hours or more of improved durability in the stack.

Prior work has been performed employing a different mitigation strategy, namely the addition of metal oxide particles to the catalyst layer of the MEA to serve as hydrogen peroxide decomposition agents. The underlying hypothesis was that the decomposition of generated hydrogen peroxide in the electrodes would lower the amount of free radicals formed in the MEA and hence the degradation rate and the FER. These methods have yielded FER reductions on the order of 30-50% [1, 2]. In contrast, the method employed here yields close to 2 orders of magnitude reduction in the FER rate and hence in the macroscopic rate of PEM degradation.

It is postulated that the presence of platinum on the CeO_2 surface enhances the rate of reduction of Ce^{4+} to Ce^{3+} ions, thereby increasing the amount of hydroxyl radical scavengers available on CeO_2 surface and thus further mitigating the chemical degradation of Nafion® membrane. This hypothesis is supported by the results of Coms and coworkers[3], who studied the mitigation of PEM degradation during fuel cell operation using Ce and Mn ions. The hypothesis is additionally supported by the work of several authors who have analyzed the mechanism of free radical scavenging by CeO_2 in biological systems[4-6]. A potential alternate explanation for the observed FER reduction could be the generation of water within the PEM due to the presence of the added inorganic additives (and hence the dilution of reactive oxygen species). This explanation has some traction when one considers the enhanced conductivities in some of the composite membranes. However the following factors militate against this being the mechanism of degradation mitigation: a) the durability tests were performed under extremely dry conditions where the conductivity of the membranes would have been uniformly low; and b) the composite membranes prepared using Pt(0.5&1wt%) on CeO_2 did not show much improvement in conductivity, but their FER was very close to the one observed for Pt(2wt%) on CeO_2.

The regenerative nature of supported Pt on CeO_2 particles in the acidic environment of PEM was also tested via a 5-day durability test. A larger than one order of magnitude reduction in total FER was observed compared to recast Nafion® throughout the experiment, confirming that Pt/CeO_2 was a regenerative free radical scavenger.

References:

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