Degradation and contamination of perfluorinated sulfonic acid Membrane due to swelling-dehydration cycles

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Introduction

Formation of sulfonic anhydride S-O-S (from the condensation of sulfonic acids) was known one of the important degradation mechanisms [i] for Nafion membrane under hydrothermal aging condition, which is especially critical for hydrogen fuel cells. Similar mechanism would also have be desirable to the membrane degradation in direct methanol fuel cells (DMFCs), where liquid water has direct contact with the electrolyte. An ex-situ experiment was established with swelling-dehydration cycles on the membrane. However, formation of sulfonic anhydride was not detected during the entire treatment; instead contamination from calcium was found the primary reason for the deterioration of the membrane properties.

Experiment

The property changes of commercially available perfluorinated sulfonic acid membrane – Nafion™ 212 were continuously monitored during over 60 times swelling (distilled water boil at 1 atm.) - dehydration (vacuum dry, 80 °C, 8*10^2 Bar) cycles. A combination of weight loss, conductivity, ion exchange capacity, fluoride release, element mapping, thermal stability and different types of microcopies and spectroscopies were applied in the study.

Results

The degradation behaviors include decreasing hydrated weight, however increasing dry weight (fig.1) decreased conductivity and water content (fig. 2), release of fluoride (XPS, fig. 3 and ion selective electrode), almost complete loose of ion exchange capacity etc. Despite only distilled water was used during the treatment, contamination from calcium was confirmed from both EDX element mapping and Raman spectroscopy (fig. 4). Calcium was found forming stable product with sulfonic group, which explains the enhanced membrane thermal property (via thermogravimetry), and also lower water content and consequently lower protonic conductivity.

Discussion

As shown in fig. 5 IR spectra, for oven baked Nafion, a clear peak indicates S-O-S bonding, which wasn’t observed for water boiled sample. This might be due to both the difficulty of water condensation in liquid environment and strong affinity between –SO3- and Ca^2+. These suggest that instead of sulfur anhydride formation, cation contamination is a more important membrane degradation mechanism in the cell where Nafion equilibrium with liquid phase, such as DMFC.