Self-healing Composite Membranes for Fuel Cell Applications

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ABSTRACT

We developed a self-healing membrane based on micro-size microcapsules prefilled with Nafion solution. The microcapsules will rupture when encounter pinholes formed in membrane, and then release the prefilled Nafion solution to heal the pinholes in-situ. Microcapsules were characterized by SEM. Fuel cell performance with 6 wt% and 10 wt% microcapsules/Nafion membranes and pure recast Nafion membrane was compared. 220 hours OCV with relative humidity cycling test confirmed that self-healing membrane could greatly extent the lift span of fuel cell membrane.

Keywords: microcapsules; Nafion; durability; self-healing; fuel cells

INTRODUCTION

Fuel cells are an important enabling technology for the nation's energy portfolio with the potential to revolutionize power generation by offering a cleaner, more-efficient alternative to the combustion of gasoline and other fossil fuels. Hydrogen-powered polymer electrolyte fuel cells (PEFCs) have already demonstrated their potential to replace the internal-combustion engine in vehicles, and provide power in stationary and portable applications because they are energy-efficient, clean, and the hydrogen fuel can be generated from a variety of domestic sources [1]. One of the main challenges to PEFC commercialization is the durability of the membrane electrode assembly (MEA) [2] which is comprised of the proton-conducting electrolyte membrane, the anode, and the cathode. The membrane typically consists of a perfluorosulfonic acid (PFSA) polymer such as Nafion® which undergoes degradation over the lifetime of the fuel cell and accounts for a large part of the overall performance degradation of MEA. The research and development of durable MEAs is thus critical for fuel cell applications. The degradation of the PFSA membrane can be classified into two categories: mechanical and chemical.

Mechanical degradation is caused by cyclical expansion and contraction of the membrane associated with alternating wet and dry conditions during fuel cell operation. Water production during fuel cell operation raises the moisture level of the MEA, followed by dry-out during periods of shutdown. The PFSA membrane has an affinity for water, and as it absorbs moisture during periods of high humidity, it swells. Subsequent dry-out leads to shrinkage. Cyclical swelling and shrinkage due to hygrothermal loading subjects the membrane to fatigue stresses which promote the formation of mechanical defects such as micro-cracks and pinholes. Long-term durability studies under various conditions have been reported in order to understand the performance decrease mechanisms of the PFSA membrane [3]. Similarly, chemical degradation is caused by chemical reactions between the membrane and harmful chemical species. It is generally believed that the PFSA membrane undergoes attack by free radicals resulting from hydrogen peroxide (H_2O_2) which forms at the cathode by the two-electron reduction of O_2 due to cross-leakage of O_2 gas. The presence of H_2O_2, which forms the reactive hydroxyl (·OH) and hydroperoxide (·OOH) radicals, has been confirmed in cathode drain water, exhaust gas, and the membrane during PEFC operation. Chemical attack by these reactive radicals thins out the membrane and exacerbates the formation of mechanical defects. Such combined mechanical and chemical degradation can result in membrane failure through the initiation and propagation of microscopic cracks and pinholes which provide a pathway for reactant gas crossover which is fatal to fuel cell operation.

Membrane defects are impossible to detect and repair in an operating fuel cell, and the only solution is to replace the entire membrane electrode assembly which is prohibitively expensive. Therefore, a solution to the issue of membrane durability in fuel cells is urgently needed. The possibility of employing self-healing polymeric materials that can heal such cracks and pinholes in-situ is an exciting prospect for extending the working life and safety of such systems.

EXPERIMENTAL

Spherical microcapsules were prepared by *in-situ* polymerization of urea and formaldehyde at 55ºC for 4 hours in an oil-in-water emulsion consisting of a solution of Nafion dispersion. The stirring speed was 1000 rpm for the samples that we used in this report. The products were then filtered with DI-water for at least five times. The microcapsules were dried in atmosphere for at one week. 20 ml of 5% Nafion solution (E.I. DuPont) was dried at 60°C to vaporize the solvent. The Nafion® resin was then dissolved in DMAC to form Nafion/DMAC solution and the previously prepared microcapsules were added to it. The mixture was stirred overnight to mix the microcapsules with Nafion. The microcapsules were mixed with Nafion solution for membrane casting, and allowed to dry slowly over 24 hours. The resultant membrane formed a pore-free solid film that was about 50μm thick and contained the microcapsules with Nafion solution in it. Then the microcapsules-Nafion solution was poured onto a glass plate and heated in an air oven at 80°C for 12 hours.

UF/Nafion membranes with 6wt% and 10wt% were prepared for compassion. Finally, the composite membrane was dried and hot-pressed between gas diffusion electrodes (GDEs) with 0.3mg/cm^2 Pt loading at 120°C for 2 mins to fabricate the membrane electrode assembly (MEAThe microstructure of the composite membrane was studied using a cross-beam SEM (Auriga-60, ZEISS) with an accelerating voltage of 3kV. The MEA's performance was then tested in a 10cm^2 fuel cell. The polarization I-V evaluation of the fuel cell was conducted and controlled by a fuel cell test station from Arbin Instruments. The H_2 and O_2 humidifiers were maintained at 70°C while the fuel cell temperature was set to 75°C to prevent condensation of water vapor. Hydrogen fuel and oxygen were fed in co-flow to the fuel cell. The fuel cell tests were conducted at ambient pressure. H_2 and O_2 flow rates were fixed at 200 and 400 sccm, respectively. The fuel cell was conditioned for 8 h at a current density of 1 A/cm^2 before collecting performance data. Durability tests were conducted by holding the cell at OCV at 90°C and RH cycling. The cell voltage was monitored throughout the test.

RESULTS AND DISCUSSION

Figures 1 shows SEM images of UF microcapsules prepared with a stirring speed of 1000 rpm. The microcapsule diameter ranges from 2µm to 10µm with an average size of 5.85µm.

The fuel cell performance of the baseline recast Nafion, 6wt% UF/Nafion, and 10wt% UF/Nafion membranes was tested at 70°C, 100% relative humidity (RH) with H_2 flow rate of 200ml/min, and O_2 flow rate of 400ml/cm^2 in a 10cm^2 cell. As shown in Figure 2, fuel cell performance with 6wt% microcapsules is similar to that of the pure Nafion membrane. However, with 10wt% microcapsules, fuel cell performance greatly decreased compared to the pure Nafion membrane. Hence, it may be concluded that the loading of UF microcapsules in composite membranes should not exceed about 6wt%.

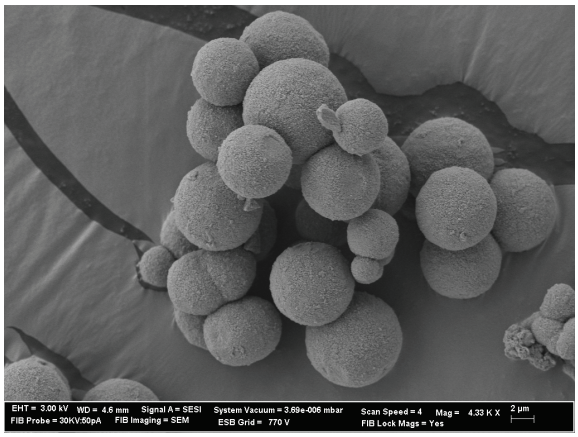

Figure 1. SEM of UF microcapsules

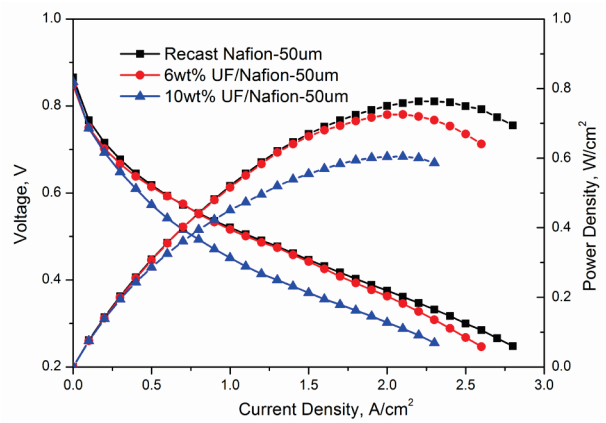

Figure 2. Fuel cell performance of recast Nafion, 6wt% UF/Nafion and 10wt% UF/Nafion

An accelerated durability test was conducted at 90°C, open circuit voltage (OCV) hold with RH cycling. Each RH cycle contained a 30 sec wet step followed by a 45 sec dry step. The protocol simulates chemical and mechanical degradation simultaneously. As shown in Figure 3, the composite membrane with 6wt% microcapsules showed a reverse trend of OCV across the entire 220 hour (10,000 cycles) test, comparing to the baseline recast Nafion which degraded rapidly owing to the formation of pinholes. The self-healing function could be the reason caused the recovery of OCV instead of decrease of the OCV. The seal-healing agents released during the accelerated test would help fix the defects, then reduced the gas cross-over to improve the OCV.

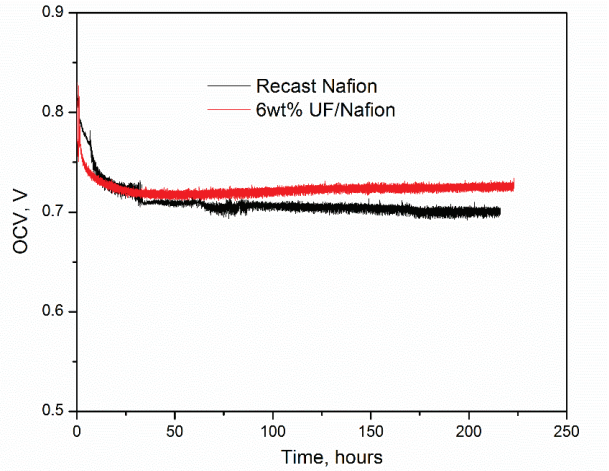

Figure 3. 220 hour accelerated durability test at OCV with RH cycling

REFERENCES

[1] U.S. Department of Energy http://energy.gov/eere/fuelcells/fuel-cells

[2] S. Vengatesan, M.W Fowler, X.Z. Yuan, H. Wang, "Diagnosis of MEA degradation under accelerated relative humidity cycling," J. Power Sources, 196, 5045, 2011.

[3] M.M. Mench, E.C. Kumbur, T. N. Veziroglu, in "Polymer electrolyte fuel cell degradation," Elsevier Inc, 2012.