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A rejuvenation process to enhance the durability of low Pt loaded polymer electrolyte membrane fuel cells

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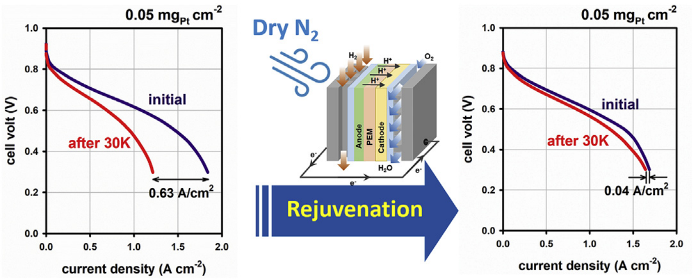
HIGHLIGHTS

- A facile and effective method to enhance the durability of fuel cells is reported.
- Cell rejuvenation is achieved by exposing the electrodes to a hot dry-N_2 stream.
- The lifetime of a low Pt loaded fuel cell is extended by a factor of 5.
- Ionomer relaxation in fuel cell electrodes plays a key role in durability.

GRAPHICAL ABSTRACT



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ABSTRACT

An effective method to enhance the durability of polymer electrolyte membrane fuel cells (PEMFCs) is reported. PEMFC performance loss is mitigated by exposing the electrodes of fuel cells to dry nitrogen gas periodically at high temperature. This method extends the lifetime of fuel cells significantly compared to their non-treated counterparts. The impact of treatment temperature and exposure time on PEMFC durability is reported, using potential cycling accelerated stress tests. The enhanced durability is attributed to the suppression of “ionomer relaxation” that occurs under the nearly water saturated operating conditions of a PEMFC cathode.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) offer one of the most promising solutions to mankind's need for the clean production of electricity [1–3]. A representative application is in automobiles, as the benefits of higher efficiencies over combustion engines, clean emissions and quieter operating conditions have made fuel cells a key technology targeted by several countries' governments [4,5].

One of the key issues to resolve for the wide spread commercialization of fuel cells in automobiles is their durability [6–8]. Several strategies have been implemented to improve fuel cell performance with regards to subzero start-up [9], acid-end group condensation of Nafion [10] and electrocatalyst impurity [11]. However, there have been few strategies to mitigate PEMFC electrode performance deterioration over time. The mechanisms of such electrode performance loss are complex, involving the complicated interactions of water, gases, metal catalyst, carbon support, ionomer, and polymer membrane. Under the dynamic conditions of a moving automobile, PEMFC cathode degradation is attributed to varying electrical voltage swings from low to high and back again, with rapid metal catalyst (usually Pt) dissolution occurring at high voltages. This dissolved Pt triggers Ostwald-like aggregations [12,13], drastically reducing the electrochemically active

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surface area of the cathode catalyst [14], gradually degrading cathode integrity which is reflected in deteriorated fuel cell performance. At low voltages, water generated by the oxygen reduction reaction (ORR) of the cathode fills the pores in the catalyst layer, which in turn inhibits gas transport, leading to depressed fuel cell performance [15]. This problem is especially apparent at low Pt loadings [16] in which the three-phase interface of catalyst-carbon support-ionomer formed in the relatively thin catalyst layer is easily disrupted by the dynamic water behavior. In such degradation pathways, the role of the ionomer is often overlooked, and as such, a topic of investigation in this study.

Ionomers such as perfluorosulfonic acid derived Nafion provide ion conduction through the catalyst layers of PEMFCs while also facilitating the transport of the gas-phase reactants and the gas- and liquid-phase product water [17–20]. Furthermore, ionomers provide mechanical integrity to the catalyst layers which impact the durability of fuel cells. Therefore, it is important to understand the relaxation behavior of ionomers. The relaxation behavior of Nafion stems from the amphiphilic nature of the polymer as its proton dissociable hydrophilic sulfonated groups are attached to an extremely hydrophobic Teflon-like polymer backbone. The Nafion dispersion, which has been the center of several previous studies over the past decades, reflects the amphiphilic nature of Nafion [20,21]. Welch studied the particle microstructure of Nafion in various dispersing agents through small angle neutron scattering experiments, showing that the dispersion particle morphology, size, and conformation could be tuned by controlling the surface energy interaction between Nafion and the dispersing agents [22]. Kim expanded upon this concept to find the dispersing agents which induced critical gelation and how various thermal treatments correlate to the mechanical properties of cast Nafion films [23]. Nafion films cast from different dispersing agents retain the characteristics derived from the Nafion-dispersing agent interaction, indicating that the microstructure and physical properties of Nafion stems from a disordered state of thermodynamic inequilibrium [24,25]. Therefore, the properties of the ionomer are governed by the colloidal particle interaction with the dispersing agent rather than polymer/solvent molecular interaction.

One well-known example of the thermodynamic inequilibrium process for Nafion is water uptake after different pretreatment conditions. Zawodzinski et al. first reported that the water uptake of Nafion strongly depends on the preheating temperatures [26]. The water uptake of Nafion after drying at room temperature is significantly lower than that after drying at 105 °C. This behavior was further examined by Alberti et al. who showed that the equilibrium water uptake of Nafion at different preheating temperatures can only be reached after a long period of time (~200 h) [27]. Furthermore, Onishi et al. measured that the time to reach equilibrium from 100% water vapor to liquid water at 30 °C is approximately 1800 h [28]. Since the relaxation of Nafion from one equilibrium state to another can take a relatively long time, various properties of Nafion (e.g. proton conductivity [29], vanadium transport [30], and mechanical properties [31]) have been studied in relation to the pretreatment history.

The impact of the relaxation behavior of Nafion on fuel cell performance and durability was first demonstrated by our research group using different catalyst/ionomer dispersing agents [32] (i.e. a water-monohydric alcohol mixture, aprotic *N*-methyl pyrrolidone (NMP) and protic glycerol or 1,2 propanediol). It was found that a cathode electrode prepared from a water-monohydric alcohol dispersing agent reached water equilibrium conditions in a relatively short time (< 20 h). A cathode electrode prepared from an aprotic NMP dispersing agent took ~120 h to reach equilibrium. In contrast, a cathode electrode prepared from protic glycerol or 1,2 propanediol did not show much change during the experimental time range (120 h). The extremely slow relaxation process of Nafion derived from the protic polar dispersing agent can enhance fuel cell durability, as demonstrated by the minimal fuel cell performance loss after 70 K potential cycles from 0.6 to 1.0 V [32]. However, one disadvantage of using the protic dispersing agent for the preparation of fuel cell electrodes is low initial high current density performance (ca. ~15%) compared to that of a fuel cell prepared from a water-based dispersing agent. This occurs because the cathodes prepared from a protic dispersing agent contain less macro-scale pores than cathodes prepared from a water-based dispersing agent.

In this study, we have developed an effective method to enhance the durability of PEMFCs fabricated with Nafion ionomers by subjecting the electrodes to a thermal treatment with inert, dry N_2 gas at high temperature. This treatment rejuvenates the fuel cell by altering the ionomer's hydrated state, giving it a new “process history”. The treatment significantly depressed fuel cell degradation during water-saturated fuel cell operating conditions, especially with low Pt catalyst loading levels. The practicality of our method, along with the significant increase in fuel cell stability during potential cycling conditions, holds great promise for future integration into automobile fuel cells.

2. Experimental

2.1. MEA fabrication

A membrane electrode assembly (MEA) was fabricated by a decal transfer process [33] onto Nafion NR-212 membrane. The catalyst inks contained a commercial water-based Nafion solution (DE 521) along with glycerol as a dispersing agent. Commercial carbon-supported Pt catalysts (ETEK) were used for the electrodes (20% Pt/C catalyst [0.2 mg_{Pt} cm^{-2}] on the anode and 5, 10 and 20% Pt/C catalyst [0.01–0.2 mg_{Pt} cm^{-2}] on the cathode). The Pt loading of the MEA was determined by X-ray fluorescence. The Pt loading of five spots of the electrode were measured with the average value reported as the actual Pt loading. The MEAs were assembled with carbon paper gas diffusion layers (SGL 25BC).

2.2. Atomic force microscopy analysis

Ionomer relaxation behavior was examined by atomic force microscopy (AFM). Thin Nafion film (~10 μm thickness) was cast from a Nafion dispersion in NMP. The cast membrane was dried at 140 °C for 6 h, then exposed to either saturated water vapor at 100 °C for 0.5–3 h or 50% RH at 30 °C for 6 months. The phase images of the Nafion films were obtained at ambient conditions after drying the sample at 60 °C for 30 min. A Veeco Metrology D3000 microscope with a Nanoscope IIIa controller and standard SFM 125 micron long silicon cantilevers with a spring constant of approximately 40 $N\,m^{-1}$ was used to obtain all images. Identical operating conditions (cantilever drive amplitude, set point, same tip) were employed for each sample.

2.3. Microelectrode experiments

Microelectrode experiments were performed with thin Nafion films according to a previously reported procedure [32]. The working electrode was a 100 μm diameter Pt microdisk (Bioanalytical Systems). Thin Nafion films (thickness ~ 5 μm) were cast on the electrode by depositing a small volume (typically 8 μl) of a commercial water-based Nafion dispersion (DE 521). The thin Nafion films were dried at 60 °C for 30 min. ORR voltammograms were measured under oxygen bubbling conditions before and after dry N_2 exposure at 80 °C for 1 h.

2.4. Electron microscopy analysis

The morphology of cathodes obtained from non-rejuvenated and rejuvenated MEAs after 30 K potential cycling tests was examined by transmission electron microscopy (TEM, Hitachi HF3300) operated at 300 kV. The TEM samples were prepared by embedding the electrodes in epoxy (Araldite 6005, SPI Supplies) and then sectioning them on a Leica Ultra Microtome.

The morphology of cathodes obtained before and after hot-dry N_2