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Repetitive hot-press approach for performance enhancement of hydrogen fuel cells

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HIGHLIGHTS

- Confirms the efficacy of the hot-pressing technique under optimal conditions.
- Two stage hot-press with hydration between presses was found to improve performance.
- Gains from hot-pressings due to the kinetic polarization suppression.
- A correlation between water content and fuel cell performance was investigated.

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ABSTRACT

For Nafion 212-based PEM fuel cells assembled with gas diffusion electrodes, two stage hot-press with conditioning or hydration between presses was found to improve performance and to allow the cell to sustain higher current densities. Testing refuted additional time as a driving factor for increased performance and the optimal hot-press time of 3 min from literature is confirmed. The two-stage hot-press process is shown to decrease ohmic resistance and to increase performance by a greater factor for Nafion 212 than Nafion 115. Tafel plots are constructed to focus on kinetics and give insight into the behavior of each membrane. Gains from hot-press and sequential hot-pressings are shown to be largely due to the suppression of kinetic overpotential. A correlation between water content and fuel cell performance in hot-press processes indicates that excessive hot-press limits the water content of a membrane, lending further support to an existence of an optimal hot-press time.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) that use hydrogen gas as fuel have received considerable attention over the past two decades due to their high energy density and low emissions [1]. Fuel cells can power vehicles, provide stationary power, reduce dependence on foreign oil and reduce air pollution. Optimization of these cells can make them a more viable alternative energy source by improving their energy density and cost [1,2]. At the heart of the PEMFC is the membrane electrode assembly (MEA) which is composed of electrocatalyst layers separated by an ion-conducting membrane. MEA hot-pressing is an important issue in fuel cell performance, as the process can help solidify the structure of the MEA and increase electrical contact [3–7]. Additionally, hot-pressing can lead to favorable polymer reconfiguration and catalyst utilization to benefit fuel cell performance [8,9]. However, excessive hot-press can lower performance by irreversibly drying out and damaging the MEA, starting at temperatures above 130 °C [2]. Tashima et al. show this damage with X-ray Photoelectron Spectroscopy and note that the CF_2/CH and CF/CH ratios decrease at 150 °C, evidencing main chain structure decomposition [2]. SEM imaging at excessive hot-press conditions showed the catalyst layer had been forced into the conductive layer and covered by Nafion, reducing the surface area and is a likely reason for decreased performance [3]. Sone et al. propose that the thermal treatment of Nafion 117 can reduce its water content through the reduction of micropores which proportionally reduces the conductivity of the cell [10]. Membrane water content is an important indicator of fuel cell health and performance, since protons are transported through the membrane while attached to water as hydronium ions [11]. A water-swollen pore increases the proton diffusion through the membrane due to the Grotthuss mechanism [12]. Studies for hot-press optimization have found pressures between 6.90 and 7.57 MPa, temperatures between 99 and 132 °C, and durations of

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2–3 min as most beneficial [2,3,13]. Other reported hot-press processes are performed between 3 and 7.57 MPa, temperatures between 99 and 135 °C, and for 1.5–3 min [4,6,14–17].

This work will analyze the effect of hot-press and repeated hot-press on fuel cell performance, the effect of conditioning, and water hydration. Hot-press techniques will be investigated, including sequential hot-presses, and their effect on the MEA will be noted.

2. Experimental

2.1. Fuel cell tests

A Scribner 850e fuel cell test system was used in our experiments. Temperatures were set to 60 °C for the cell and the anode and cathode humidifiers to ensure 100% relative humidity. The flow rates of hydrogen and oxygen were 100 sccm, while back pressure was regulated at 15 psi. Each MEA was conditioned before its first test at a constant 0.6 V and 50 sccm flow rate until the maximum attainable current developed. This typically took 12–24 h. In assembly, the test fixture was tightened to 6 Nm of torque on each of the eight bolts in the cell frame. A model 4386 Carver hot-press equipped with a digital pressure gauge was used for hot-pressing the membranes at a temperature of 132 °C and a force of 300 lb_f (1335 N). Membrane thickness was measured before and after presses with a caliper with an accuracy of ±0.0005 in (0.0127 mm).

Hand sprayed, conventional gas diffusion electrodes (GDEs) were fabricated. AVcarb™ GDL was uniformly sprayed with a 50% Pt/C ink dispersed in a water/IPA/liquid ionomer mixture in 5 min increments until the target loading of 0.1 mg cm^{-2} of platinum was reached on the GDL. The GDL was cut into 1 cm^2 squares for the construction of the MEA.

2.2. Membrane water content tests

1 cm × 3.5 cm rectangular strips were cut from a sheet of Nafion 212. After the appropriate hot-press procedure, the membranes were placed in separate, labeled, open, glass containers with silica gel beads to aid the dehumidification of the Nafion. These were then dried in a Yamato oven at 80 °C for three days. Five total measurements of the dry weight of the Nafion strip were taken after an initial measurement; one after each passing hour. The membranes were placed back into the oven between measurements. After the conclusion of the dry weight measurements, the strips were placed in water and allowed to soak on a hot plate at 80 °C for 2 h. After soaking, the membranes were left in water for five days at room temperature to fully hydrate. For the wet weight measurements, the Nafion strips were removed from the water containers, wiped until no visible moisture could be seen, weighed, and then returned to the water containers. Ten measurements of each membrane were taken and outlier values were discarded. The values are compared using the equation for water content [11],

$$W_c = \frac{100\%\ (W_w - W_D)}{W_D} \tag{1}$$

where W_w and W_D are the respective wet and dry sample weights. The standard deviation was calculated by taking into account the standard deviations of the dry weight and wet weight, as described by D.C. Baird [18]:

$$\sigma = \sqrt{\left(\frac{\partial W_c}{\partial W_w}\right)^2 \sigma_{W_w}^2 + \left(\frac{\partial W_c}{\partial W_D}\right)^2 \sigma_{W_D}^2} \tag{2}$$

3. Results and discussion

3.1. Effects of hot-press on the power and polarization behavior for N212 and N115 based cells

Hot-press has been shown to result in performance increase in hydrogen fuel cells by mitigating the kinetic and ohmic losses that shape the polarization curve [3,6,9]. Power is a key figure of merit in energy conversion systems and portrays the rate at which energy is produced, where the current density and potential are simply multiplied together [19]. Fig. 1 shows our polarization testing of Nafion 212 (N212) and Nafion 115 (N115) membranes at conditions described in Experimental section 2.1 before and after 3 min of hot-press time. Gains in maximum power density can be seen in both membranes after the hot-press procedure. The maximum power increased 143% from 206 to 500 mW cm^{-2} for N212. The maximum power increased 42% from 287 to 408 mW cm^{-2} for N115. However, the power increase in the Nafion 212 is disproportionately larger due to hot-press than the increase in the Nafion 115. This could be due to the differences in the behavior of the membranes under thermal and compressive stress. For example, the tensile strength of N212 is 23.9 MPa [20] and 29 MPa for N115 [21], which implies that N212 may flow more easily and better reconfigure under hot-press (HP) [22]. Higher potential is evident in the polarization plot. Using a reference point of 400 mA cm^{-2}, the HP N212 has a potential of 0.727 V compared to 0.486 V before hot-pressing, a gain of 49.6%. At the same reference point for N115, the HP has a potential of 0.706 V compared to 0.636 V before hot-pressing, a gain of 10.9%. Additionally, operation is sustainable at a higher current in both instances.

3.2. Effects of hot-press on the Tafel response on N212 and N115 based cells

In order to extract information about performance losses in the activation polarization dominated region, a correction is made for IR loss to get the Tafel plot, which focuses on kinetics losses (Fig. 2). It is believed that the increased contact from hot-press results in a greater number of available reaction sites that improve the kinetics of a cell, [3,6,19] and this improvement is shown in our measurements. For example, at a current density of 100 mA cm^{-2}, which is taken to be within the kinetic domain, the IR-free potential of the N212 cell after hot-press increased 2.9% to 0.812 V compared to a corrected potential of 0.790 V before hot-pressing. With the same reference point, the IR-free potential of N115 with hot-press increased 2.6% to 0.847 V, compared to a corrected potential of 0.826 V before hot-press. These slight improvements in IR-free potential can be attributed to reduced losses in the activation polarization region.

Each Tafel plot can be modeled using Butler–Volmer kinetics and mass transport effects as defined by Bard and Faulkner [23].

$$V_{\mathrm{IR-Free}} = E_a - b\log(i) + C\log\left(\frac{i_{\lim} - i}{i_{\lim}}\right) \tag{3}$$

where

$$E_a = E_{\mathrm{theor}} + b\log(i_0) \tag{4}$$

These equations define b as the Tafel slope, C and $i_{\lim}$ as mass transport limiting conditions and i is the operating current. E_{theor} is the theoretical, open circuit potential and i_0 is the exchange current density and describes the reaction rate at the electrode surface [24].

The IR corrected potential becomes consistently larger once cells have become hot-pressed (Table 1). Higher Tafel slopes can be