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Investigation of the Proton Exchange Membrane Fuel Cell Performances by Optimization of the Hot-pressing Process for Membrane Electrode Assembly Fabrication#

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ABSTRACT

The efficiency of proton exchange membrane fuel cells (PEMFC) is influenced by both the components of the membrane electrode assembly (MEA) and the fabrication process of the MEA, which in turn impacts the characteristics and structure of the electrode. This study examines the impact of hot-pressing temperatures on the gas diffusion layer (GDL) and catalyst-coated membrane (CCM). Proper hot-pressing is essential for optimizing performance. The ideal hot-pressing temperature identified is 100 ℃, resulting in a maximum power density of 1.228 W/cm^2 for the MEA, representing a 4.9% improvement compared to MEAs without hot-pressing. While hot-pressing does increase the ohmic resistance of the MEA across all humidity levels, appropriate hot-pressing temperatures can notably enhance the electrochemical surface area (ECSA) by 16.3% and reduce charge transfer resistance. Additionally, mass transfer resistance can be minimized, potentially due to the narrowing of the interface gap between the catalyst layer (CL) and GDL. These findings offer valuable insights for MEA fabrication processes and can serve as a valuable resource for practical applications.

Keywords: MEA fabrication, hot-pressing, CCM, Interface, PEMFC

NONMENCLATURE

Abbreviations	
CV	Cyclic voltammetry
CL	Catalyst layer
CCM	Catalyst coated membrane
ECSA	Electrochemical Active Surface Area
GDE	Gas diffusion electrode
GDL	Gas diffusion layer
MEA	Membrane electrode assembly
PTFE	Polytetrafluoroethylene
RH	Relative humidity

1. INTRODUCTION

The proton exchange membrane fuel cell (PEMFC) has garnered significant interest in the automotive and stationary power generation sectors due to its favorable characteristics such as reduced emissions, high energy density, quick response time, and minimal noise levels [1,2]. A crucial element of the PEMFC is the membrane electrode assembly (MEA), which comprises a proton exchange membrane (PEM), a catalyst layer (CL), and a gas diffusion layer (GDL). Hydrogen passes through the anode GDL and breaks down into protons and electrons at the anode CL. Protons and electrons are transported to the cathode through the PEM and the external circuit, respectively. Oxygen passes through the cathode GDL, then reacts with protons and electrons to form water at cathode CL [3,4].

The performance of PEMFC is influenced by both the components of the MEA and the fabrication process of the MEA, which in turn impacts the properties and structure of the electrode. Hot-pressing is a commonly used technique for MEA fabrication and plays a significant role in fuel cell performance [5,6]. While many studies have examined the effects of hot-pressing on MEAs prepared using the gas diffusion electrode (GDE) method, there is limited research on MEAs prepared using the catalyst coated membrane (CCM) method, which is a well-established and widely used technique. D. DeBonis et al. [6] investigated the changes in Naion conductivity in GDE method MEAs resulting from hot-pressing, attributing improvements in reaction activation polarization and concentration polarization to a reorganization of the membrane polymer near the CL. Ayşe Bayrakçeken et al. [7] identified the optimal hot-pressing pressure for the GDL in contact with either the

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membrane or CCM, noting that appropriate hot-pressing enhanced the performance of GDE method MEAs but had adverse effects on CCM method MEAs. Samaneh Shahgaldi et al. [8] arrived at a similar conclusion, highlighting that hot-pressing not only decreases the porosity of the CL in CCM method MEAs but also raises the diffusion resistivity of reactants.

It is imperative to study the hot-pressing based on CCM. This study delves into the fabrication of MEAs on GDL and CCM at varying hot-pressing temperatures. Findings indicate an optimal hot-pressing temperature for MEA fabrication. The study reveals that differences in MEA performance can be ascribed to membrane alterations, CL structure variations, and CL-GDL interface configurations. This investigation is poised to advance the optimization of MEA fabrication for practical applications.

2. MATERIAL AND METHODS

2.1 Preparation of MEAs

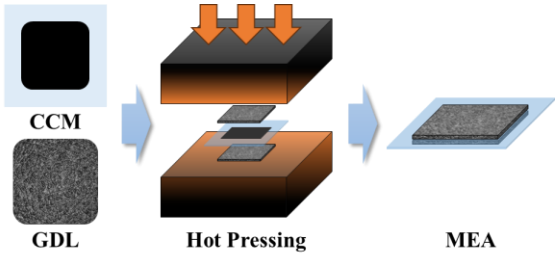

Fig. 1 MEAs fabrication process

Commercial CCM is with an active area of 25 cm^2. The GDL was placed on both sides of the CCM. As shown in Fig. 1, MEA was fabricated by hot-pressing at various temperature under a pressure of 4 MPa. MEA without hot-pressing was denoted as w/o HP. MEAs hot pressed at 100 ℃ and 130 ℃ were denoted as HP100 and HP130, respectively.

2.2 Electrochemical measurements

Single cell tests were conducted to assess the performance of the fuel cells. Hydrogen and air were supplied with a stoichiometry ratio of 1.3 for the anode and 1.8 for the cathode. The backpressure was 1.5 bar. The operating temperature of the single cell was maintained at 80 ℃. Electrochemical impedance spectroscopy (EIS) measurements were conducted at current densities of 0.2 and 2.0 A/cm^2. The disturbance current was 5% of the direct current. The frequency was scanned from 10 kHz to 0.1 Hz. Cyclic voltammogram (CV) was carried out at 80 ℃, 100%RH, H_2 and N_2 for anode and cathode, respectively. CV was carried out in a voltage range of 0.07~1.0 V (vs. RHE) at a scan rate of 50 mV/s.

3. RESULTS

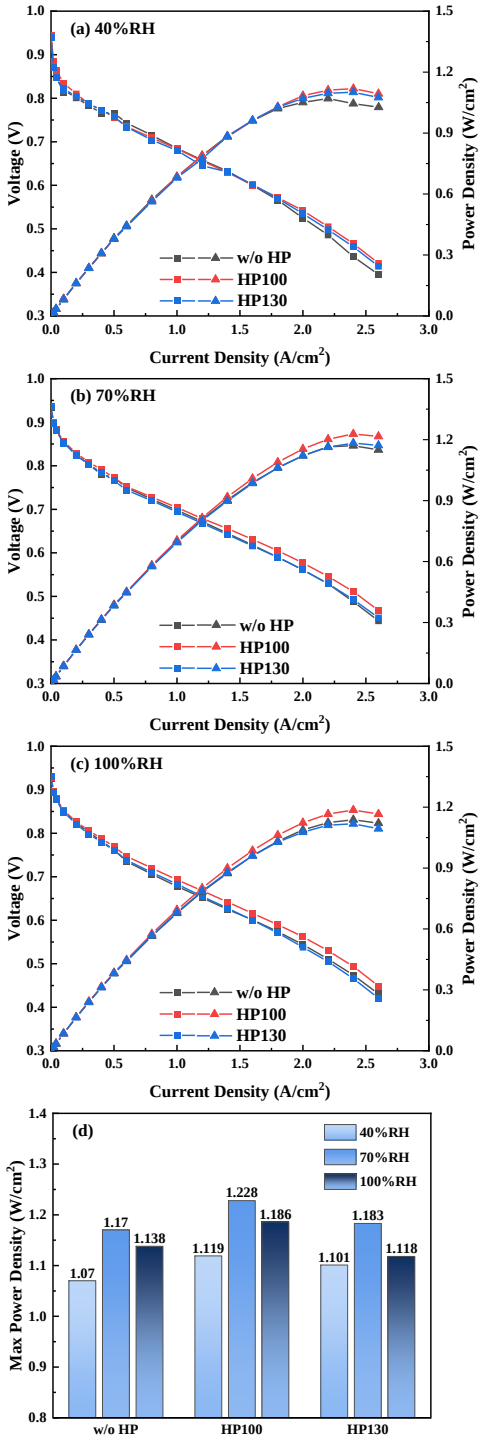

Fig. 2 Polarization curves of various MEAs under (a) 40%RH; (b) 70%RH; (c) 100%RH; (d) Max power density of MEAs under various

Fig. 2 illustrates a comparison of polarization curves and maximum power density of different MEAs at

varying relative humidity levels of 40%, 70%, and 100%. The results depicted in Fig. 2(a), (b), and (c) indicate that the performance of the three MEAs is similar in the low current density range (0 ~ 0.5 A/cm^2), with distinctions becoming evident in the intermediate and high current density ranges, specifically in the ohmic polarization and concentration polarization regions. Notably, the HP100 MEA exhibited superior performance, particularly at high current densities (>2A/cm^2). As shown in Fig. 2(d), the performance of the MEAs improved from 40%RH to 70%RH, followed by a decline from 70%RH to 100%RH. The maximum power densities of w/o HP, HP100 and HP130 under 70%RH are 1.17,1.228 and 1.183 W/cm^2, respectively, representing increases of 9.3%, 9.7%, and 7.4% compared to the lowest performance observed at 40%RH. Notably, HP100 demonstrated the best performance at 70%RH, exhibiting a 4.9% improvement over MEA w/o HP under the same conditions.

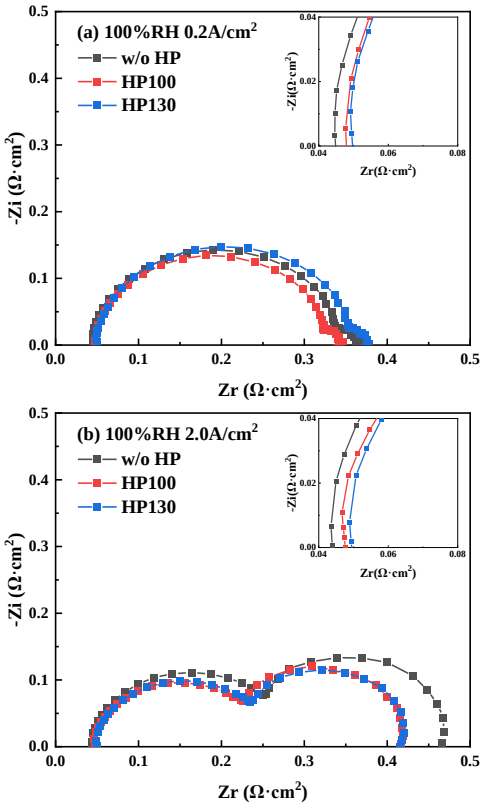

Fig. 3 EIS curves of MEAs under 100%RH, at (a) 0.2A/cm^2; (b) 2.0A/cm^2

The EIS curves under 100%RH were presented in Fig. 3. The intersection of EIS curves with the real axis represents the ohmic resistance. The radius of arcs indicates the magnitude of the resistance. The first semicircle represented the charge transfer resistance (R_{ct}), and the second semicircle represented the mass transfer resistance (R_{mt}). To assess the disparity in R_{ct} and mitigate the impact of R_{mt}, EIS measurements were conducted at a low current density of 0.2 A/cm^2. In Fig. 3(a), the first semicircle of the MEA without hot-pressing treatment (w/o HP) was marginally smaller than that of HP130, whereas HP100 exhibited the smallest semicircle. It indicated that HP100 had the lowest R_{ct}. At high current density as 2.0 A/cm^2, the mass transfer resistance became more pronounced. Fig. 3(b) reveal that the mass transfer resistance of w/o HP was the highest. And the mass transfer resistance of HP130 and HP100 were almost the same under 100%RH. The ranking of ohmic resistance from high to low, across test current densities was HP130, HP100, w/o HP.

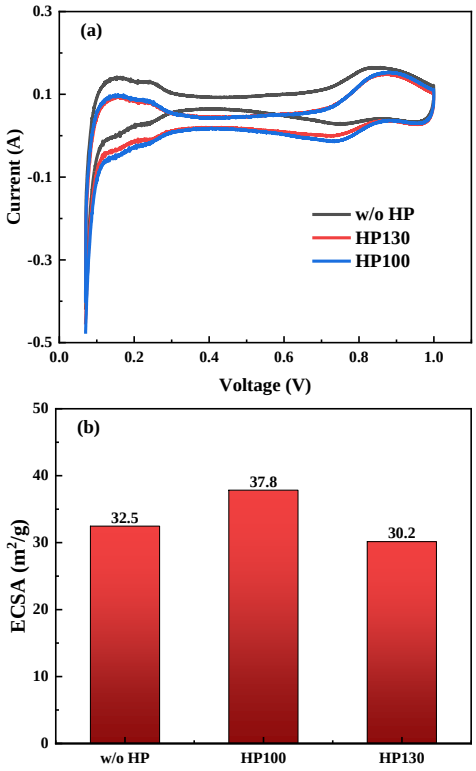

Fig. 4 (a) CV curves of MEAs; (b) ECSA of MEAs

In Fig. 4, it is evident that the hot-pressed MEAs exhibited notably lower values on the left side of the curve compared to the MEA that without hot-pressing. This observation suggests a modification in the adsorption-desorption characteristics of hydrogen. The calculated Electrochemical Surface Area (ECSA) is presented in Fig. 4(b). Specifically, the ECSA of HP100 is measured at 37.8 m^2/g, representing a 16.3% increase in comparison to the non-hot-pressed MEA, whereas the ECSA of HP130 shows a decrease of 7.1%.

4. DISCUSSION

The data presented in Fig. 2 suggests that the performance of a MEA can be enhanced through hot

pressing at an appropriate temperature, while excessively high hot-pressing temperatures can diminish MEA performance. Through a comprehensive analysis, the impact of hot-pressing on MEA can be summarized as follows.

Hot-pressing influences the characteristics of the proton exchange membrane. Elevated hot-pressing temperatures can induce a more crystalline morphology [9] and reduce the water content of the membrane [10], thereby lowering proton conductivity. This phenomenon elucidates the observed increase in MEA ohmic resistance with rising hot-pressing temperatures, as depicted in Fig. 3. However, this is not the primary factor contributing to MEA performance difference.

Furthermore, hot-pressing can alter the structure of the CL, which shares the same composition, Nafion, as the membrane [11]. Appropriate hot-pressing temperatures can optimize the electrode interface structure comprising platinum catalyst, carbon, and Nafion [9,10]. This optimization results in a high ECSA and low R_{ct}, as illustrated in Fig. 4(b) and Fig. 3(a). Conversely, excessive hot-pressing temperatures can disrupt the surface structure of the electrode, diminishing proton conductivity and yielding an adverse effect. This discrepancy in ECSA and R_{ct} between hot-pressing at 100°C and 130°C is evident.

Moreover, hot-pressing can enhance the mass transfer process within the MEA. As shown in Fig. 3(b), the mass transfer resistance of hot-pressed MEAs is lower compared to the MEA without hot-pressing. This partially accounts for the superior performance of hot-pressed MEAs in high current density regions. It means that the structure of GDL after hot-pressing has not been obviously damaged and is still valid. The hot-pressing temperature is significantly below the melting point of the hydrophobic Polytetrafluoroethylene (PTFE) in the GDL. Consequently, the hydrophobicity of the internal GDL structure undergoes minimal alteration. The enhancement in mass transfer capability is attributed to the improved interface structure of the CL-GDL. The presence of a gap at the CL-GDL interface leads to liquid water accumulation [12,13]. Hot-pressing facilitates closer contact between the GDL and CL, with deformation compensating for the interface gap to some extent. This reduction in liquid water accumulation during operation enhances gas transmission and improves the mass transfer ability of the MEA.

5. CONCLUSIONS

The study examined how the temperature used during hot-pressing affects the fabrication of MEAs. Differences in performance were linked to changes in the membrane, the structure of the CL, and the interface structure of CL-GDL. Performance variances were illustrated using polarization curves. EIS and CV were conducted to understand the mechanisms behind performance enhancements.

The findings indicate that an appropriate hot-pressing temperature can enhance MEA performance. The ideal hot-pressing temperature was determined to be 100℃, resulting in a maximum power density of 1.228 W/cm^2, which is 4.9% higher than that of MEAs fabricated without hot-pressing under the same conditions. Hot-pressing was found to increase the ohmic resistance of MEAs. The right hot-pressing temperature could enhance the ECSA of MEAs by improving the electrode interface's microstructure and reducing R_{ct}. The ECSA of MEAs hot-pressed at 100℃ was 16.3% higher than those without hot-pressing. Hot-pressing could help minimize the interface gap, decrease liquid water accumulation, improve the CL-GDL interface structure, and reduce mass transfer resistance.

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