

Supporting Information

Design of an Advanced Membrane Electrode Assembly Employing a Double-layered Cathode for a PEM Fuel Cell

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authors.

EXPERIMENTAL SECTION

MEA preparation

Figure S1 shows the MEA fabrication processes used in this work. The inner layer was fabricated by applying Pt/C slurry to a Kepton film and then transferring the prepared electrode to a membrane (*Nafion 111*) by hot pressing at a pressure of 15.7 MPa and a temperature of 140 °C for 1 min; this layer is referred to as the decal layer (Figure S1(a)).¹ The outer layer was fabricated by applying Pt/C slurry to a GDL (*SGL 10BC*, 5 wt.% PTFE); this layer is referred to as the catalyst-coated GDL (CCG) layer (Figure S1(b)), for which the GDL was not hot-pressed. The Pt/C catalyst slurry ink used for both of the layers is composed of commercial Pt/C powder (*Tanaka*, 45.8 wt.% Pt), isopropyl alcohol (IPA), deionized (DI) water and *Nafion* ionomer (*Aldrich*, 20 wt.% *Nafion* in solution). The content of *Nafion* in all the catalyst layer was constant to be 25 wt.%. The catalyst slurry was coated on the GDL or on the membrane at a constant coating speed using an automatic doctor blade and then dried in a vacuum oven for 24 h.

Five types of MEAs were designed. The total Pt loading of each cathode is 0.4 mg cm⁻² Pt. The Pt loadings in the inner/outer layer were 0.4/0.0 (a single-layered decal electrode), 0.3/0.1, 0.2/0.2, 0.1/0.3, and 0.0/0.4 (a single-layered CCG electrode) mg cm⁻² Pt, as described in Figure 1. Pt loading of anode was fixed to 0.25 mg cm⁻² Pt. The active area of the prepared MEA was 5 x 5 cm².

Firstly, anode (0.25 mgPt cm⁻²) and cathode inner layers (0.1, 0.2, 0.3 and 0.4 mgPt cm⁻²) were coated on substrate films. Then, through hot-pressing at 140 °C and 15.7 MPa for 1 min, they were transferred onto the both sides of the membrane, respectively, as illustrated in Figure S1(a).

The sandwiched membrane with the anode and the cathode inner layer, the CCL GDL (cathode outer layer) and bipolar plates were assembled at a compressed pressure of about 1.51 Mpa.

Preparation of single cells

The prepared MEAs were assembled with GDLs and graphite bipolar plates (BPs) with serpentine flow fields under the compressed pressure of 1.51 Mpa. The single cells were activated at 0.4 V for 24 h using hydrogen and air with a relative humidity (RH) of 100 %.²⁻⁴ The operating temperature was 65 °C. The stoichiometric ratios (SRs) of fuel (H₂) and oxidant (air) were 1.5 and 2.0, respectively, with a RH of 100 %.

Electrochemical characterizations

Current density-voltage (i-V) measurements, electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) were performed to characterize the electrochemical properties of the single cells employing the prepared MEAs. The i-V curves were plotted by measuring voltage (V) with increasing current (I). The duration time at each current depends on the applied current to get stabilized voltage values; 1 min at 0 /0.1 /0.5 /1 /2 A, 2 min at 4/ 6/ 8 A, 4 min at 10 A, 6 min at 12 A, 8 min at 16 A, and 10 min at 10/ 20/ 30 A.

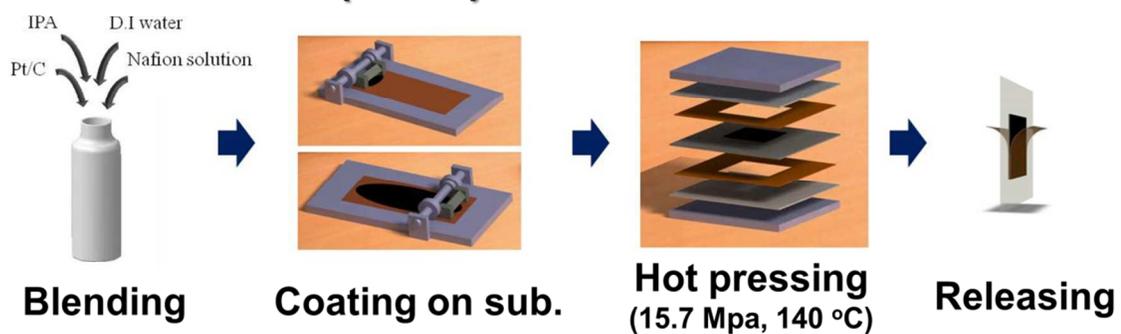
EIS was performed in the frequency range from 10 kHz to 10 mHz with a 5 mV amplitude of the sinusoidal tension signal at an applied potential of 0.85 V.³⁻⁴ The anode served as both the reference and counter electrode, and the cathode served as the working electrode under the assumption that the reactions at the anode were negligible.⁵ The CV was measured from 50 mV

to 1.2 V at a scan rate of 50 mV s⁻¹ while humidified N₂ gas was fed to the cathode. CV was used to measure the electrochemically active surface area (EAS) of the cathode using the coulombic charge for the hydrogen desorption (Q_H). The surface area of Pt was 112 m² g⁻¹, based on a commercial Pt/C catalyst, and the surface charge of Pt was 220 μC cm².⁶⁻⁷

Surface analyses

Cross-sectional images of MEAs and the Pt distribution in MEAs were analyzed by scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA). To observe the cross-sectional images, the fabricated MEAs were placed in liquefied nitrogen for 1 min and cut in the vertical direction.

(a) Decal transfer (CCM)



(b) Catalyst-coated GDL (CCG)

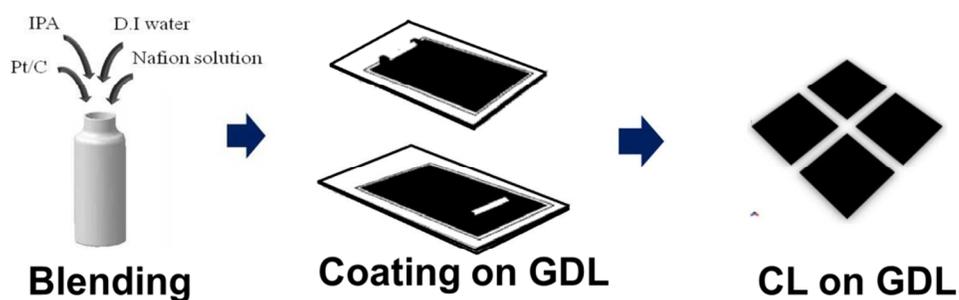


Figure S1 Illustrations of both MEA fabrication processes used in this work; (a) decal transfer catalyst-coated membrane (CCM) method and (b) catalyst-coated GDL (CCG) coating method.

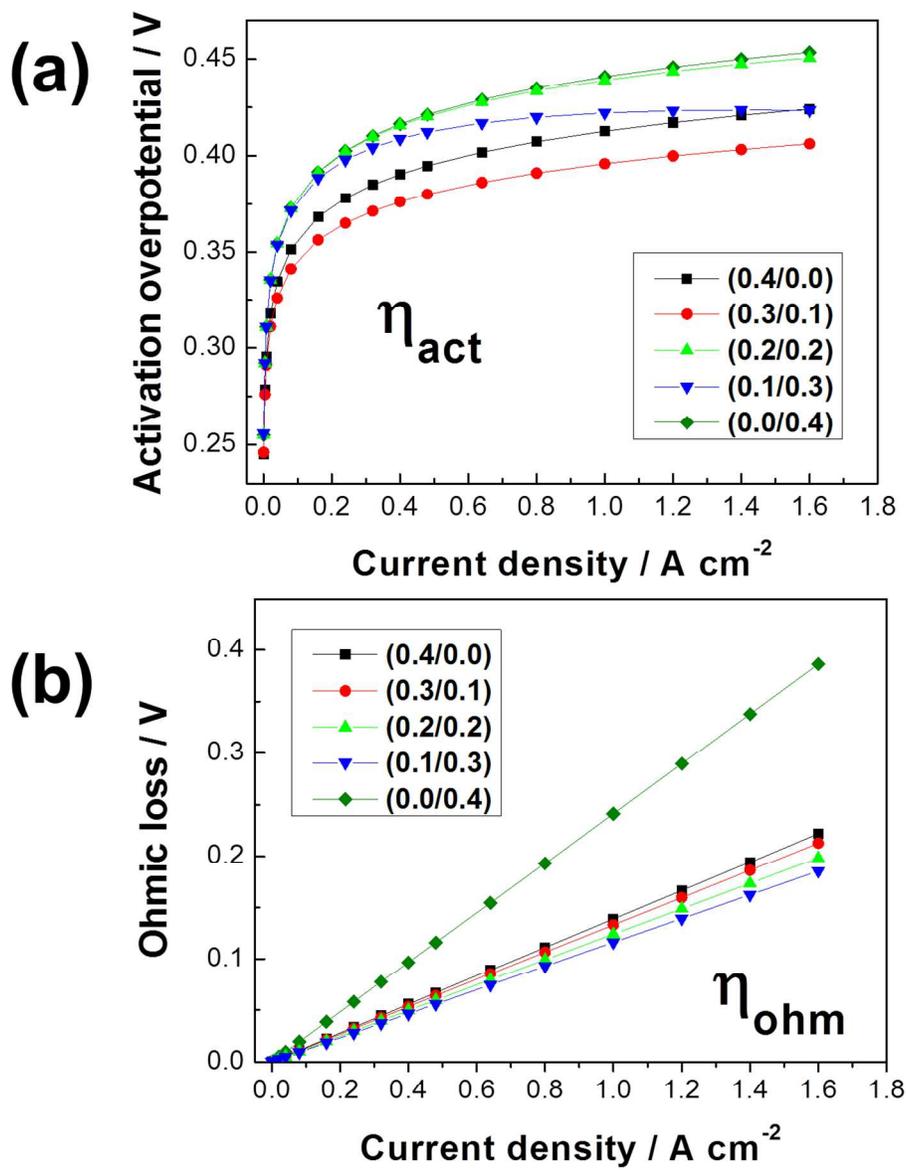


Figure S2 (a) Activation overpotential (η_{act}) and (b) ohmic loss (η_{ohmic}) of the single PEMFCs employing single-layered CCM (0.4/0.0) and CCG (0.0/0.4) and double-layered electrode of (0.3/0.1), (0.2/0.2), and (0.1/0.3) as a function of current density.

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