Journal of Power Sources 363 (2017) 153–160

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Reduction of methanol crossover by thin cracked metal barriers at the interface between membrane and electrode in direct methanol fuel cells

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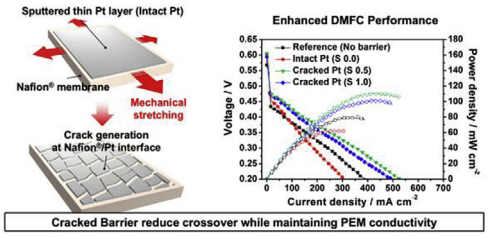
HIGHLIGHTS

- A thin, cracked metal layer on PEM is fabricated by simple method.
- The cracked metal layer reduces fuel crossover without affecting PEM conductivity.
- A MEA with the layer shows superior performance compared to conventional one.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 13 July 2017
Accepted 20 July 2017

Keywords:
Direct methanol fuel cell
Methanol crossover
Metal crack
Membrane electrode assembly
Mechanical stretching

ABSTRACT

This work reports the successful reduction in methanol crossover by creating a thin cracked metal barrier at the interface between a Nafion® membrane and an electrode in direct methanol fuel cells (DMFCs). The cracks are generated by simple mechanical stretching of a metal deposited Nafion® membrane as a result of the elastic mismatch between the two attached surfaces. The cracked metal barriers with varying strains (~0.5 and ~1.0) are investigated and successfully incorporated into the DMFC. Remarkably, the membrane electrode assembly with the thin metal crack exhibits comparable ohmic resistance as well as reduction of methanol crossover, which enhanced the device performance.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been extensively studied over several decades as an alternative energy device for stable production of electricity by refilling methanol, as a fuel without pollutant emissions except for carbon dioxide, and as a portable power supply for applications such as mobile phones and

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http://dx.doi.org/10.1016/j.jpowsour.2017.07.071
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laptop computers [1,2]. Regarding the commercialization of DMFCs, there are several technical issues such as the formation of mixed potential due to methanol crossover through an electrolyte membrane [3–6], mass transport in the membrane electrode assembly (MEA) [7], decreased ohmic resistance of the electrolyte membrane [8], and catalyst poisoning [9–11]. Among these, the methanol crossover through the membrane severely affects the performance of DMFCs. When the unreacted methanol permeates into the cathode from the anode (through a commonly used polymeric electrolyte membrane mainly due to diffusion), methanol oxidation occurs due to reaction with platinum catalyst sites on the cathode. This induces mixed potential at the cathode and critically reduces the performance of the device. In order to prevent methanol crossover in DMFCs, there have been several approaches including the development of organic/inorganic composite Nafion® membranes [12–14] and incorporation of a barrier layer onto the electrolyte membrane surface [15–17]. However, maintaining both high proton conductivity and low methanol crossover in DMFC has still remained a challenge. The transport of hydrogen ions takes place by transport of water molecules, which should result in the electrolyte membrane being swollen sufficiently with water to achieve high proton conductivity [18,19]. In contrast, to reduce methanol crossover, the electrolyte membrane should block water and disallow methanol molecules from penetrating through the membrane. Generally, low methanol crossover and high proton conductivity, which is same as low membrane resistance, are in a trade-off relationship.

Recently, there have been novel studies to apply nano-/micro-cracks that used to be considered as defects [20,21] into proton exchange membrane fuel cells (PEMFCs) [22,23]. Park et al. reported a cracked hydrophobic layer on an electrolyte membrane by directly depositing C_4F_8 gas onto the membrane. The generated nano-cracks effectively worked as nanoscale valves to delay water desorption and to maintain ion conductivity of the membrane [23]. Recently, our research group performed cracking of the catalyst layer in MEA and verified the effectiveness of the micro-cracks in a PEMFC by simultaneously achieving enhanced mass transport and reduced ohmic resistance [22]. To assess the effectiveness of the crack strategy for a DMFC with low methanol crossover and high proton conductivity, we simply stretched out a metal deposited Nafion® membrane in order to deliberately generate a thin cracked metal layer on the membrane. The as-fabricated MEA with the thin cracked metal barrier successfully showed reduced methanol crossover as well as comparable ohmic resistance compared to the conventional MEA, which led to enhancement of the device performance.

2. Experimental

2.1. Generation of metal cracked barrier by stretching out the metal deposited membrane

A ~35 nm thick Pt metal film was deposited onto as-prepared Nafion® 115 membrane using a sample sputter coater (Q300T D, Quorum Technologies, UK). A ~30 nm thick Au metal film was deposited onto the membrane using a vacuum thermal evaporator (Selcos, South Korea). Before the metal film deposition process, the Nafion® membrane was pretreated with a 3 wt% hydrogen peroxide solution for 1 h at 80 °C, followed by a 0.5 M sulfuric acid solution for 1 h at 80 °C. Then, the metal deposited membranes were stretched out by a universal material testing machine (3342 UTM, Instron Corp., US) which provides a uniform strain to the membrane and a strong clamping force to the mechanical wedge grips. We fixed bottom and top side of the metal deposited membrane by pressing two mechanical wedge grips (~0.6 MPa) with a width of ~5 cm at each side (Fig. S1). Then, in order to generate metal cracks, mechanical stretching was applied to the metal deposited membrane where the top side was stretched and the bottom side was fixed. The metal coated membranes were stretched out with variation of the strains (~0.5 and ~1.0). Additionally, pre-stretched Nafion® membrane (with strains of ~0.5 and 1.0) without depositing the metal film were also prepared for figuring out the membrane thinning effect to the device performances.

2.2. Preparation of the MEA

Catalyst ink was prepared by mixing water, 5 wt% Nafion® solution (DuPont) and isopropyl alcohol (IPA) (Aldrich) with the catalyst. 75 wt% PtRu/C (HiSPEC 12100, Johnson Matthey Co.) for the anode side and 60 wt% Pt/C (HiSPEC 9000, Johnson Matthey Co.) for the cathode side were used for catalyst inks. The prepared catalyst ink was blended by ultrasonic treatment and sprayed onto the prepared or bare Nafion® membrane to fabricate MEAs. The noble metal loadings were 2.0 mg cm^{-2} in the anodes (including the Pt film) and 1.0 mg cm^{-2} in the cathodes of the MEAs, respectively. These catalyst-coated membranes (CCMs) were dried at room temperature for more than 12 h. Then, each CCM was sandwiched between the anode gas diffusion layer (GDL) (TGPH-060-020, Toray) and cathode GDL (Sigracet 35 BC, SGL group) without a hot-pressing process. The active area of the MEAs was 5.0 cm^2.

2.3. Physical analysis

Field emission-scanning electron microscopy (FE-SEM) was conducted using a SUPRA 55VP microscope (Carl Zeiss) to examine the morphology of the various samples used in this paper. The samples were observed in the SE mode without any additional coating processes.

2.4. Electrochemical measurements

Each Prepared MEA was inserted between two graphite plates with a one channel, serpentine type flow field. The single cell was assembled with identical torque and connected to a fuel cell test station (CNL Energy). To measure the single cell performance, the methanol solution was fed to the anode at flow rates of 1.5 mmol min^{-1} by varying the concentration of the methanol solution (1.5 M, 3.0 M, and 6.0 M) and non-humidified air without back pressure was fed to the cathode at flow rates of 200 mL min^{-1}, respectively. The temperature of the cell was kept at 70 °C. Polarization curves were measured by applying different currents and measuring the correspondent cell voltages. To confirm the stability of the cracked Pt film, durability test was conducted for 50 h at a constant current density of 0.2 A cm^{-2} with 1.5 M methanol feed concentration. Electrochemical impedance spectroscopy (EIS) (Zennium, Zahner) of the single cells was conducted at 0.4 V with an amplitude of 10 mV. The measurement was conducted in the frequency range from 0.1 Hz to 100 kHz. Linear sweep voltammetry (LSV) was used to analyze the extent of methanol crossover. Methanol solution and fully humidified nitrogen gas were supplied to the anode and cathode, respectively. The cathode was used as working electrode and the anode was used as counter electrode. A positive potential was applied to the cathode from 0 V to 0.75 V vs. the anode at a scan rate of 2 mV s^{-1}. The measurement was committed at a temperature of 70 °C. To obtain the cyclic voltammograms of PtRu/C electrode (including Pt film), hydrogen gas was supplied to the Pt/C electrode (cathode in DMFC operation) and nitrogen gas was supplied to the PtRu/C electrode (anode in DMFC operation), respectively. Both gases were fully humidified and the

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