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Characterization of electrode structures and the related performance of direct methanol fuel cells

C.Y. Chen*, C.S. Tsao

Institute of Nuclear Energy Research (INER), 1000, Wenhua Rd., Chiaan Village, P.O. Box 3-14, Lungtan, Taiwan

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Abstract

The performance of membrane electrode assemblies (MEAs) in fuel cells is substantially affected by the structures of the electrodes. An increase of about 25% in power performance was achieved merely by controlling the pressure of hot press in the MEA fabrication process for a given Pt loading, instead of by employing pore formers and heat treatment-a widely accepted method-to modify the structures of the electrode. The microstructures of the different hot-pressed electrodes were examined by transmission electron microscopy, scanning electron microscopy, and small angle X-ray scattering to assess the effect of the pressure on the structures of the electrodes. Based on experimental observations, the improved performance of the MEA is attributed to the porosity of the cathode electrode, in which a network of macrofissures and sub-microfissures allows air to penetrate the electrode. Emphasis is also placed on the relationship between the total porosity of the electrodes and the MEA performance. Results of this study demonstrate that the specific power density nearly doubles when the total porosity increased from 57% to 76%. Also, the MEAs mounted in an air-breathing DMFC small pack were fabricated in-house to supply power for a mobile phone.

Keywords: Direct methanol fuel cell; Proton exchange membrane fuel cell; Membrane electrode assembly; Porosity; Electrode structure

1. Introduction

The direct methanol fuel cell (DMFC) and the proton exchange membrane fuel cell (PEMFC) are two low temperature fuel cells suitable for portable and transportation applications [1–4]. The PEMFC consumes gas fuel (hydrogen), while the DMFC is directly fuelled by liquid fuel (methanol). The use of liquid fuel is considered to be essential for commercial use due to its ease of carriage, less safety concern, and existing supply infrastructures (petroleum distribution network). Furthermore, DMFCs do not require any fuel processing equipment to convert a liquid hydrocarbon fuel into hydrogen, which significantly reduces the cost and complexity of the fuel cell system. Although the DMFC has many advantages over the PEMFC, it is mainly limited by its poor performance because it typically produces only 1/4 to 1/2 of the PEMFC's power density [5]. This has hampered the development of commercial DMFCs. Therefore, great efforts have been made to increase the power performance close to that of the PEMFC. Many works have sought for more active electrode electrocatalysts [6–9] and have addressed ways to increase the dispersion of such electrocatalysts [10] to promote methanol electro-oxidation. They have also considered the modification of Nafion membranes [11–13] and the development of new proton-conducting polymers [14] to reduce methanol crossover.

To enhance the performance of the DMFC, electrocatalysts in both electrodes usually have high Pt loadings of 5–10 mg Pt cm^{-2} to increase the electrochemical activities of the electrodes. However, high Pt loading raises a problem

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* Corresponding author.
E-mail address: cychen@iner.gov.tw (C.Y. Chen).

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of the cost in commercially exploiting the DMFC. Improving electrode structures in the MEA can greatly mitigate this problem. If the electrode structures of the MEA are designed to allow more efficient diffusion of both the liquid fuel and the gas oxidant into the electrocatalyst layers, then the performance of the MEA can be improved by limiting the mass transport losses. Accordingly, the Pt loadings in the electrodes can be considerably reduced.

This study neither develops new electrocatalysts or membranes, nor utilizes any complicated approaches, such as manufacturing multi-layer electrodes or (and) adding pore-formers to improve the MEA performance [15–17]. Instead, the pressure of hot press and Pt loadings in the MEA fabrication process are simply manipulated to increase the performance of MEA. This study aims to characterize the electrode structures and thus elucidate the mechanism of the improvement in the performance of the MEA. Various techniques including transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and scanning electron microscopy (SEM) are employed to investigate the Pt nanoparticles and electrode structures in different hot-pressed electrodes. Although laborious experiments are commonly used to improve MEA performance, a better understanding of the structures of electrodes would accelerate MEA development for high-performance DMFCs. Additionally, the MEAs fabricated in-house were applied to an air-breathing DMFC power pack to demonstrate their operability in mobile phones.

2. Experimental

2.1. Electrocatalyst preparation and characterization

40 wt% Pt–20 wt% Ru and 50 wt% Pt electrocatalysts both supported on a conductive carbon black with a high surface area, together with 60 wt% Pt–30 wt% Ru and 100 wt% Pt electrocatalysts were purchased from Johnson Matthey Inc. The mean particle sizes of the electrocatalysts range between 2.5 and 3.5 nm. The anode electrocatalyst was prepared from a mixture of 40 wt% Pt–20 wt% Ru/carbon black, 60 wt% Pt–30 wt% Ru and 5% Nafion solution (DuPont) to enable the electrodes of the MEA to be fabricated at various Pt concentrations and Pt loadings. The cathode electrocatalyst was obtained from the mixture of 50 wt% Pt/carbon black, 100 wt% Pt and 5% Nafion solution. The electrocatalysts were rigorously stirred until the mixture became a smooth paste. The microstructures of the as-received electrocatalysts and those on MEAs were examined using a JOEL 2000FX TEM, a HITACHI S-800 SEM and a SAXS instrument.

2.2. Fabrication of the membrane electrode assembly

After Nafion 117 membranes (DuPont) were cleansed by boiling in deionized water, 3 wt% H_2O_2, 3 wt% H_2SO_4, deionized water and deionized water again for 1 h in each step, a thin layer of electrode was coated on each surface of the membrane by screen printing with the prepared electrocatalysts. The MEA was then obtained by hot pressing at 120 °C and 5–100 kg cm^{-2} for 2–3 min. The active area of the MEA was 4 cm^2 with the same Pt loading of about 2–5 mg cm^{-2} in each electrode.

2.3. Performance test

After the MEA was fabricated in-house, it was sandwiched between carbon cloths (purchased from ElectroChem. Inc. and used as diffusion layers) and then installed in a single cell test fixture with two current collectors. The current collectors were made of 1.2 mm stainless steel plates with a series of 3 mm diameter holes drilled to enable the fuel or ambient air to flow through. The cell was held together between acrylic plates using a set of four retaining bolts positioned at the periphery of the cell. To reduce the testing instability, the power density of the cell was obtained at a constant voltage after 30 min of operation. The voltage was conducted at about 0.23 V as determined from the peak power density in the polarization curves. In this short-term (30-min) stability test, the cell was connected to a simple flow rig, which consisted of a Eyela MP-3N peristaltic pump, to supply the aqueous methanol solution from a reservoir ($\sim$ 50 cm^3) at a rate of $\sim$ 10 ml/ min. This process eliminated the influence of the changes and heterogeneity of the methanol concentration. Tests on air-blown DMFCs were carried out at 30 °C by a test station equipped with a Chroma 63030 electronic load.

3. Results and discussion

3.1. Performance of various MEAs

A short-term stability test of a DMFC with 3 wt% MeOH was conducted at 0.23 V and 30 °C. Fig. 1 shows the typi-

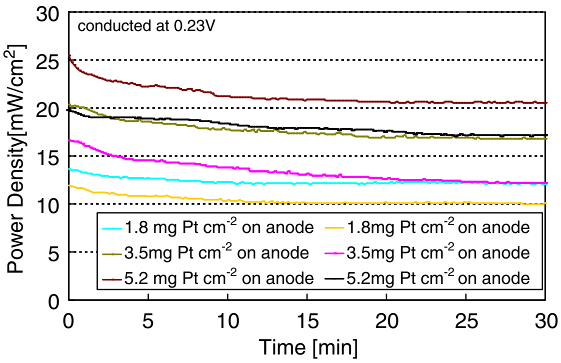

Fig. 1. Typical variation of the power density with time for MEAs with various amounts of Pt at 30 °C and ambient pressure.