

Short communication

High performance membrane-electrode assembly based on a surface-modified membrane

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Abstract

A surface-modified membrane is prepared using a sputtering technique that deposits gold directly on a Nafion[®] 115 membrane surface that is roughened with silicon carbide paper. The surface-modified membranes are characterized by means of a scanning electron microscope (SEM), differential scanning calorimetry (DSC), and water contact-angle analysis. A single direct methanol fuel cell (DMFC) with a surface-modified membrane exhibits enhanced performance (160 mW cm^{-2}), while a bare Nafion[®] 115 cell yields 113 mW cm^{-2} at 0.4 V and an operating temperature of 70 °C. From FE-SEM images and CO_{ad} stripping voltammograms, it is also found that the gold layer is composed of clusters of porous nodule-like particles, which indicates that an anode with nodule-like gold leads to the preferential oxidation of carbon monoxide. These results suggest that the topology of gold in the interfacial area and its electrocatalytic nature may be the critical factors that affect DMFC performance.

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1. Introduction

A number of studies that seek to improve direct methanol fuel cell (DMFC) performance have focused on increasing the efficiency of the catalyst, reducing methanol crossover, controlling mass transport, and increasing the durability of the membrane-electrode assembly (MEA) [1–5]. Among these issues, the interfacial properties of the MEA for durability have been recognized as a critical determinant of DMFC performance [6]. In fact, good adhesion of the electrocatalyst to the membrane is required to reduce ohmic losses and to support the high mechanical stresses produced during cell operation. The grow-

ing interest in the interfacial properties has promoted work on the surface-modification of membranes. For instance, a MEA that employed a Pd-deposited Nafion[®] membrane was found [7,8] to be effective in suppressing methanol crossover at high methanol concentrations. Haug et al. [9] observed that Pt deposition on a membrane by a sputter-deposition method formed a layer with a columnar structure, and reported that loading of the catalyst via this method gave a high efficiency of catalyst performance [9]. Despite these improvements, the increased resistance of the metal-deposited membrane and cracks in the metal layer are critical issues that need to be resolved for high performance in fuel cells. Metals such as gold, ruthenium and tungsten are of particular interest because of their effective catalytic oxidation [10–13]. From cyclic voltammograms, Umeda et al. [14] confirmed that for Pt–Ru alloy, the use of a Au substrate significantly decreases methanol oxidation current density [14].

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In the present study, surface-modified membranes are prepared by depositing a gold layer on a membrane that is roughened with silicon carbide paper. It is anticipated that the introduction of gold sputtered on the roughened membrane might offer other advantages with respect to the above-mentioned surface-modified membrane. The topological effects of the gold particles on DMFC performance and electrochemical properties are investigated.

2. Experimental

2.1. Membrane preparation and modification

Commercial Nafion[®] 115 membranes were treated according to the membrane cleaning procedure detailed elsewhere, i.e., by boiling for 2 h in each step in 2% H₂O₂ solution at 95 °C, deionized (DI) water, 1 M H₂SO₄, and again in DI water. The pretreated membranes were stored separately in water prior to use. Before the deposition of Au, both sides of the membrane surface were roughened manually with #1000 silicon carbide paper. Then, one side of the membrane was deposited with Au by the sputtering method.

2.2. Methanol permeability

Methanol permeation rates were measured using an in-house permeation cell at 50 and 60 °C. A methanol solution (0.5 or 1 M) was fed to one side of the membrane and pure water was circulated through the other side. The concentration of methanol in the permeate stream increased with time and was measured by a refractive index detector. The instrument was connected to a computer running a program that calculates methanol permeability.

2.3. Preparation of membrane-electrode assembly (MEA)

Electrocatalysts used in the anode and cathode were unsupported PtRu black (Johnson Matthey, HISPEC 6000) and Pt black (Johnson Matthey, HISPEC 1000) respectively. A catalyst slurry containing Nafion solution (DuPont, 5 wt%) was directly scattered on the Nafion membrane or the modified Nafion membrane using a spray device (Nordson Co., Japan). The catalyst, Nafion solution (Dupont, 5 wt%), distilled water, and isopropyl alcohol were mixed at a weight ratio of 1.0/0.12/1.0/9.0, and the mixture was homogenized with a microfluidizer (Microfluidics). The resulting ink was sprayed by using a pulsed spray coating machine (Nordson, Japan). The diffusion layers used were 25BC (SGL, Germany) and 10DA (SGL Germany) for the anode and cathode, respectively. A microporous layer that consists of Vulcan XC-72 (Cabot, USA) and PTFE (XC-72:PTFE = 1/1(wt/wt)) on 10DA (carbon loading level: 1.3 mg cm⁻²) was applied prior to the catalyst coating. A MEA was fabricated by placing a Nafion[®] 115 membrane between a Pt–Ru black (5 mg cm⁻²) anode and a Pt (6 mg cm⁻²) cathode followed by hot pressing at 135 °C, 10 kg_f cm⁻² for 180 s.

The cell was fitted with a MEA sandwiched between two graphite blocks that had serpentine channel flow fields for

methanol and air. The cell performance of the DMFC system was investigated with an electrochemical measuring system (Wona Tech.).

2.4. Carbon monoxide stripping voltammetry

The in situ electrochemical activities of the PtRu anode catalysts with Au particles on the membrane surface were measured using a potentiostat/galvanostat. Carbon monoxide stripping voltammetry was carried out at 30 °C using a single-cell configuration with a 2 cm² active area, with H₂O fed to the anode serving as the working electrode. Humidified hydrogen was fed to the Pt black cathode at a rate of 50 ml min⁻¹ (zero back-pressure), which then acted as a counter and a pseudo-reference electrode (dynamic hydrogen electrode, DHE). The Baseline curve was obtained with H₂O fed to the anode using a Masterflex liquid micro-pump at a rate of 2 ml min⁻¹ from 0.0 to +1.2 V. Carbon monoxide was adsorbed on to the PtRu catalyst by flowing 20% CO in nitrogen at a rate of 50 ml min⁻¹ (zero back-pressure) through the anode for 20 min, while holding the anode electrode potential at 0.1 V versus DHE. The gas was then switched for 2 min to argon at a flow rate of 50 ml min⁻¹, with the potential still held at 0.1 V, to remove non-adsorbed CO from the gas phase. The CO-stripping voltammogram was recorded by scanning the potential from 0.0 to 1.2 V at 20 mV s⁻¹.

2.5. Differential scanning calorimetry analysis and water-contact-angle measurements

The thermal characteristics of the membranes were studied using a Perkin-Elmer DSC-7, which was precalibrated with indium and zinc standards. Upon heating, the samples were raised to a temperature of 300 °C at a rate of 10 °C min⁻¹. Water contact angles were determined by means of the sessile drop method. The water droplet was limited to about 0.5 μl to prevent gravitational distortion of its spherical profile. Each determination was actually the average of at least four measurements.

2.6. Scanning electron microscopy of surface-modified membrane and MEAs after durability test

The morphological variation of the membrane surface and the interfacial surface of MEAs was investigated using scanning electron microscopy (SEM) (JEOL JSM-6340F, Tokyo, Japan). The MEAs used for SEM observation were fractured under liquid nitrogen and then dried in a vacuum oven at room temperature for 24 h. Finally, the samples were gold-coated using ion sputtering.

2.7. Wide angle X-ray diffraction analysis

Microstructural changes were investigated by using wide angle X-ray diffraction (WAXD). Spectra were taken at room temperature at a scan rate of 10° min⁻¹ over the range of 2 to 80° using an X-ray diffractometer equipped with nickel filtered Cu K α radiation (40 kV, 30 Ma) (Rigaku Denki, Model DMAX 2000).

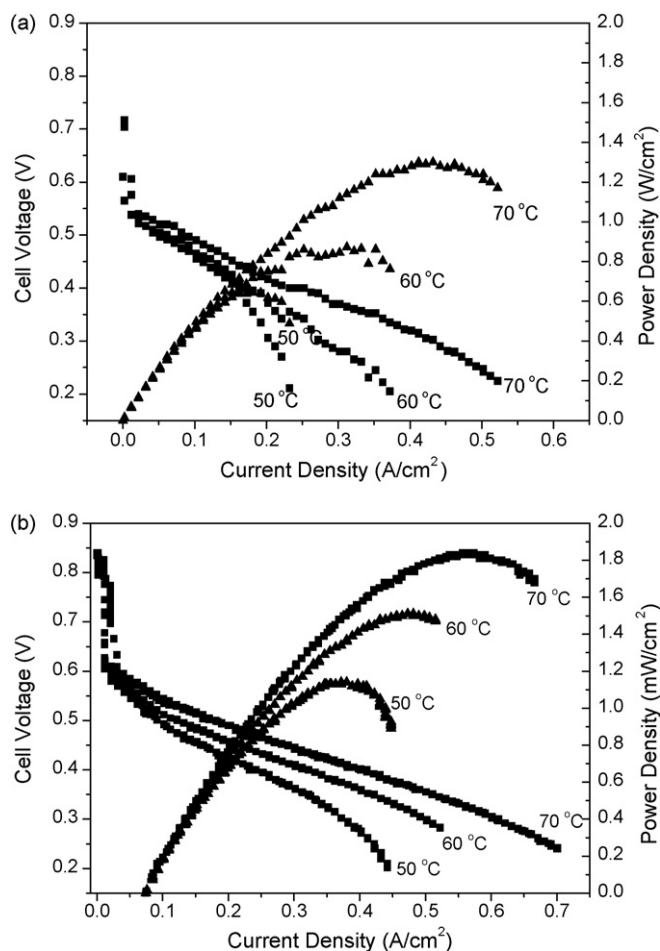


Fig. 1. DMFC performance with (a) bare Nafion 115 and (b) surface-modified membrane at increasing operating temperature.

3. Results and discussion

Steady-state polarization curves for MEAs employing a surface-modified membrane under operating conditions comprising a 1 M methanol solution as the fuel and air as the oxidant at a cell temperature of 50, 60, and 70 °C, are shown in Fig. 1. In the case of MEAs with the surface-modified membrane, a power density above $\sim 160 \text{ mW cm}^{-2}$ can be achieved at a cell voltage of 0.4 V under an operating temperature of 70 °C. From morphological observation of the interfacial area between the membrane and the electrode, it appears that strong adhesion between the membrane and the electrode contributes to the improved MEA performance. As shown in Fig. 2(a) and (b), SEM images of the interfacial area between the membrane and the electrode after the MEA performance test shows evidence of strong adhesion.

The untreated MEA exhibits a particularly unfavorable adhesion state, with the catalyst layer being almost completely separated from the membrane. Conversely, the MEA with a surface-modified membrane remains perfectly intact with no detectable flaw after the performance test. Another possible explanation for the improved MEA performance is that Au on the roughened membrane may play a role as a catalyst or a promoter for catalytic activation. The electrode reaction of gold is

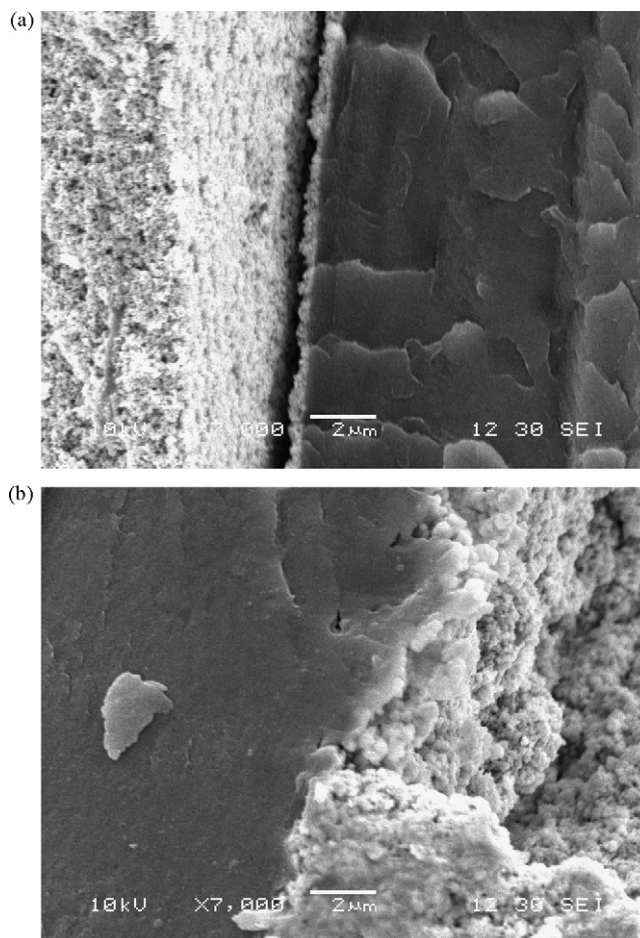
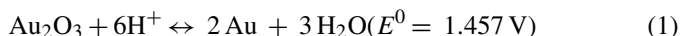


Fig. 2. SEM images of interfacial area between electrode and membrane: (a) MEA with the bare Nafion 115; (b) MEA with surface-modified membrane.

expressed as follows [8]:



From this reaction and experimental data, Mohamedi and coworkers [14] reported that Au does not participate directly in the formation of M-OH_{ad} ($\text{M} = \text{Ru}, \text{Sn}, \text{W}, \text{Mo} \dots$) but may indirectly affect the quantity of M-OH_{ad} . This species offers advantages via a bifunctional effect (see below).

Various studies concerning the electrodes manufactured using a vapour deposition or sputtering method, have been well explored in recent years. As mentioned in the above, general deposition of metal on the membrane may bring about a significant increase in the resistivity. In the present study, to minimize this disadvantage, Au was sputtered on the roughened membrane with a surface-roughness of 200 nm to 3 μm.

An electron micrograph of the surface of a surface-modified membrane is shown in Fig. 3. The interfacial surface seems to be composed of Au clusters of porous nano-nodules on the roughened membrane. Haug et al. [9] have reported that sputter deposition of Pt on the flat surface of Nafion 117 forms columnar structures due to an agglomeration of Pt islands [9]. This morphological difference is thought to be a characteristic of Au on the roughened membrane, which would induce an increase in the surface area adjacent to the catalysts.

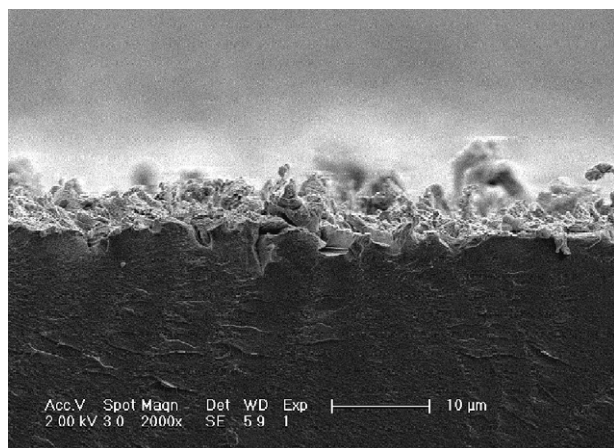


Fig. 3. FE-SEM image of interfacial area of Nafion 115 Au-sputtered after roughening process.

Differential scanning thermograms show that the membranes dried and swelled at 60 °C. As shown in Fig. 4(a) and (b), the endothermic peak of the modified membrane, C, has a higher intensity compared with those of bare Nafion 115 and the roughened membrane.

These results, together with the observation that the modified membrane shows the lowest water contact angle (Table 1), indicates that the nodule-like Au particles cause a strong interaction with water. The permeability values at 50 and 60 °C are listed in Table 1. The surface-modified Nafion 115 membrane displays lower methanol permeability compared with other membranes. Generally, the roughening process increases the specific surface area. The methanol permeability is proportional to the surface area of the membrane, and inversely proportional to the permeation length. Furthermore, the fusion enthalpy of the modified membrane after swelling is 211.2 J g⁻¹, which represents an increase of about 55% compared with that of bare Nafion® 115 (Fig. 4(b)). In the present study, although the sand-papery process causes an increase in the surface area of Nafion® that contacts directly with methanol and an increase in hydrophilicity arising from the Au layer, this layer may be responsible for the reduction of methanol permeability.

Voltammograms of CO_{ad} oxidation on anode electrodes employing PtRu black catalyst on surface-modified Nafion® 115 and bare Nafion® 115 are shown in Fig. 5. The onset potential of CO_{ad} oxidation for the anode electrode with bare Nafion 115 is observed at 386 mV versus RHE, while the onset potential of

Table 1

Water contact angle and methanol permeability of bare Nafion 115 and surface-modified membranes

Membranes	Water contact angle (°)	Methanol permeability (cm ² s ⁻¹)	
		50 °C	60 °C
Nafion® 115	62	2.38 × 10 ⁻⁶	3.03 × 10 ⁻⁶
R-Nafion 115 ^a	56	2.23 × 10 ⁻⁶	2.86 × 10 ⁻⁶
R-Au-Nafion 115 ^b	44	2.07 × 10 ⁻⁶	2.57 × 10 ⁻⁶

^a R-Nafion 115 indicates Nafion 115 roughened with silicon carbide with depth of 20 nm to 3 μm.

^b R-Au-Nafion 115 indicates Nafion 115 Au-sputtered after surface roughening.

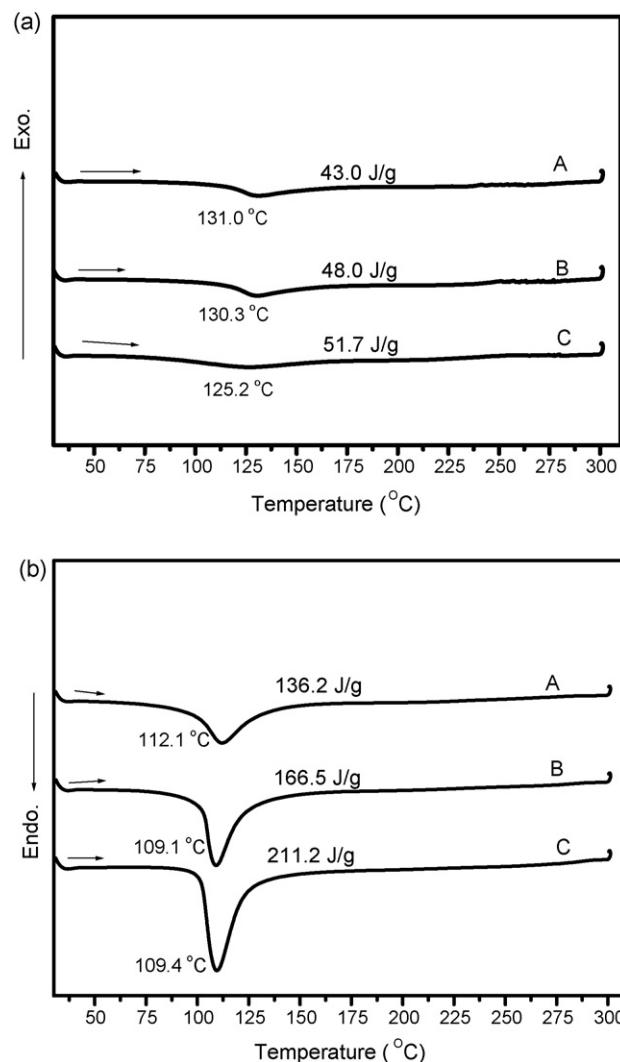


Fig. 4. DSC traces of membranes at heating rate of 10 °C min⁻¹. (A) Bare Nafion 115; (B) roughened Nafion 115; (C) Au-sputtered Nafion 115 after roughening process: (a) samples dried at 60 °C for 1 h; (b) samples immersed in water at 60 °C for 1 h.

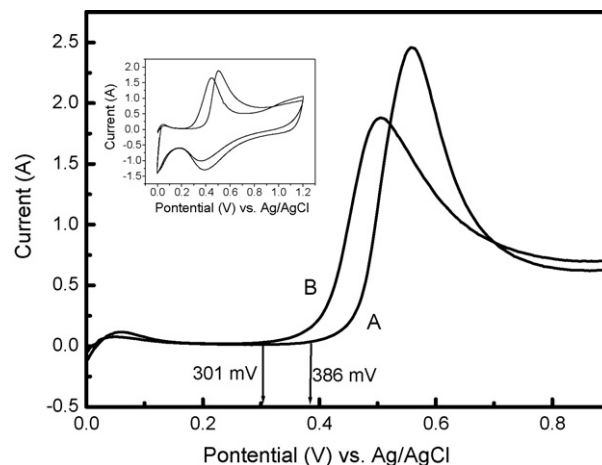


Fig. 5. Pre-adsorbed CO (CO_{ad}) stripping voltammogram at 70 °C: (A) bare Nafion 115; (B) surface-modified membrane.

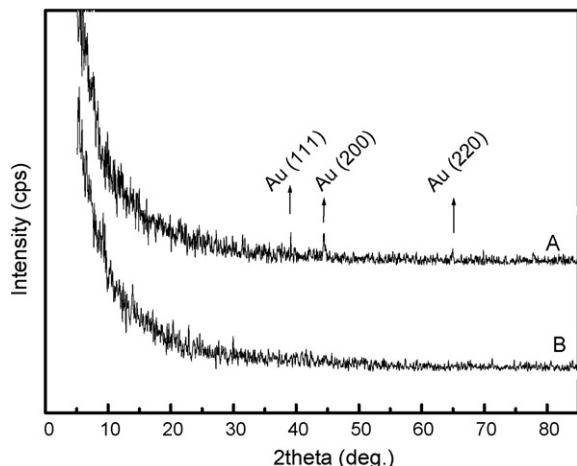


Fig. 6. WAXD patterns of membranes: (A) Au-sputtered after roughening; (B) Au-sputtered without roughening (B).

the anode electrode with the surface-modified membrane significantly shifts towards a lower potential of 301 mV. According to a previous study [14], alloying second metals such as a Ru, Co, Au and W with Pt activates the anode electrode for the CO oxidation by a bifunctional mechanism in which a OH species is provided from water adsorption. The findings discussed above indicate that nodule-like Au particles have the ability to promote the electrooxidation of adsorbed CO at low potentials. On the other hand, another noteworthy difference is found in the WAXD patterns. As shown in Fig. 6, the WAXD pattern of the Au-sputtered membrane after roughening exhibits relatively distinct small peaks at 40° , 45° , and 65° , which are assigned to (1 1 1), (2 0 0), and (2 2 0), respectively. Strbac and Adzic [15] previously reported that the potential of OH^- adsorption depends largely on the crystallographic orientation corresponding to Au(1 0 0) and Au(1 1 1). Based on these considerations, it can be concluded that the nodule-like Au particles deposited on the roughened membrane are crystalline with regularity in d -spacing, and serves as additional sites for CO_{ad} oxidation.

4. Conclusions

Membrane-electrode assemblies built from sputter-deposited Au on roughened Nafion 115 demonstrate a significant improve-

ment in DMFC performance. X-ray diffraction analysis shows that distinct crystalline peaks appear for the surface-modified membrane with nodule-like Au. This suggests that this structural characteristic of nodule-like Au may serve as additional sites for OH species. From examination of these morphologies and CO_{ad} stripping voltammograms, it is concluded that the nodule-like Au particles cause an effective electrocatalytic activation at the anode and an increase in water content within the membrane.

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