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O_2-Enhanced Methanol Oxidation at Pt-Ru-C Ternary Sputtered Electrode

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We have developed a novel anode catalyst for the direct methanol fuel cell (DMFC). Pt-C and Pt-Ru-C electrodes were prepared by a co-sputtering technique. These electrodes with a specific atomic ratio showed a remarkable O_2-enhanced methanol oxidation performance and the reaction selectivity by O_2 addition for methanol as a fuel. For practical utilization, the relationship between the O_2-enhanced methanol oxidation activity and the thermal stability of the Pt-C and Pt-Ru-C sputtered electrodes were evaluated by a post-annealing treatment. It is found that the O_2-enhanced methanol oxidation activity of the Pt-Ru-C electrodes is retained if the annealing temperature is less than or equal to 100°C. Finally, the DMFC performance was assessed using a single DMFC cell incorporating a membrane electrode assembly with Pt-Ru-C which was hot pressed at 100°C.

Introduction

The mixed reactant fuel cell (MRFC) has attracted much attention as a significant technology to downsize the direct methanol fuel cell (DMFC) (1-3). For realizing the MRFC, the anode and cathode are required to possess a reaction selectivity for the methanol oxidation reaction (MOR) and O_2 reduction reaction (ORR), respectively, because a mixture of methanol and O_2 is fed to each electrode of the MRFC. Therefore, it is important for the MRFC electrode to possess a reaction selectivity.

In our previous study, we reported that the Pt-C and Pt-Ru-C sputtered electrodes show an O_2-enhanced MOR activity with an MOR selectivity in the presence of methanol and O_2. The Pt-C and Pt-Ru-C electrodes with a specific Pt:Ru:C atomic ratio have a remarkable methanol oxidation performance, which is enhanced by the added O_2 (4,5). The reaction mechanism of the O_2-enhanced MOR is also discussed.

To characterize the practical performance, a hot-press process is indispensable to incorporate the Pt-C and Pt-Ru-C electrodes into a single DMFC cell. It is not well known what properties the prepared Pt-C and Pt-Ru-C by a co-sputtering technique possess.

In this study, we first focused our attention on a Pt-C electrocatalysts for the heat effect. The sputtered Pt-C electrode underwent a post-annealing treatment at various temperatures. The crystal structure and electric state of the Pt-C electrode were investigated using XRD and XPS measurements. We then prepared an MEA of the

Pt-Ru-C sputtered electrode and performed a power generation test using the single DMFC cell.

Experimental

Preparation of co-sputtered electrodes

The Pt-C and Pt-Ru-C thin-layer electrodes were prepared using a multi-target sputtering system (ULVAC, CS-200S) (6,7). A Pt disk, Ru disk, and two graphite carbon disks were used as the sputtering targets. The diameters of all the targets were 8 cm. An Au foil (8-mm diameter, 0.05-mm thickness), a glassy carbon plate (10 × 10 mm^2 area, 1-mm thickness; Tokai Carbon, GC-20SS), and a carbon paper (23 × 23 mm^2 area, Toray, TGP-H-060H) were used as the sputter-deposition substrates for the electrochemical measurements. Before the sputtering, these substrates were washed by ultrasonic agitation in acetone and then in Milli-Q water for 10 min each.

The experimental procedure for the sputter deposition is described as follows. A rotating holder bearing the substrates was installed in a vacuum chamber, then the chamber was evacuated by rotary and turbo-molecular pumps to a base pressure of 3 × 10^{-4} Pa. Subsequently, 99.999% Ar gas was introduced into the chamber to a pressure of 3 Pa, then the substrate was exposed to an inverse sputter etching process to remove any residue on the surface. This pre-sputtering was conducted at the DC power of 200 W for 120 s. After the etching, Pt, Ru, and C were simultaneously sputtered onto the substrate under the conditions listed in Table 1, while the substrate holder was rotated at 10 rpm. During the sputtering, an RF power was supplied to the Pt and Ru targets, and a DC power was supplied to the C targets. After the sputtering, the pressure in the chamber was allowed to return to atmospheric pressure before the samples were removed. The formed Pt-C and Pt-Ru-C layer had a 5-mm diameter with 50-100-nm thickness on the Au and the glassy carbon.

The MEA (geometric electrode area, 5 cm^2) used in this study was prepared as follows (8,9). Nafion 117 (Dupont) was used as the polymer electrolyte membrane. The membrane (5 cm × 5 cm) was boiled in 0.5 mol dm^{-3} H_2SO_4 for 1 h and then washed twice by boiling in pure water for 1 h. The above-prepared Pt-Ru-C on carbon paper was used as the anode. A commercially available Pt/C (amount of deposited Pt: 45.9 wt. %, Tanaka Kikinzoku Kogyo) catalyst was used as the cathode. The Pt/C was dispersed using a ball mill in a 5 wt. % Nafion solution (Wako Pure Chemical Industries) diluted by a mixed solvent of methanol, 2-propanol, and Millipore water (1:1:1 weight ratio). The dispersed solution was spread on the carbon paper over a 5-cm^2 area. The amount of the spread Pt was adjusted to 1.0 mg cm^{-2}. Subsequently, the pretreated Nafion 117 membrane was sandwiched between the two catalyst-loaded carbon papers and then hot-pressed at 7.5 kN and 100ºC for 10 min.

Characterization of co-sputtered electrodes

The atomic ratios of the co-sputtered electrodes were analyzed using an energy-dispersive X-ray analyzer (EDS: JEOL, JED-2300) combined with a scanning electron microscope (SEM: JEOL, JSM-6060A). The analyzed data are listed in Table 1. The

crystal structures of the prepared Pt-C layers were evaluated by X-ray diffraction (XRD: Shimadzu, XD-D1) at 30 mA and 30 kV using Cu-Kα radiation. The XRD patterns were measured in the range of 2θ = 20−80 degrees. X-ray photoelectron spectroscopy (XPS) (JEOL, JPS-100SX) was conducted to investigate the electronic structure of the co-sputtered layer. Prior to the measurement, the sample surface was cleaned by Ar ion etching, then the XPS spectra were obtained using Mg-Kα irradiation to induce excitation of the photoelectrons.

Electrochemical measurements

The electrochemical properties of the sputter-deposited Pt-C and Pt-Ru-C electrodes were evaluated using a three-compartment electrochemical cell. A supporting electrolyte of a 0.5 mol dm^{-3} H_2SO_4 solution was prepared by diluting concentrated H_2SO_4 (Wako Pure Chemical) with Milli-Q water. An Ag/Ag_2SO_4 (8,10-12) and a Pt coil were used as the reference and counter electrodes, respectively. The Pt-C and Pt-Ru-C sputtered electrodes were used as the working electrodes and their potentials were controlled by a potentiostat (Hokuto Denko, HAB-151). All the electrochemical measurements were conducted at 25 ± 1ºC and the electrode potentials in this report are referenced to the normal hydrogen electrode potential (NHE) at the same temperature. The measured currents were normalized by the geometric surface area of the sputtered electrode, which was exposed to the electrolytic solution (0.196 cm^2).

The electrochemical measurements were conducted as follows. The sputtered electrodes were pretreated by potential cycling at the rate of 10 mV s^{-1} in N_2-saturated 0.5 mol dm^{-3} H_2SO_4 solution until the voltammogram was unchanged, so that the electrode surface could be stabilized. The potential cycling was reversed from the cathodic sweep to the anodic sweep immediately before the H_2 evolution and the anodic sweep was conducted up to 0.75 V vs. NHE to prevent the Ru from dissolving (13). Methanol oxidation at the sputtered electrodes was evaluated in N_2- and O_2-saturated 0.5 mol dm^{-3} H_2SO_4 + 1 mol dm^{-3} CH_3OH solutions. The measurement was conducted at the sweep rate of 10 mV s^{-1} after the pretreatment.

The prepared MEA was installed in a single cell (Electrochem Inc., EFC05-01SP) to measure its current-voltage (i-V) characteristics using a cell operation system (FC Development Company, HPE-1000) in combination with a potentiostat/galvanostat (HAB-151, Hokuto Denko), and the data were collected using a datalogger (NR-2000, Keyence). A fully humidified N_2 gas was supplied to the Pt-Ru-C sputtered electrode at 50 cm^3 min^{-1} and a fully humidified H_2 gas to the counter electrode at 50 cm^3 min^{-1}. Thus, a background cyclic voltammogram of the Pt-Ru-C sputtered electrode was measured. The N_2 gas was then changed to an Ar- and O_2-saturated 1 mol dm^{-3} methanol solution at the rate of 50 cm^3 min^{-1} in order to compare the methanol electrooxidation at the Pt-Ru-C sputtered electrode under the Ar and O_2 atmospheres. The cell temperature was controlled at 60ºC. For the voltammetry measurements, the Pt-Ru-C electrode potential was controlled versus the counter electrode, which is considered to be a dynamic hydrogen electrode (DHE). Next, the H_2 gas supplied to the counter electrode was switched to a fully humidified O_2 gas at 50 cm^3 min^{-1}. Thus, the DMFC power generation was then conducted at the cell temperatures of 60ºC. During the power generation, the i-V and current–power (i-P) curves were measured by feeding an Ar- and O_2-saturated 1 mol dm^{-3} methanol solution to the anode and the fully humidified O_2 gas to the cathode.

All the measured currents were normalized by the geometric surface area of the Pt-Ru-C electrode, which was in contact with the polymer electrolyte membrane (5 cm^2).

TABLE 1. Sputtering conditions[a] and Pt:Ru:C[b] atomic ratios of Pt-C and Pt-Ru-C co-sputtered electrodes.

Output power / W			Sputtering time / min	Atomic ratio of Pt:Ru:C
Pt[c]	Ru[c]	C[d]		
52	0	500	30	56:0:44
50	120	500	30	61:34:5

[a] Ar gas pressure and temperature were fixed at 3 Pa and room temperature, respectively.
[b] The atomic ratios of Pt, Ru, and C were estimated by EDS.
[c] Pt and Ru were sputtered using RF power generators.
[d] C was sputtered using two graphite carbon target plates and a DC power generator.

Results and discussion

Thermal stability of O_2-enhanced MOR at Pt-C electrode

The Pt-C electrodes were prepared by the co-sputtering technique. The results of the electrochemical measurements are shown in Figure 1(A). These voltammograms of curves (a) and (b) were measured in O_2- and N_2-saturated 1 mol dm^{-3} methanol + 0.5 mol dm^{-3} H_2SO_4, respectively. The voltammogram of curve (c) was measured in O_2-saturated 0.5 mol dm^{-3} H_2SO_4. Curve (a) in O_2 atmosphere has a higher methanol oxidation current than curve (b) in the N_2 one at > 0.6 V vs. NHE. Such an O_2-enhanced methanol oxidation has not been observed when using commercial Pt supported carbon catalysts (Pt/Cs) (14). The mechanism of the O_2-enhanced methanol oxidation has been reported elsewhere (4).

Next, the prepared Pt-C electrode was post-annealed at 100 and 120°C, then the MOR and ORR activities measured, as shown in Figures 1(B) and 1(C). When the methanol oxidation voltammogram of Figure 1(A) is compared to that of Figure 1(B), almost the same characteristics are observed in terms of the methanol oxidation current density, onset potential (0.52 V vs. NHE), and O_2-enhanced methanol oxidation effect. In contrast, the O_2-enhanced methanol oxidation effect disappears despite the current density increases in the methanol oxidation voltammogram of Figure 1(C). Therefore, XRD and XPS measurements were carried out to investigate this phenomenon.

Characterization of the post-annealed Pt-C electrode

We performed the XRD and XPS measurements to observe the crystal structure and electronic state of the post-annealed Pt-C electrodes. Figure 2 shows the XRD patterns of the Pt-C electrodes with and without the heat-treated Pt-C. Also, that of Pt is shown as a reference. To compare the Pt and Pt-C without the heat treatment, the peak of Pt(111) at around 40 degree shifts toward to low degree at the Pt-C electrode. After the heat treatment, there is no change in the full-width at half-maximum of the (111) peak, but the peak positions are 39.66, 39.97, and 39.95 degrees at with no heat treatment, 80, and

160°C, respectively. Due to the heat treatment, the peak position shifts toward that of the Pt electrode. Therefore, the crystal structure of Pt in the Pt-C electrode changes to that of elemental Pt by the heat treatment even at 80°C. When comparing the temperature dependence of Figure 2 and that of Figure 1, there is a difference in the inflection temperature point. We assumed that there is no relationship between these crystal structures and the O_2-enhanced MOR activity.

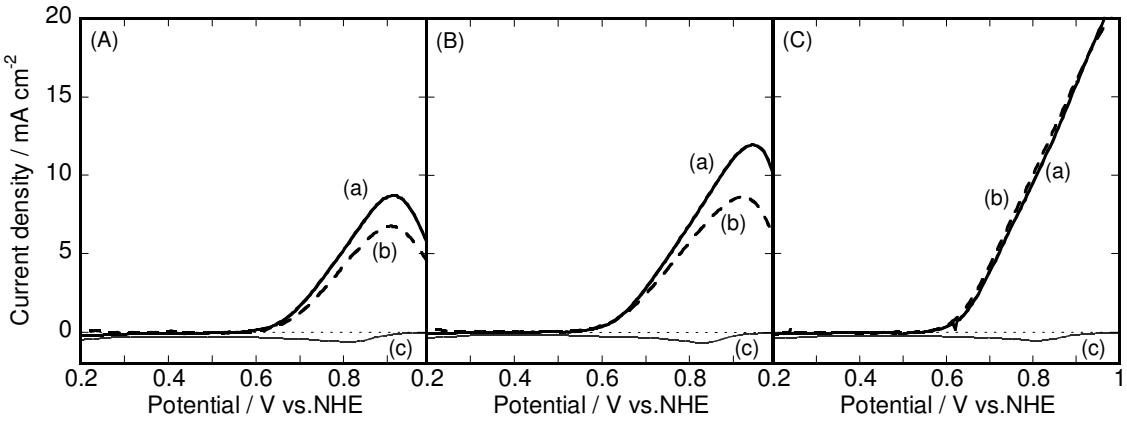

Figure 1 Voltammograms of methanol oxidation and oxygen reduction at (A) the sputtered Pt-C electrode, (B) the post annealed Pt-C electrode at 100°C, and (C) at 120°C in (a) O_2-saturated 1 mol dm^{-3} methanol + 0.5 mol dm^{-3} H_2SO_4, (b) N_2-saturated 1 mol dm^{-3} methanol + 0.5 mol dm^{-3} H_2SO_4, and (c) 0.5 mol dm^{-3} H_2SO_4. The sweep rate is 10 mV s^{-1}.

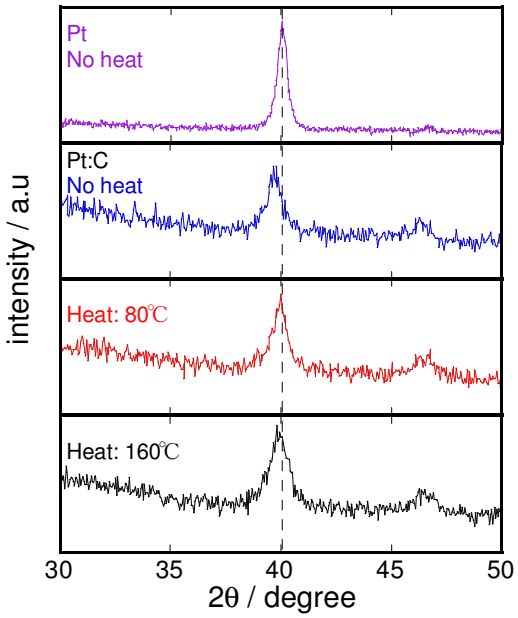

Figure 2 XRD patterns of sputtered Pt and Pt-C electrodes with and without post-annealing at 80 and 160°C. The dashed line denotes Pt(111) peak.

The XPS spectra of Pt $4f_{5/2}$ and $4f_{7/2}$ are shown in Figure 3(A). The Pt 4f peak position of the prepared Pt-C electrode is shifted toward a higher energy when compared

to that of the Pt sputtered electrode. The spectrum of the post-annealed Pt-C electrode at 80°C has almost the same peak position as that of the Pt-C electrode before annealing. On the other hand, the spectrum peak of the post-annealed electrode at 160°C is located between that of the Pt and the Pt-C electrodes. The peaks of C 1s are not changed for the post-annealed and before annealing at the Pt-C electrodes (Figure 3(B)). There seems to be little electronic interaction with between C and Pt. By high temperature treatment, the electric state of Pt in the Pt-C electrode changes and shifts toward the Pt metal state. Therefore, it is considered that the O_2-enhanced MOR effect disappeared at greater than 120°C.

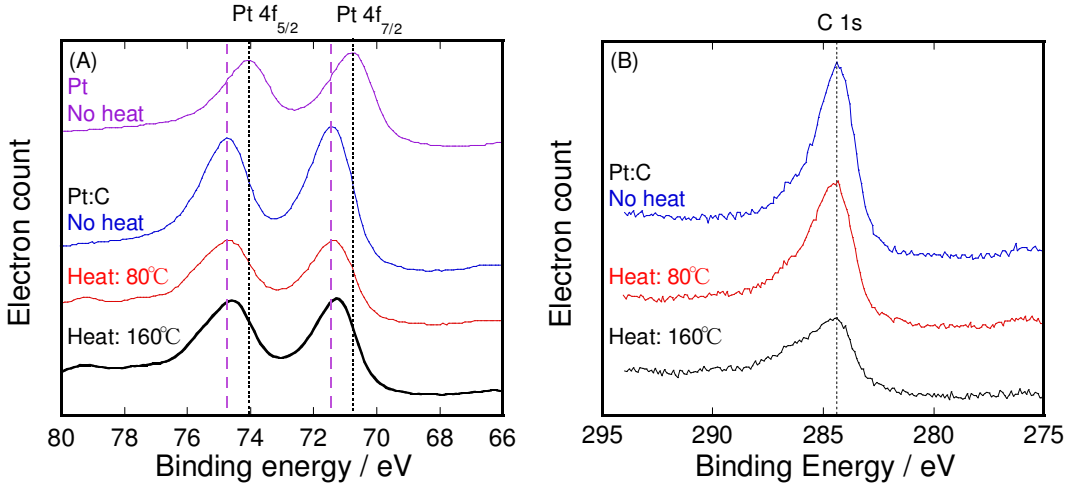

Figure 3 XPS spectra of sputtered Pt and Pt-C electrodes with and without post annealing at 80 and 160°C, (A) is Pt 4f and (B) is C 1s. Tthe dotted line and dashed line denote the peak position of Pt 4f or 1C and the Pt-C before the annealing, respectively.

Thermal effect of O_2-enhanced MOR activity at Pt-Ru-C electrode

Next, the effect of Ru addition to the Pt-Ru-C electrode was investigated. The results of the electrochemical measurements are shown in Figure 4. By comparing Figure 4 with Figure 1(A), the MOR onset potential of Pt-Ru-C (0.3 V vs. NHE) shifts toward the cathodic direction by the addition of Ru. In Figure 4, the O_2-enhanced MOR is also observed for the Pt-Ru-C electrode. Curve (a) in the O_2-saturated atmosphere is higher than curve (b) in the N_2-saturated 1 mol dm^{-3} methanol and 0.5 mol dm^{-3} H_2SO_4.

Similar to the Pt-C electrode, the effect of heat treatment on the Pt-Ru-C electrode was investigated. Figure 5 shows each current density for the methanol oxidation in O_2 and N_2 atmospheres at 0.6 V vs. NHE and the ratio of the current density ($i(O_2)/i(N_2)$). If the ratio is higher than 1, it is suggested to possess an O_2-enhanced MOR activity. This ratio decreases with the increasing post-annealed temperature. Finally, the O_2-enhanced MOR activity almost disappears at greater than 120°C. The effect of the O_2-enhanced MOR is assumed to be the same mechanism as that of the Pt-C electrode. Therefore, when we make an MEA incorporating the sputtered Pt-Ru-C, a hot-press treatment should be performed at a temperature lower than 100°C.

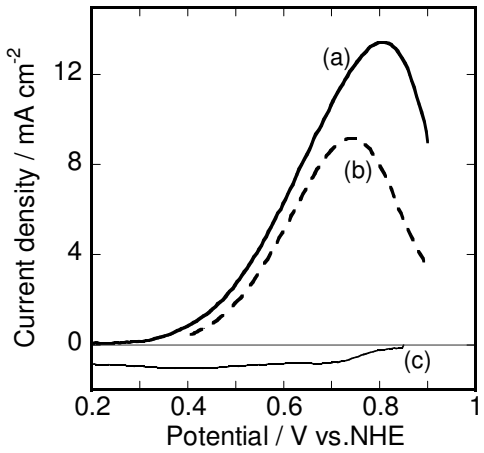

Figure 4 Voltammograms of methanol oxidation and oxygen reduction at the sputtered Pt-Ru-C electrode in (a) O_2-saturated 1 mol dm^{-3} methanol + 0.5 mol dm^{-3} H_2SO_4, (b) N_2-saturated 1 mol dm^{-3} methanol + 0.5 mol dm^{-3} H_2SO_4, and (c) 0.5 mol dm^{-3} H_2SO_4. The sweep rate is 10 mV s^{-1}.

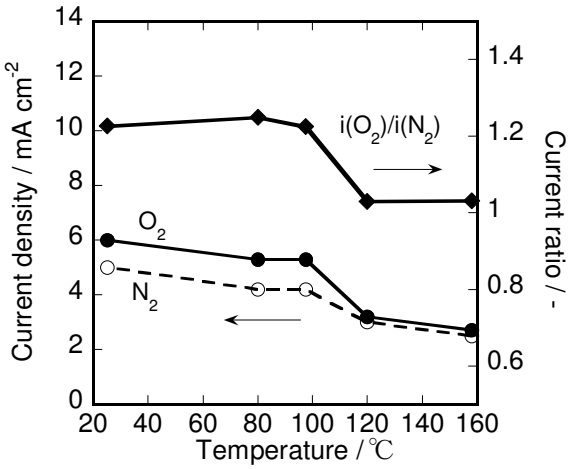

Figure 5 Annealing temperature dependence of the MOR current at 0.6 V vs. RHE in O_2- and Ar-saturated solutions, and the MOR current ratio. The electrochemical measurements were carried out at 25°C.

DMFC cell performance equipped with Pt-Ru-C electrocatalyst

The Pt-Ru-C was sputtered on carbon paper, and used as the anode of a DMFC by a hot-pressing procedure conducted at 100°C. Figure 6 shows the linear sweep voltammograms measured at the Pt-Ru-C in a single DMFC cell. During the measurement, H_2 gas was fed to the counter electrode. The MOR current measured by feeding O_2-saturated methanol exceeded that measured by feeding Ar-saturated methanol. The O_2-enhanced MOR mechanism is considered to be the same as that of Pt-C.

In Figure 7, the DMFC power generation performance measured by supplying O_2 gas to the cathode is shown. A higher power generation is observed when the O_2-saturated methanol is fed to the anode. Consequently, the O_2-enhanced MOR is clearly observed at the Pt-Ru-C of the single DMFC cell, which can be preferentially used as the MRFC anode.

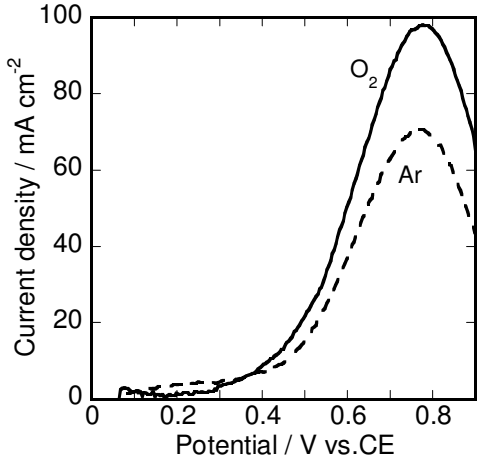

Figure 6 Current-potential curves of methanol oxidation at Pt-Ru-C electrode of an MEA installed in a DMFC single cell. Measurements were carried out at 60°C by feeding O_2- and Ar-saturated 1 mol dm^{-3} methanol solution to the anode and humidified H_2 gas to the counter electrode. Sweep rate is 50 mV s^{-1}.

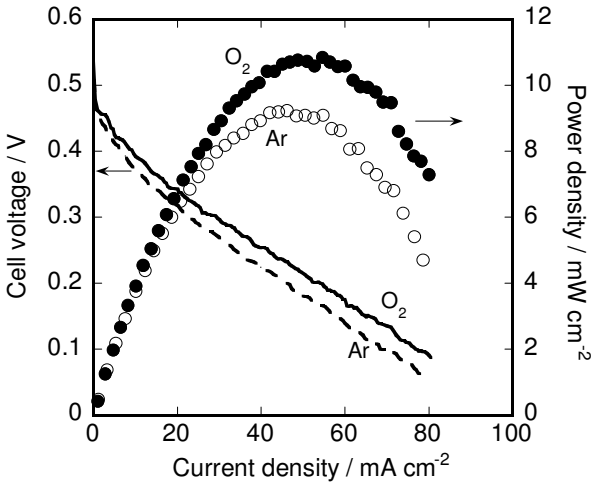

Figure 7 Current-voltage characteristics of a DMFC single cell incorporating an MEA which has a sputtered Pt-Ru-C anode catalyst layer. Symbols denote the cell voltage and power density. Measurements were carried out at 60°C by feeding O_2- and Ar-saturated 1 mol dm^{-3} methanol solution to the anode and humidified O_2 gas to the cathode.

Conclusions

We successfully prepared useful Pt-C and Pt-Ru-C electrodes using a multi-target sputtering system for the DMFC anode. The obtained electrodes possess an O_2-enhanced methanol performance and a reaction selectivity for the methanol oxidation under an O_2 atmosphere. It is confirmed that the O_2-enhanced methanol oxidation effect remains up to a 100°C heat treatment. Therefore, the single DMFC cell incorporated the 100°C hot-pressed MEA containing the Pt-Ru-C electrode. Finally, the O_2-enhanced methanol oxidation activity is clearly observed at the Pt-Ru-C of the single DMFC cell. The presented Pt-Ru-C electrode can be used as an efficient DMFC anode by feeding the methanol and O_2 mixture.

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