Short communication

Electrode/matrix interfacial characteristics in a phosphoric acid fuel cell

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1. Introduction

Among the several types of fuel cells, the phosphoric acid fuel cell (PAFC) has been developed most widely due to its commercial viability. PAFC has problems regarding high cathodic overpotential resulting from the slow oxygen reduction rate and rapid degradation of cell performance after long operating times [1].

In this work three different types of electrode/matrix interfaces in a PAFC, produced by the direct tape-casting of a matrix based on SiC whisker on an anode, a cathode, or both electrodes, were investigated with regard to their influence on electrical properties. A desirable form of the cell is discussed in conjunction with microstructural characteristics and impedance evaluation at the interface between the electrolyte and electrode.

2. Experimental details

A highly porous matrix based on a commercial SiC whisker (TWS-100, Tokai whisker Co.) and PES (polyethersulfone) as a binder was produced on the Pt–C electrode by the tape-casting method described previously [2, 3]. Pt–C electrode sheets of thickness about 250 μm were prepared by a rolling method and heat treated at 350 °C for 30 min. The amount of platinum loaded on carbon paper was 1 mg cm^{-2}. A slurry for the porous matrix was prepared by mixing 75 wt% SiC whisker with organic materials such as 15 wt% polyester sulfone (PES as a binder), 7.5 wt% triphenyl phosphate (TPP as a plasticizer), and 2.5 wt% Span 80 (sorbitan monooleate as a surfactant). Span 80 was first dissolved in dichloromethane (as solvent), followed by adding the SiC whisker to form a slurry. A solution of PES and TPP in dichloromethane was separately prepared by an ultrasonic agitation method. The solution was then mixed with the SiC slurry. Mixed slurry was cast directly on the Pt–C porous electrode. The dried thickness of the matrix on the electrode was 250 to 300 μm. Heat treatment was performed in two steps; first at 220 °C for 30 min to eliminate the solvent and then at 300 °C for 30 min to aid integration of the binder into the matrix. The heating rate was 100 °C h^{-1}.

Three different types (denoted OC, HC and DC) of the single cells were produced as follows. In the case of OC, the matrix was cast on the cathode (oxygen electrode). HC corresponds to the single cell containing the matrix that was cast on the anode (hydrogen electrode). In the third type labelled as DC, the matrices were cast on both electrodes. The matrices on electrodes (OC, HC and DC) were immersed in a liquid electrolyte (phosphoric acid) and constructed into a single stack with bipolar plates. Bipolar plates having a ribbed structure on one side distributed the reactant gases to the individual electrodes and also served as current collector. Pure hydrogen and oxygen were used as fuel and oxidant, respectively. Current–voltage characteristics of the PAFC single cell were measured at 170 °C under atmospheric pressure using a multimeter (HP 34401A) and an a.c. amperemeter (Keithley 177 DMM). To evaluate the relative electrochemical reaction area (three phase contact region), the adsorption charge of hydrogen on Pt was obtained using cyclic voltammetry. The effective Pt surface area can be estimated through the charge needed for monolayer coverage of its surface by hydrogen adsorption.

For simplicity, Pt is assumed to have the same crystal index plane and its surface to consist of the (1 0 0) plane. The charge of a hydrogen monolayer adsorbed on the (1 0 0) planes of Pt is 210 mC cm^{-2} [4]. The area of the three phase contact region obtained from the modified cyclic voltammetry was expressed as the roughness factor. The roughness factor is the ratio of the electrochemical reaction area to the apparent area of an electrode [5]. The single fuel cell was further characterized by a.c. impedance spectroscopy in the frequency range from 10^{-3} Hz to 100 kHz. The set-up for the a.c. impedance measurement included a potentio/galvanostat (model 273, EG&G) and a frequency analyser (Schlumberger 1255 HF).

3. Results and discussion

The different microstructures (region 1 and region 2) of the tape-cast matrices are shown in Figure 1. The
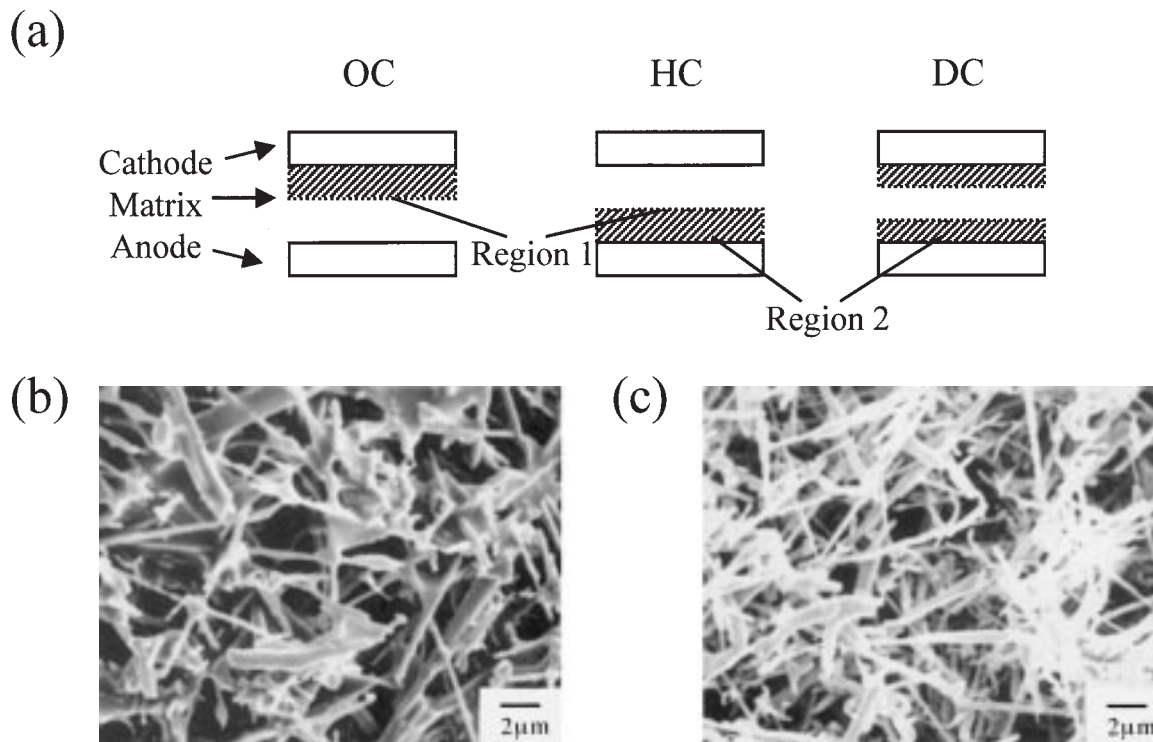
(a)

(b)

(c)

Fig. 1. (a) Schematics of three different cell structures, OC, HC, and DC, and (b, c) SEM photographs of the SiC matrix; (b) region 1 and (c) region 2 of the matrix of Figure 1(a) (Note that the region 2 represents a dense region adhering to the electrode).

region 1 represents the surface region of the matrix tape-cast on the electrode. The region 2 indicates an interface area between the tape-cast matrix and the electrode. The region 2 corresponding to Figure 1(c) shows a denser microstructure of the SiC whisker matrix compared to the region 1 of Figure 1(b). This is a reasonable observation due to the whisker particles accumulated easily during the tape-casting process on the electrode surface. Therefore, region 2 has a smaller cross-sectional area of the electrolyte near the electrodes than that of region 1. However, region 2 is expected to have a larger three phase contact region due to better adherence to the electrode surface. Consequently, in the case of OC, the cathode adheres to region 2 while the anode adheres to region 1 when a single cell is completed. However, both electrodes of the DC will contact with region 2 (see Figure 1(a)).

Figure 2 shows the cyclic voltammograms of regions 1 and 2. Region 2 exhibited a larger roughness factor (3985) than that of region 1 (2780). Such quantitative comparison shows that region 2 has a larger three phase contact area.

Figure 3 shows the I/V characteristics of the three different types OC, HC and DC. A voltage of ~0.9 V was found for the open circuit voltage (OCV) regardless of the cell type. The current tended to increase with decreasing potential below the OCV. Table 1 summarizes the results of electrical measurements for the three types. Different current densities at operating potentials were obtained according to the cell type. This indicates that the different interface characteristics

influenced the I/V behaviour. OC exhibited the highest current density of 503 mA cm^{-2} at 0.7 V, desirable for this application.

Figure 4 shows the plots of the impedance spectra measured at two potentials of 0.9 V (near the open circuit potential) and 0.7 V (near the operating potential) for each cell type. The first intercept of each plot (at high frequencies) on the real resistance axis refers to the electrolyte resistance (R_e) known to depend on the amount of phosphoric acid [6]. The second intercept (at low frequencies) indicates the sum of R_e and two
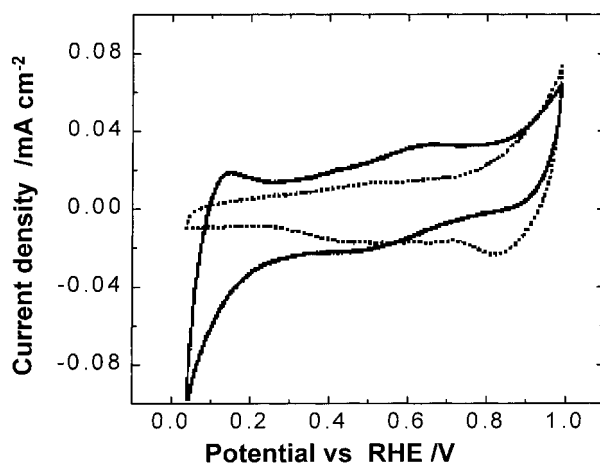

Fig. 2. Cyclic voltammograms of the interfaces between the matrix and the electrode (Note that roughness factors of the region 2 and the region 1 were 3985 and 2780, respectively). Key: (———) region 1; (- - - - -) region 2.
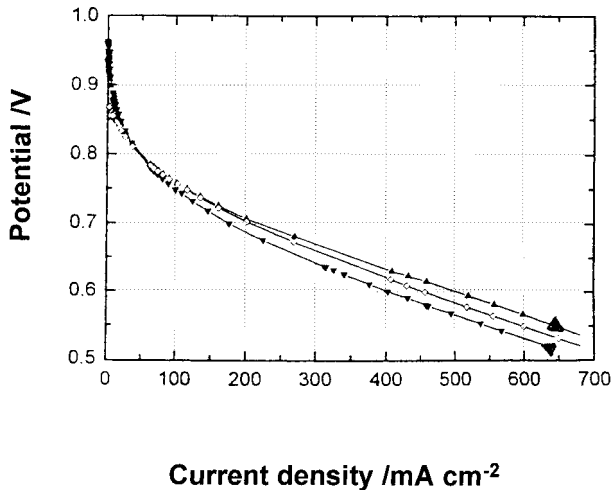
Fig. 3. Characteristics of the three different cell types: (-▲-) OC, (-▼-) HC and (-◇-) DC.

polarization resistances at the anode ($R_{P,a}$) and cathode ($R_{P,c}$) interfaces. In addition, the double layer capacitance, C_{dl}, corresponding to an electrochemically active area was evaluated using the impedance spectra. By assuming that only the cathodic double layer capacitance was dominant, C_{dl} was calculated from the resonance frequency and the cathode polarization resistance from the equation [7, 8]

$$C_{dl} = 1/(2pf_{max}R_{P,c}) \tag{1}$$

where f_{max} is the frequency of the maximum point of a semicircle, the resonance frequency. Detailed descriptions of the impedance spectra can be found in previous work [3]. On the one hand, the values obtained from the impedance plots are given in Table 1. R_e was found not to be influenced by the single cell type because it depended only on the amount of electrolyte (Table 1). On the other hand, the polarization resistance (R_p) depended on the single cell types. In this study, OC

Table 1. Results of electrical measurements for three different cell types

| Cell type	OC	HC	DC
Matrix thickness/μm	265	260	320
Current density/mA cm^{-2}			
at 0.7 V	220	178	209
at 0.6 V	503	404	461
Electrolyte resistance/Ω cm^2			
at 0.9 V	0.25	0.28	0.27
at 0.7 V	0.23	0.25	0.25
Anodic polarization resistance/Ω cm^2			
at 0.9 V	0.10	0.87	0.15
at 0.7 V	3.26×10^{-2}	17.69×10^{-2}	6.10×10^{-2}
Cathodic polarization resistance/Ω cm^2			
at 0.9 V	4.23	13.26	9.69
at 0.7 V	0.11	0.47	0.27
Double layer capacitance /mF cm^{-2}	202	131	173
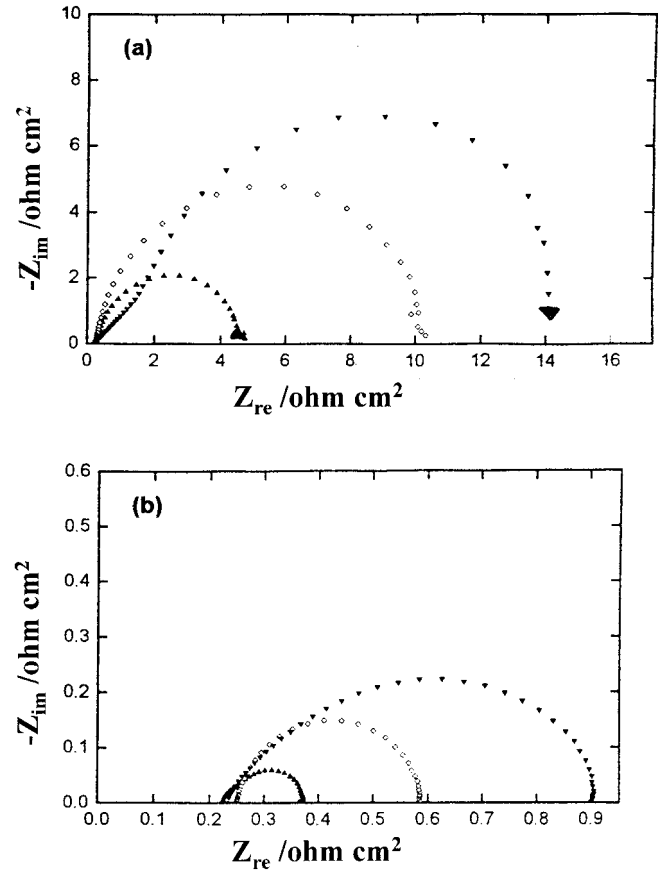
Fig. 4. Impedance spectra of the three different cell types measured at (a) 0.9 V and (b) 0.7 V. Key: (▲) OC, (◇) DC and (▼) DC.

showed the smallest cathodic and anodic polarization resistance compared to those of HC and DC. The largest three phase contact region from region 2 resulted in the smallest cathodic polarization resistance. This observation was confirmed by the C_{dl} values in Table 1. However, the smallest anodic polarization resistance in OC can be attributed to the high mobility of H$^+$ generated by the anodic reaction (H$_2 \rightarrow$ 2H$^+$ + 2e$^-$) not to the three phase contact region. This high mobility of H$^+$ is thought to be mainly due to the high absorbency of the phosphoric acid in the porous region 1. It is reasonable to conclude that the HC type (the opposite case of OC) showed the highest resistance values as shown in Table 1. HC is believed to have the smallest three phase contact region at the cathode and small acid absorbency near the anode.

Acknowledgement

References

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