Dissolution and migration of platinum after long-term operation of a polymer electrolyte fuel cell under various conditions

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ABSTRACT

The distribution patterns of Pt crystals that have moved from electrodes to the membrane phase of membrane electrode assembly (MEA) are monitored using transmission electron microscopy (TEM) after long-term operation (>1000 h) of a polymer electrolyte membrane fuel cell (PEMFC) at various operating and feed conditions. The dissolution of cathode Pt and subsequent migration to the membrane is readily observed when residual oxygen concentrations inside the cathode are kept high under low current density conditions. Dissolution of anodic Pt can also be observed under constant-current operation when hydrogen feed is kept low to induce a hydrogen shortage on the Pt surface. It is postulated that the Pt at the both electrodes is dissolved by chemical oxidation to PtO in the presence of residual oxygen. The Pt ions that are dissolved in water migrate to the membrane phase and undergo repeated oxidation/dissolution and reduction/deposition by crossover of oxygen and hydrogen, respectively. As a result, the distribution patterns and crystal sizes of the migrated Pt are strongly dependent on the relative concentrations of the crossover oxygen and hydrogen. The final position of the deposited Pt band is located at the point where crossover oxygen becomes depleted, typically between 1 and 10 μm from the cathode–membrane interface. Higher concentrations of oxygen and hydrogen in the membrane yield sharper and narrower Pt bands with large Pt aggregates, whereas lower concentrations yield wider distribution bands with smaller Pt crystals.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) has attracted much attention since its first development by General Electric in the 1960s. In order to make commercialization of PEMFCs feasible, extensive research has focused on improving the system performance by changing either the catalyst, the electrode or the stack design. Cell durability is an additional important issue, particularly within automobiles due to the harsh environment therein. Accordingly, there has been increased focus on the study of cell degradation phenomena. Nevertheless, cell deterioration phenomena are still not fully understood due in part to the difficulty of *in situ* analysis of the membrane electrode assembly (MEA) structure. Based on the present data, MEA degradation may result from: (i) activity loss of the electrocatalyst; (ii) carbon corrosion; or (iii) degradation of the polymer electrolyte membrane and ionomer in the catalyst layer by the formation of hydrogen peroxide and the generation of heat [1–10]. Among these, activity loss of the electrocatalyst is believed to be the most significant. It is well known that the particle size of the Pt electrode catalyst increases during PEMFC operation. This is claimed to occur either by Ostwald ripening or by crystallite migration [1,5,11]. This process has been shown to cause subsequent loss of catalyst activity [1,5,7].

Recently, Pt dissolution phenomena have become an area of interest, as they are directly related to a gradual loss of electrode catalyst during a long-term operation. In order to investigate Pt dissolution in Pt/C electrodes, researchers have employed a method of potential cycling, or potential holding at a high potential to observe rapid Pt dissolution over a short time interval [12,13]. A Pt/C electrode immersed in perchloric acid electrolyte gave the highest measured dissolution rate at a high potential of 1.1 V [14]. Further, Akita et al. [15] reported transmission electron microscopy (TEM) images and electron diffraction (EDS) patterns of deposited Pt in the membrane phase after 86 h of accelerated testing at a constant voltage of 1.0 V [15].

During PEMFC operation, the Pb cathode in a MEA is gradually dissolved and migrates into the membrane phase where it is chemically reduced by crossover hydrogen from the anode [5,13,15]. Yasuda et al. [13] and Akita et al. [15] have shown that the deposition position of the reduced Pt in the membrane is affected by the gas compositions at both the anode and cathode. To date, Pt dissolution during PEMFC operation has been observed in the cathode,

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except by Xie et al. [3] who found anodic Pt dissolution after 1000 h of operation using a MEA with Pt/C at the anode and Pt$_3$Cr/C at the cathode [3].

Despite increasing efforts in this area, little is known about the cause and mechanism of Pt dissolution in the electrodes and the migration to the membrane phase. This is due in large part to the lengthy testing periods required and the difficulty in observing Pt dissolution and deposition *in situ* during the cell operation. The work presented herein seeks to elucidate further the mechanism of Pt dissolution in the electrodes and deposition in the membrane phase. To this end, a study is made of membrane deposition of Pt from the cathode and anode of a MEA during long-term operation of a PEMFC at various feed and cell operating conditions.

2. Experimental

2.1. Activation of commercial MEA

A single-cell system was employed with a commercial MEA (Gore, 25 cm^2 surface area at both electrodes). The catalyst loading was 0.4 mg Pt cm^{-2} in both the anode and the cathode (15 μm thickness for each electrode). The thickness of the Nafion membrane was 25 μm with a Teflon band incorporated at the centre. An in-house test station using a dc electronic load (DAE GIL Co., Ltd. EL-1000P) was employed for PEMFC operation. Before long-term operation, all the cells were operated for 8 h at a constant voltage (0.4 V) to activate the fresh MEA.

2.2. Long-term operation of activated MEAs

Cell operation was carried out with inlet gases humidified at 70 °C under either open-circuit voltage (OCV) or constant-current (80 mA cm^{-2} at about 0.7–0.8 V) conditions. Pure hydrogen gas was fed to the anode side usually at a 200% excess amount (stoichiometric ratio (SR) = 3), except in the case of lean hydrogen conditions. Either air or pure oxygen was fed to the cathode at a 300% excess (SR = 4), apart from one test under oxygen-rich conditions, in which pure oxygen (SR = 8) was employed. During the long-term operation, polarization curves were taken at regular intervals to investigate the degradation tendencies of the cell. The polarization curves should be taken restrictively, however, as the process could affect the cell performance. Table 1 summarizes the conditions of feed, operation and running period for five different operations.
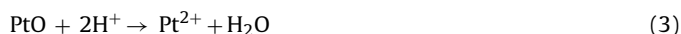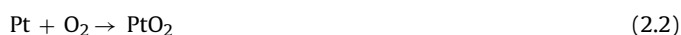
2.3. TEM–EDS analysis

After long-term operation, the MEA was removed from the cell housing and the carbon paper was eliminated from the both sides. Next, a small piece of the MEA was embedded in epoxy resin (Araldite 502 embedding kit, Luft's Formula, Polyscience Inc.), dried for 30 min, and cured at 60 °C for 12 h. This was followed by a sectioning process using an ultra-microtome with a diamond knife (DIATOME). The sliced sample (50–100 nm thickness) was posi-

tioned on a copper grid (150 meshed) for TEM (PHILIPS-CM200) analysis. Micro-scale morphology and Pt concentration in the cross-section of the MEA was subsequently observed. The TEM was equipped with energy dispersive X-ray spectroscopy (EDS) for elemental analysis, which allowed measurement of the deposited Pt.

3. Results and discussion

3.1. Platinum dissolution at constant current

Fresh MEA was operated at a constant current of 80 mA cm^{-2} with excess feed gases (SR = 3 for hydrogen, and SR = 4 for air: operation #1). Cell decay was monitored by measuring polarization curves during 1784 h of operation. The Pt particle size grew rapidly from 1.5 to 3.5–4.0 nm during the initial operation period of within 380 h, after which time the Pt size remained constant. Thus, after 380 h of operation, the cell decay was deemed slow at a constant rate of about 25 mV per 1000 h. This was presumed to be caused by dissolution of Pt from the electrode. At the end of the long-term operation period, the cross-sectional area in a sliced portion of the MEA was monitored with TEM. Fig. 1(a) shows the cross-section of the cathode (dark coloured) and the membrane phase (Nafion and Teflon), and Fig. 1(b) shows that of the anode (dark coloured) and the membrane phase. Platinum dissolution appears to occur only at the cathode side as deposited Pt can be seen in the membrane phase. Long-term operation for 1780 h allows for deposition of migrated Pt ions at approximately 1 μm from the cathode–membrane interface. After this point, a widespread Pt band is formed at the centre of Teflon phase. The Pt particle size in the deposited Pt band decreases gradually with distance from the cathode. From these results, it is concluded that several processes are taking place in the membrane phase: (i) reduction of migrated Pt ions by crossover hydrogen from the anode; (ii) re-oxidation of the deposited Pt by crossover oxygen from the cathode; (iii) re-dissolution of the formed PtO. These are expressed as follows.

$$Pt^{2+} + H_2 \rightarrow Pt + 2H^+ \tag{1}$$

$$Pt + \frac{1}{2}O_2 \rightarrow PtO \tag{2.1}$$

$$Pt + O_2 \rightarrow PtO_2 \tag{2.2}$$

$$PtO + 2H^+ \rightarrow Pt^{2+} + H_2O \tag{3}$$

Magnified TEM images (Fig. 1(c) and (d)) indicate that the deposited Pt particles have the same crystal shape as those of Akita et al. [15], which suggests that the Pt ions grow as a single crystal during the repeated process of reduction and oxidative dissolution. Many researchers have reported observing the electrochemical dissolution of Pt by employing potential cycling or potential holding at high potentials [12–17]. This can occur in the anodic current region if the potential is above 1.15 V, as shown in the following equations:

$$Pt \rightarrow Pt^{2+} + 2e^- \quad 1.188 \text{ V vs. SHE} \tag{4}$$

$$Pt \rightarrow Pt^{4+} + 4e^- \quad 1.15 \text{ V vs. SHE} \tag{5}$$

Table 1
Operation conditions of each MEA

Operation #	Stoichiometric ratio of H$_2$ and O$_2$ feed (80 mA cm^{-2} basis)		Operating condition	Operation time (h)
	H$_2$	O$_2$ (air)		
1	3	4 (air)	80 mA cm^{-2} (constant current)	1784
2	3	4 (air)	0A (OCV)	1484
3	3	8 (O$_2$)	80 mA cm^{-2} (constant current)	1384
4	3 (initial)/1.5 (additional)	4 (air, initial)/4 (O$_2$, additional)	80 mA cm^{-2} (constant current)	320 (initial)/187 (additional)
5	1.35	4 (air)	80 mA cm^{-2} (constant current)	333

It has also been observed that water in humidified nitrogen could react with Pt to form PtO (or PtO_2) when the anodic current displayed with a potential increase from 0 to 1.5 V (Eq. (6)) [16–18].

$$Pt + H_2O \rightarrow PtO + 2H^+ + 2e^- \quad 0.98\,V\ vs.\ SHE \tag{6}$$
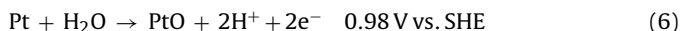
However, PEMFC operated with a dc electronic load must be different from potential cycling using a potentiostat. In our cell operation with a dc electronic load, the constant current ($80\,mA\,cm^{-2}$) was adopted at potentials in the range between 0.7 and 0.8 V, that is, significantly lower than the potentials required for anodic Pt dissolution, Eqs. (4)–(6). Since platinum dissolution is observed only at the cathode (under a reduction current) during long-term cell operation, we must consider the possibility of electrochemical dissolution of Pt at this side. Therefore, we postulate

that in order for the cathode Pt to be dissolved during the PEMFC operation, it must be chemically oxidized after adsorbing oxygen dissolved in the water or present in the air feed (Eqs. (2.1) or (2.2)). The oxidized Pt may be dissolved electrochemically at the cathode by Eq. (7) [16–18], i.e.,

$$PtO_2 + 4H^+ + 2e^- \rightarrow Pt^{2+} + 2H_2O \quad 0.837\,V\ vs.\ SHE \tag{7}$$
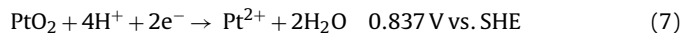
The 0.837 V reaction potential is higher than our cell operation voltage of 0.7–0.8 V. Thus, the oxidized PtO (or PtO_2) may be dissolved chemically in the presence of water at the cathode.
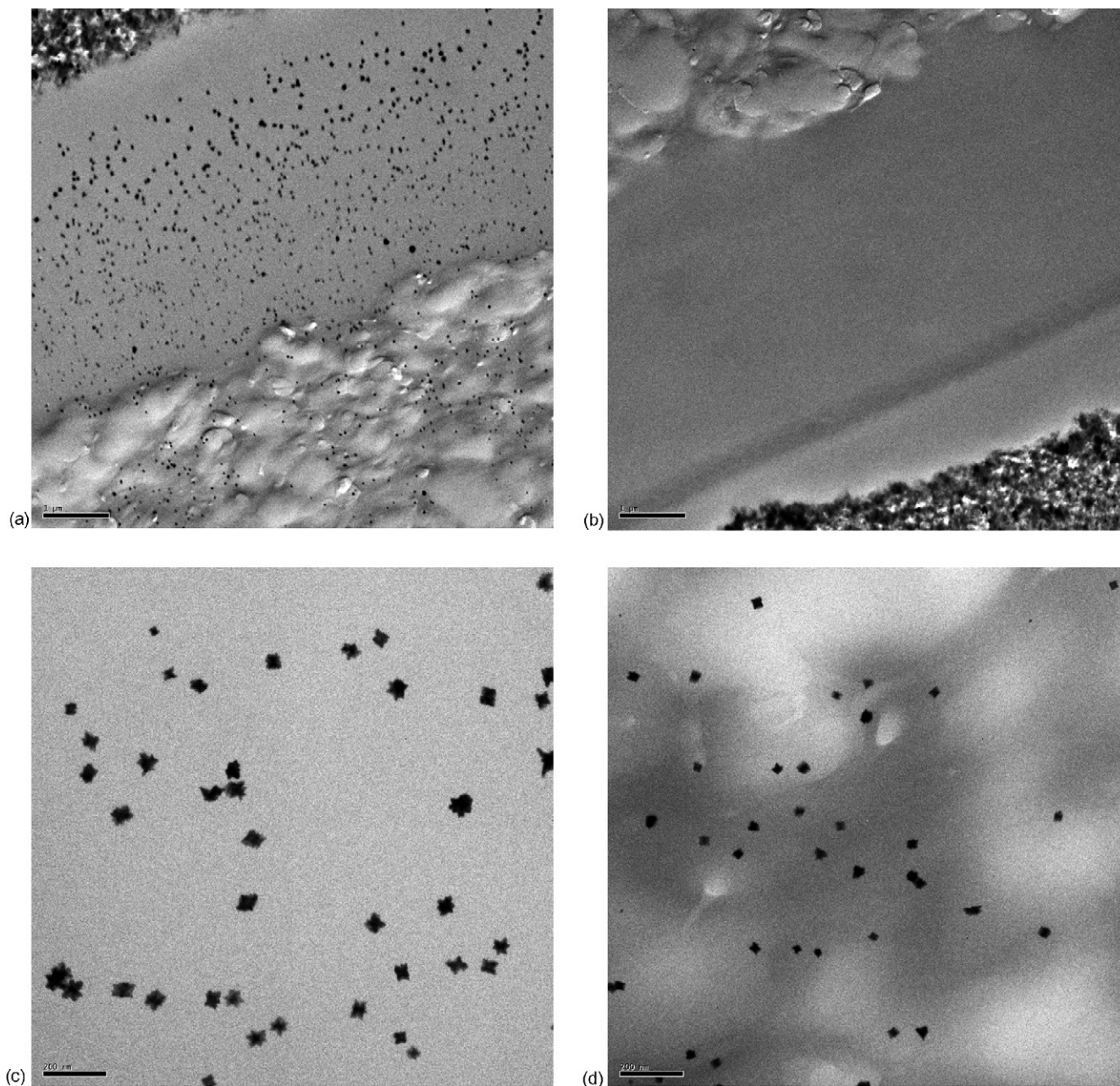
$$PtO_2 + 4H^+ \rightarrow Pt^{4+} + 2H_2O \tag{8.1}$$

$$PtO + 2H^+ \rightarrow Pt^{2+} + H_2O \tag{8.2}$$

Fig. 1. TEM images of a cross-section of MEA after operation at $80\,mA\,cm^{-2}$ under constant-current conditions with air: (a) between cathode interface and membrane; (b) between anode interface and membrane; (c) (magnified image) in membrane near cathode interface; (d) (magnified image) in PTFE layer.

Platinum dissolution by chemical processes such as those described above had been observed experimentally under acidic conditions [16,19,20].

3.2. Platinum dissolution under OCV condition

In order to verify the above hypothesis, cell operation was carried out under OCV for 1500 h. Feed conditions were kept the same as previously described (SR = 3 for hydrogen, and SR = 4 for air, based on 80 mA cm^{-2} current consumption: operation #2). TEM images of the cross-sectional MEA after the long-term operation are shown in Fig. 2(a)–(c). Fig. 2(a) indicates that large particles of Pt aggregates (50–190 nm) are formed with a sharp band (0.5 μm in thickness) located at 2.3 μm from the cathode. The Pt aggregates are not only large in size, but nearly all are linked together continuously. Simi-

larly, Ferreira et al. [5] detected the formation of a deposited Pt band in the membrane phase along the cathode interface by SEM analysis after 2000 h at OCV. Compared with constant-current operation (operation #1), the amount of dissolved Pt is significantly greater after the OCV operation, in accord with the observation that cell degradation is accelerated under the latter condition [4,21]. During our long-term operation, the cell degradation rate at OCV is 50 mV for 1000 h, which is twice that found with constant-current operation.

The Pt aggregates in the membrane phase were investigated by EDS analysis to ascertain their composition. The results in Table 2 document compositions of the Pt aggregates shown in Fig. 2(c). Apart from Pt, carbon, fluorine and a small amount of potassium impurities are detected. These elements are likely decomposition products of the membrane phase promoted by the presence of a
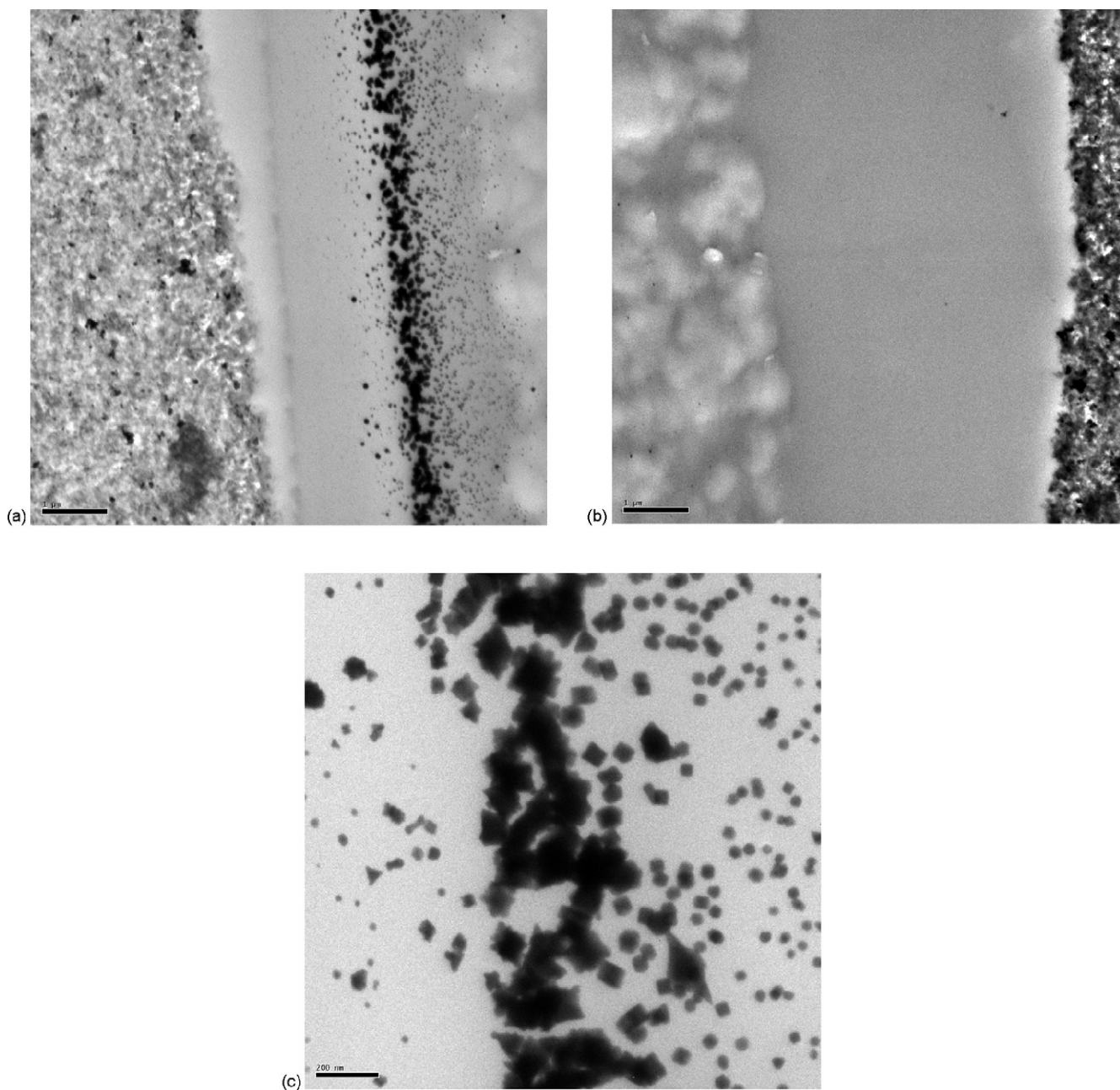

Fig. 2. TEM images of cross-section of MEA after operation under OCV conditions: (a) between cathode interface and membrane; (b) between anode interface and membrane; (c) magnified image of Pt band.

Table 2
EDS analysis of Pt aggregates in membrane phase after OCV operation

Element	Weight%
C	9.81
F	8.45
K	0.86
Cu	36.11
Pt	44.77
Total	100.00

Pt catalyst and a high concentration of crossover oxygen from the cathode during OCV operation [22].

Under OCV conditions, the exchange current is too small to dissolve appreciable quantities of cathode Pt, even though the cell voltage is sufficiently high. It is thus clear that the cathode Pt is likely oxidized to PtO (or PtO$_2$) through the adsorption of oxygen (Eqs. (2.1) and (2.2)), which must be followed by chemical dissolution in the acidic aqueous solution (Eqs. (8.1) and (8.2)). The oxidation of Pt can be accelerated by the absence of the cathode reduction current, which would prohibit the chemical oxidation of Pt. In comparison with the constant-current operation (operation #1), in which Pt begins to be widely deposited 1.0 μm from the cathode end, the deposited Pt band under the OCV operation is very sharp with a narrower width, located 2.3 μm from the cathode end. Without current generation, the feed of excess oxygen and hydrogen to the electrode channels must result in very high partial pressures of crossover oxygen and hydrogen in the membrane phase. Thus, a strong oxidizing force by the oxygen and subsequent dissolution of oxidized PtO will push the deposited Pt farther from the cathode, which can be halted by the strong reduction force of the Pt ion (or PtO) by crossover hydrogen from anode. The concentration of the crossover hydrogen from the anode is higher than that of the crossover oxygen from the cathode, due to a higher
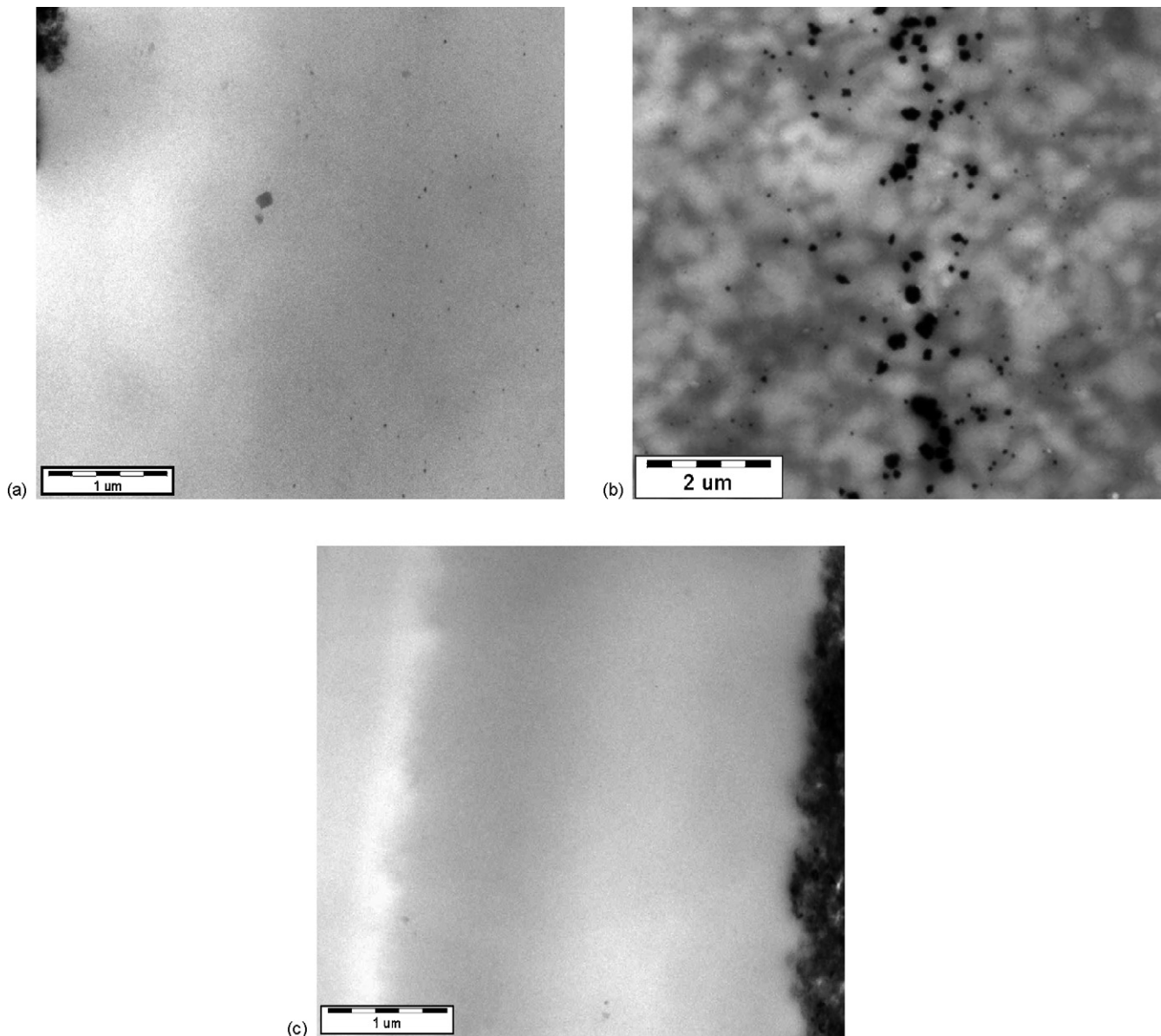

Fig. 3. TEM images of cross-section of MEA after operation at 80 mA cm^{-2} under constant-current conditions with pure oxygen: (a) between cathode interface and membrane; (b) in TPFE layer; (c) between anode interface and membrane.
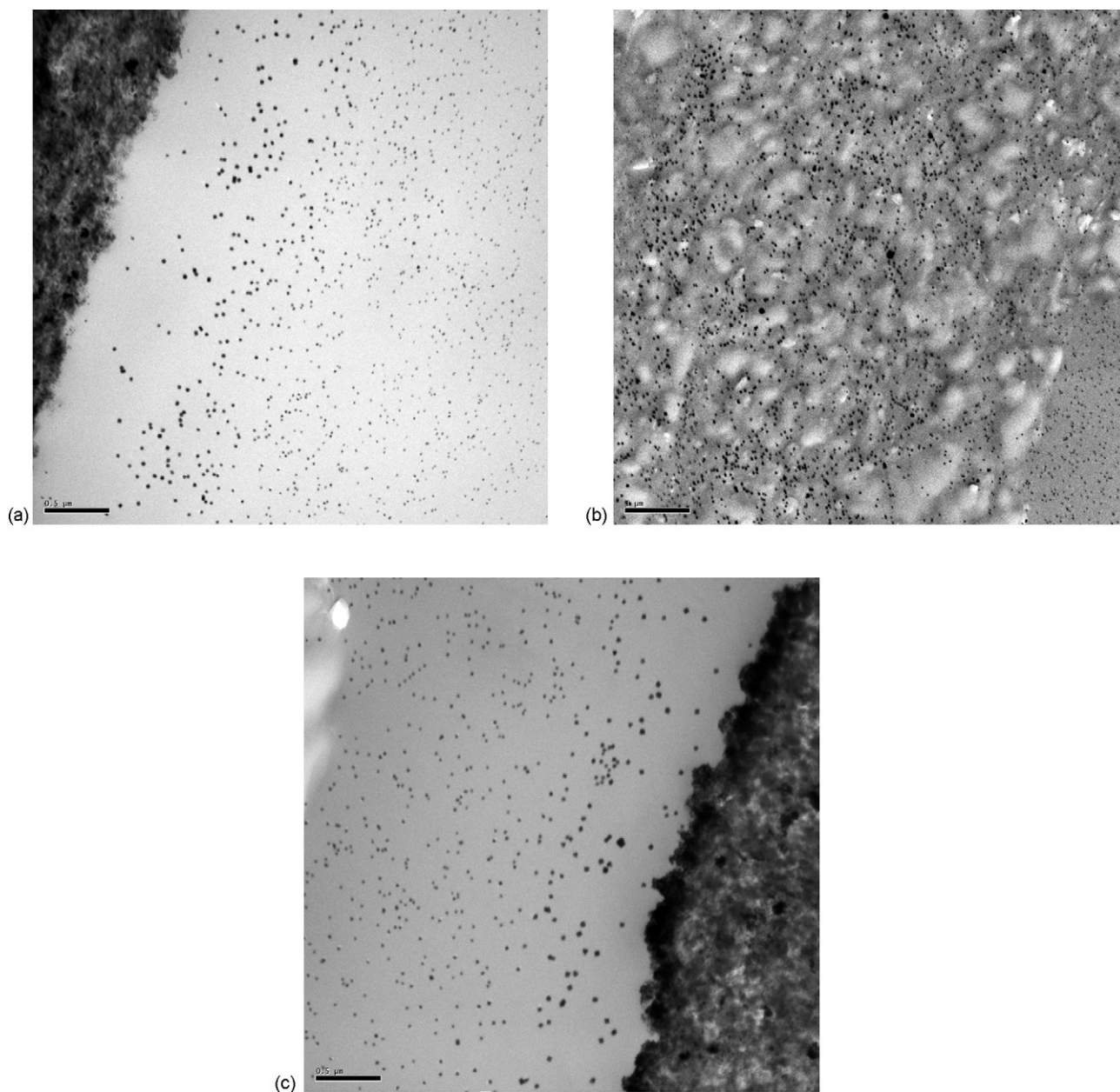
Fig. 4. TEM images of cross-section of MEA after operation at 80 mA cm^{-2} under constant-current conditions (with air for first 320 h and with oxygen for additional 170 h): (a) between cathode interface and membrane; (b) in PTFE layer; (c) between anode interface and membrane.

diffusivity and pure feed of hydrogen. Therefore, the concentration of crossover oxygen drops sharply at the location of the deposited Pt band where reaction of oxygen with excess hydrogen is promoted on the Pt surface, stopping migration of the band beyond a distance of 2.3 μm. Repeated reactions of dissolution and deposition at the 2.3 μm location eventually lead to growth of the Pt particles.

3.3. Platinum dissolution under higher oxygen partial pressure conditions

To ascertain the chemical dissolution of the cathode Pt, pure oxygen was fed to increase the partial pressure of crossover oxygen. To this end, the cell was operated for 1384 h at 80 mA cm^{-2} constant-current with SR = 3 (200% excess stoichiometric value) for hydrogen and SR = 8 (700% excess) for the pure oxygen feed (operation #3). The pure oxygen feed alone increases the oxygen partial pressure

fourfold relative to the air feed. Together with the 700% excess feed, the concentration of the crossover oxygen in the membrane phase will be significantly higher than under OCV operation. Fig. 3 indicates that the deposited Pt forms a sharp, 1.6 μm thick band (also with a large particle size of 70–310 nm), which is similar to that found with OCV operation. As expected, the location of the Pt is moved 12 μm farther from cathode, and deposited in the Teflon phase due to the higher partial pressure of the crossover oxygen.

To confirm the postulated oxygen-induced dissolution mechanism, the cell was operated initially under the same conditions as operation #1 (SR = 3 for hydrogen and 4 for air) during first 320 h phase. This was followed by a second 187 h phase with hydrogen (SR = 1.5) and pure oxygen (SR = 4.0), both at reduced flow rates (operation #4). Fig. 4(a) indicates that the Pt distribution in the membrane phase near the cathode under these conditions is similar that of operation #1. The Pt particles are largest (20–50 nm) near

the cathode, and the size decreases gradually towards the membrane phase. In addition, another deposition band of Pt appears in the Teflon phase, located at the centre of the membrane phase. This is not shown in the case of the operation #1. The band is probably formed during the second 187 h phase of operation described above. During the second phase operation, the location of Pt deposition has moved to the anodic side, due to the increased concentration of the crossover oxygen and the decreased concentration of the crossover hydrogen. Thereby, the final confrontation front with negligible oxygen concentration is established at the centre of the membrane phase (Fig. 4(b)). In addition, some of the Pt deposited near the cathode side in the membrane during the first 320 h phase must also be dissolved away in order to move to the anode side. Surprisingly, Pt deposition is also observed near the anode side of the membrane phase (Fig. 4(c)). The deposited Pt has a similar particle-size distribution to Pt deposited near cathode side of the membrane (*vide supra*). The deposited Pt shown in Fig. 4(c) has not originated from the cathode Pt, but rather results from migration of Pt dissolved from the anode electrode.

3.4. Anode platinum dissolution under lean hydrogen conditions

There have been numerous observations of cathode Pt dissolution and migration to the membrane phase. By contrast, there exists only a single report of Pt dissolution at the anode. Xie et al. [3] indicated that by employing Pt_3Cr/C at the cathode and Pt/C at the anode, the anode Pt migrates to the anodic end near the membrane interface after 500 h of PEMFC operation. Next, after an additional 500 h, a smaller number of Pt particles migrate to the membrane phase, up to 3 μm from the anode end. This phenomenon was rationalized by electrochemical oxidation. Since the anode cell potential (0.06 V vs. SHE) is below the redox potential of Pt (~1.03 V vs. SHE at a pH of 0.6–1.4), the authors postulated that Pt nanoparticles, unlike Pt bulk, undergo a shift in reduction potential of more than −1.0 V to induce oxidation of Pt to Pt^{2+}. However, these results were obtained with cells operated at a constant current, with a high current density of 1.07 A cm^{-2}, which is significantly higher than our operating conditions of 0.08 A cm^{-2}. Although excess air and hydrogen were employed (SR = 6.2 for air, and 3.6 for hydrogen), this high current density might induce a supply shortage of both hydrogen and oxygen on the Pt surface due to mass transfer limitations at local points on the electrodes. Despite excess oxygen feed, migration of cathode Pt to the membrane phase is not detected in this study, providing indirect evidence for the shortage of these gases. Depletion of oxygen at the Pt surface, particularly in the proximity of the cathode and membrane interface, may prevent dissolution and migration of cathode Pt to the membrane phase.

To confirm further the anode Pt dissolution due to hydrogen shortage, the MEA was operated for 333 h at the same constant current as that of operation #1 (0.08 A cm^{-2}) and with the same
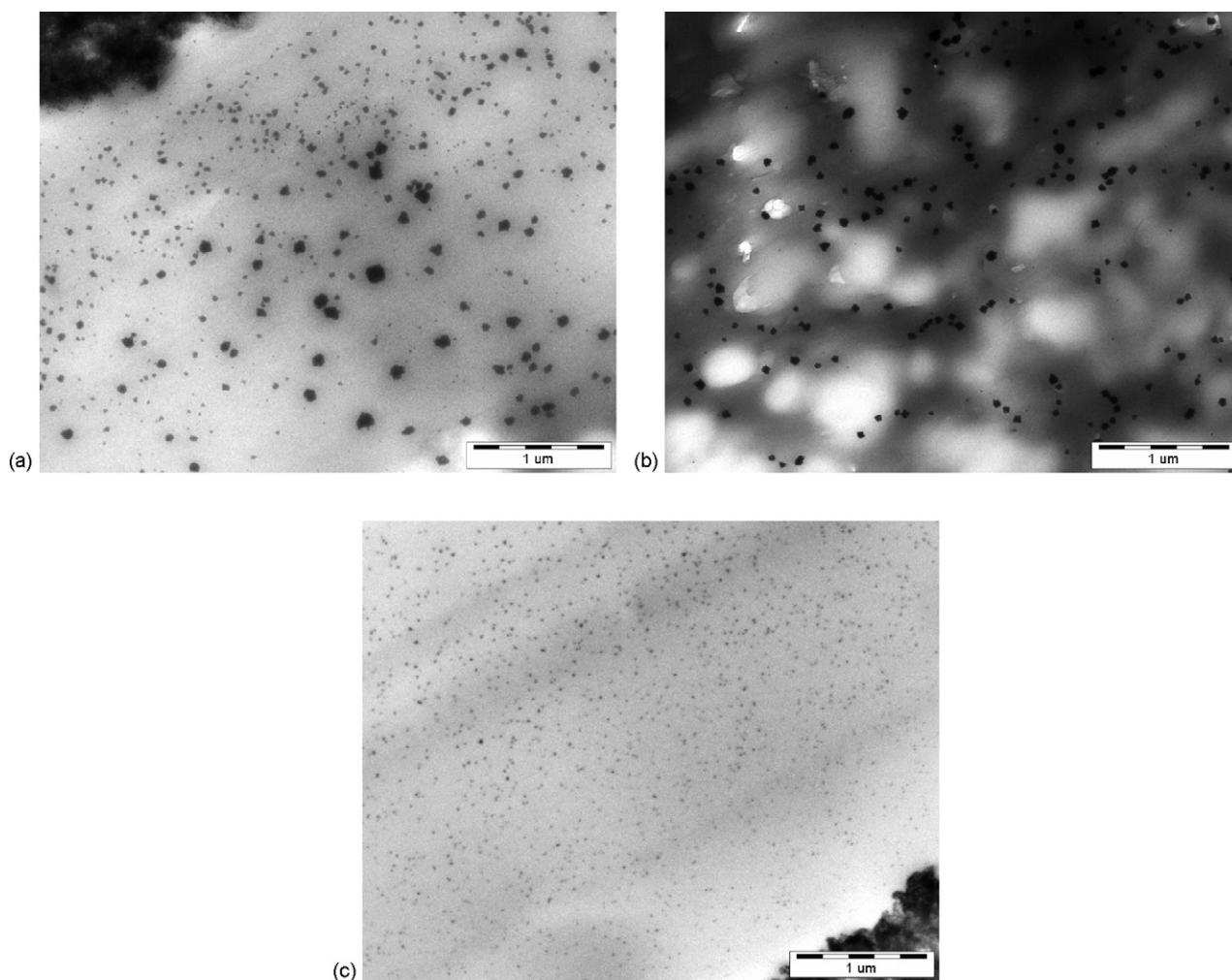

Fig. 5. TEM images of cross-section of MEA after operation at 80 mA cm^{-2} under constant-current conditions with 35% excess hydrogen: (a) between cathode interface and membrane; (b) in PTFE layer; (c) between anode interface and membrane.

air feed (SR = 4). However, a much leaner hydrogen feed was utilized (SR = 1.3). Under these conditions (operation #5), Pt is also well distributed in the full membrane region (Fig. 5(a)–(c)), and well-distributed Pt aggregates can be seen at anodic side of the membrane. Hence, it is proposed that Pt near the anode side of the membrane results from the present anodic Pt. When operating a PEMFC under constant current, a fuel shortage at the anode electrode means that an additional fuel supply is required to keep the current production at a constant level. At a localized Pt surface where a severe shortage of hydrogen is experienced, Pt may be oxidized electrochemically to produce protons and current, as indicated in Eq. (6). An alternative process would be to decompose water electrochemically to generate oxygen, H+, and current, i.e.,

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{9}$$

The produced oxygen may be involved in oxidizing Pt to PtO. From this point, oxidized PtO will be dissolved in the acidic solution to yield Pt^{2+} ions, which move towards the membrane phase due to an electro-osmotic water flux dragged by protons. Under either scenario, it is evident that the anode potential increases, and cell reversal should be observed [23]. Fig. 6 shows the cell voltage during the 333 h operation. The voltage is very unstable showing cell reversal in a short time interval, rather than a continuous pattern. At present, we cannot explain the exact mechanism of dissolution and migration of the anode Pt, and as such, this is an active area of research in our laboratory.

3.5. Effect of operating conditions on Pt distribution pattern

Fig. 7 summarizes the results of the effect of operating conditions on the Pt distribution pattern in the membrane phase. Crossover oxygen moves the Pt band in the membrane towards the anode, while hydrogen moves it towards the cathode. The final location of the Pt band is localized at the point where the crossover oxygen is depleted. Operation #1 (80 mA cm^{-2} constant current) displays a wider Pt band, that is formed close to the cathode side, because crossover oxygen and hydrogen are at relatively low concentrations. At the same feed condition as that of operation #1, but under OCV operation, higher concentrations of crossover oxygen and hydrogen lead to the formation of a narrower Pt band located farther from the cathode side. Operation #3 involves a pure oxygen feed, and at constant current of 80 mA cm^{-2}. Compared with operation #2, the Pt band has moved farther from the cathode due to increased crossover oxygen, and decreased crossover hydrogen. Operations #4 and #5 show Pt dissolution and migration from the anode at reduced feed rates of hydrogen (from 200% excess feed
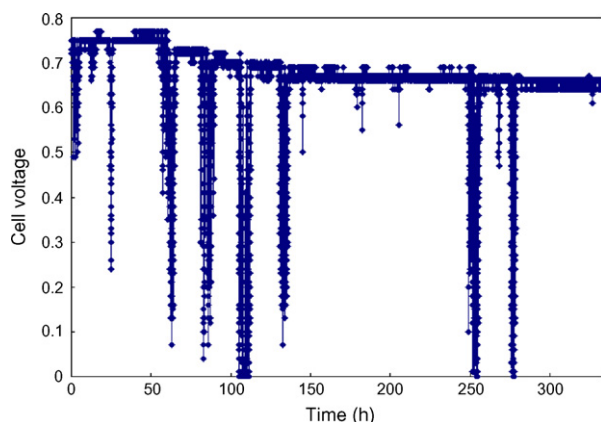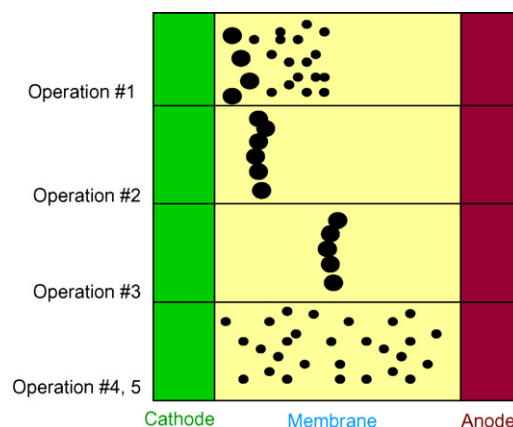

Fig. 7. Distribution patterns of Pt band in membrane phase under various operation conditions.

to 35–50% excess). The results indicate that crossover hydrogen to the membrane phase may exceed more than 30%, which results in a shortage of hydrogen on the Pt surface inside the anode.

4. Conclusions

Detailed studies of the dissolution of Pt from the cathode and anode, distribution patterns, and particle sizes of the migrated Pt in the membrane phase are performed using TEM after long-term operations of PEMFCs under various operating and feed conditions. Experimental results indicate that large quantities of cathode Pt can be dissolved when the residual oxygen concentration inside the cathode electrode is kept high, while maintaining a low reduction current density. Dissolution of Pt at the cathode proceeds primarily by chemical oxidation in the presence residual oxygen in the electrode. Dissolution and migration of anodic Pt can be possibly observed under constant-current operation if current density is kept high while maintaining low hydrogen concentrations. Hydrogen shortage at the Pt surface results in electrochemical decomposition of water to produce an additional current, protons, and oxygen. The produced oxygen causes oxidation of Pt to PtO, which undergoes anodic Pt dissolution, and eventual migration to the membrane phase.

Platinum that has migrated from the cathode to the membrane phase undergoes repeated oxidation/dissolution by crossover oxygen, and reduction by crossover hydrogen. Therefore, distribution patterns and the particle size of migrated Pt are strongly dependent upon the relative concentrations of the crossover oxygen and hydrogen from the two electrode sides. Crossover oxygen not only pushes Pt particles in the membrane toward the anode side via oxidation and dissolution mechanisms, but also promotes degradation of the Nafion membrane in the presence of Pt. Crossover hydrogen reduces migrated Pt ions, and stops the movement of dissolved Pt toward the anode. Therefore, the final position of the deposited Pt band is located at the point where oxygen concentrations are depleted, generally 1–10 μm from the cathode–membrane interface. Higher concentrations of crossover hydrogen and oxygen yield sharper and narrower Pt bands with larger Pt aggregates, while lower concentrations yield wider distributions with smaller Pt crystals.

Acknowledgements

Fig. 6. Cell voltage during 333 h operation at constant-current (80 mA cm^{-2}) with lean hydrogen feed (35% excess feed).

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