Methanol adsorbates on the DMFC cathode and their effect on
the cell performance

J. Prabhuram, T.S. Zhao *, H. Yang

Department of Mechanical Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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Abstract

A drastic decline in the performance of a direct methanol fuel cell (DMFC) occurred after the cell had been operated at a higher
temperature with higher methanol concentrations as compared with the polarization data collected under the original condition of a
lower methanol concentration and room temperature. Both the linear sweep voltammetry (LSV) and cyclic voltammetry (CV) inves-
tigations suggest that the deterioration in the cell performance was due to the permeated methanol adsorbates on platinum sites of
the cathode, which impede the oxygen reduction reactions (ORRs) by creating a large overpotential. The CV technique has further
been utilized to get rid of the methanol adsorbates from the cathode electrochemically by sweeping from 0 to 1.0 V. After this pro-
cedure, both the open circuit voltage (OCV) and performance of the DMFC were found to be improved substantially.

Keywords: Direct methanol fuel cell; Methanol adsorbates; Cyclic voltammetry; Oxygen reduction reaction

1. Introduction

Direct methanol fuel cells (DMFCs) are attractive
electrochemical devices for transportation and portable
applications as they offer many advantages, such as
elimination of fuel reforming, ease in refueling, and sim-
plified system design [1]. In DMFC, methanol is oxi-
dized at the anode according to the reaction

$$\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{(anode)} \quad (1)$$

while oxygen is reduced at the cathode according to the
reaction

$$3/2\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{(cathode)} \quad (2)$$

As such, the overall reaction in the cell is given by

$$\text{CH}_3\text{OH} + 3/2\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(cell)} \quad (3)$$

These electrochemical reactions, however, are kinetically
sluggish on the respective electrodes due to formation of
intermediates; particularly, the intermediates formed
during the methanol oxidation can seriously poison
the anode Pt and its alloys, eventually limiting the effi-
ciency of the cell [2,3]. Another serious problem is meth-
anol crossover through the Nafion type membranes to
the cathodic side, which resulted in reduction in the volt-
age and efficiency of the cell [4–8]. In order to circum-
vent the latter problem, many researchers have taken
effort to modify the Nafion type membranes by chemical
and physical means [9–13]; and found its effect on
improving the performance of the cell [12]. In this con-
text, it is essential to mention some of the recent studies
[14–17], where Pd and its alloy thin films have been
deposited on the Nafion type membranes for reducing
methanol crossover that resulted in enhanced DMFC
performance. In this direction, we have employed Pd–
Cu (6:4) alloy of thickness 0.3 μm sputtered Nafion
115 membrane to investigate the methanol crossover

* Corresponding author. Tel.: +852 2358 8647; fax: +852 2358 1543.
E-mail address: metzhao@ust.hk (T.S. Zhao).
phenomenon using high concentrations of methanol (2 and 4 M) at 70°C (the Pd–Cu alloy of ratio 6:4 has been chosen as the barrier for methanol permeation because it has a similar type of hydrogen diffusion property with that of the Pd) [18]. Surprisingly, after these high temperature and high concentration operations, the open circuit voltage (OCV) and cell performance were found to be deteriorated in the subsequent operations when the operating condition was set back to room temperature. This problem of deterioration in the cell performance has been noticed repeatedly, whenever the operating condition was changed from high temperature and high concentrations to low temperature and low concentrations. A series of experiments were conducted to dig into the cause for the performance deterioration, and finally, it was detected to be due to the existence of methanol adsorbates in the cathode of the cell, which permeated during the operations with high concentrations at high temperature. This severe crossover problem occurred even after using the modified membrane, from which one can realize how serious the methanol crossover problem is in the case of using unmodified Nafion type membranes. Recently, Qi et al. [19] reported that the DMFC performance was declined (over 20%) at 72°C, after cathode of the cell was being diffused with 1 M methanol solution during the overnight idle period; they concluded that the flooding of methanol solution on the cathode side was responsible for the decline in the performance of the cell. In the above condition, we suspect that there would also exist a possibility of the formation of methanol intermediates on Pt sites of the cathode, which is in the atmosphere of flooded methanol solution and may also lead to the decline in the performance. It should be mentioned that although many researchers have studied the methanol crossover problem [20–23], these previous studies have focused mainly on crossover effect on the cell voltage during the course of the cell operation only. To the best of our knowledge, to date, no study has been reported on the formation of methanol intermediates on Pt sites of the cathode and their post effect on the cell performance.

In this paper, we show that a drastic decline in the performance of a DMFC occurred after the cell had been operated at a higher temperature with higher methanol concentrations as compared with the polarization data collected under the original condition of a lower methanol concentration and room temperature. Our linear sweep voltammetry (LSV) and cyclic voltammetry (CV) investigations suggest that the deterioration in the cell performance was due to the permeated methanol adsorbates on platinum sites of the cathode, which impede the oxygen reduction reactions (ORRs) by creating a large overpotential. Furthermore, we also suggest a simple remedial measure to get rid of these methanol adsorbed species from Pt sites of the cathode by using the CV technique to improve the cell performance.

2. Experimental

A commercial Nafion 115 membrane (Electrochem Inc.) was treated according to the membrane cleaning procedure given elsewhere [24]. Briefly, the Nafion 115 was boiled at 80°C for 1 h in each step in 5% H2O2 solution, deionized water (DI), 0.5 M H2SO4 solution and again in DI water. Further, a thin layer of Pd–Cu (6:4) alloy of thickness 0.3 µm was deposited on one side of the cleaned and dry membrane by a sputtering technique (Model DVI SJ/24LL, Denton), under a system vacuum of 6.67 × 10⁻⁵ Pa at a temperature less than 100°C.

For both the anode and cathode, the commercial grade 30 wt% Teflon treated carbon cloth (E-TEK) was employed as the backing layer. The gas diffusion layers (GDL) were fabricated on one side of the carbon cloth comprising of Vulcan XC-72 carbon (4 mg cm⁻²) and Teflon content of 20 and 30 wt% in the anode and cathode, respectively. To fabricate anode and cathode catalyst layers, the anode and cathode inks were prepared by mixing 20 wt% of Pt–Ru/C (atomic ratio 1:1) and 20 wt% of Pt/C catalysts (both from E-TEK) with 30 wt% of Nafion solution in the solvent isopropanol. The prepared anode and cathode inks were uniformly brushed on the GDL of area 5 cm² to give the approximate loading of 2.1 mg cm⁻² of Pt–Ru on the anode and 1.8 mg cm⁻² of Pt on the cathode, respectively. Finally, 0.5 mg cm⁻² of Nafion was uniformly coated on the anode and cathode catalyst layers and dried at 80°C in a vacuum oven for 30 min. After that the Pd–Cu (6:4) alloy sputtered Nafion 115 membrane was sandwiched between the anode and cathode, in such a way that the Pd–Cu alloy barrier was placed on anode side of the catalyst layer and was hot pressed at 135°C at a pressure of 4 MPa for 3 min.

The MEA was inserted into a single cell fixture (consisting of graphite plates with an active area of 5 cm², Electrochem, Inc.) having three-pass serpentine flow channels with both width and depth of 0.7 mm. The MEA was initially activated at the loading current density of 200 mA cm⁻² and at 50°C for 20 h by feeding with H2 and O2, which were humidified at 60°C. After the activation process, the DMFC was tested by feeding diluted methanol solutions at a flow rate of 1 ml min⁻¹ using a high-pressure piston pump (Model Series III, Scientific Systems Inc.). Dry oxygen (having a high purity of 99.999%) was fed into the cathode inlet at a flow rate of 50 ml min⁻¹ at ambient pressure. Polarization curves were recorded by fixing the load current, which was controlled with an electric load system (BT2000, Arbin Instrument Inc.) as per the detailed procedure given elsewhere [25].

Linear sweep voltammetry and cyclic voltammetry experiments were conducted on the fuel cell by using the potentiostat (EG&G Princeton, Model 273 A) to
measure the oxidation current of the methanol adsorbates and to electrochemically remove the methanol adsorbates from cathode of the fuel cell. Prior to the LSV and CV experiments, the cathode of the cell was fed with humidified N₂ for 15 min. The cathode was connected to the working electrode, while the anode was connected to the reference and counter electrodes of the potentiostat, respectively. Both the LSV and CV experiments were conducted by applying voltage in the range from 0 to 1.0 V and at a scan rate of 25 mV s⁻¹. During the forward sweep of the LSV and CV experiments, the methanol adsorbates present in the cathode of a cell were oxidized; the resulting protons migrated to the anode, where they were reduced to hydrogen gas and acted as a reference electrode.

The methanol crossover was evaluated by a voltammetric method using the DMFC configuration under the open circuit condition (the permeation cell) as reported elsewhere [7]. The experiment was conducted on the permeation cell by using a potentiostat to measure the limiting current density (LCD) of the permeated methanol through the thin layer of Pd–Cu alloy sputtered Nafion 115 and unmodified Nafion 115 membranes both at room temperature and at 70 °C. During the course of the experiments, the anode of the cell was fed with 4 M methanol concentration at a flow rate of 1 ml min⁻¹ and the cathode of the cell was fed with humidified N₂ at a flow rate of 50 ml min⁻¹. The experiments were performed by connecting, respectively, the cathode of the cell to the working electrode and the anode to the reference and counter electrodes of the potentiostat. The current densities for the methanol oxidation on the cathode of the cell were measured by feeding 4 M methanol to the anode side and applying the voltage from 0 to 1.0 V at scan rates of 25 mV s⁻¹.

CV experiments were conducted at the scan rate of 25 mV s⁻¹ and (B) after operating the cell with 2 and 4 M methanol at 70 °C.

For high temperature operations, the cell was changed back to be operated at room temperature with 1 M methanol; the corresponding performance is represented by curve A in Fig. 1. The OCV value is found to be slightly lower (0.43 V) and this might be due to the presence of lower amount of catalyst loadings both on the anode and cathode of the MEA used in this work. To study the methanol crossover phenomenon for the Pd–Cu (6:4) alloy sputtered Nafion 115 membrane, the cell was subjected to operation at 70 °C using higher concentrations of methanol (first 2 M and then 4 M). After carrying out the high temperature and high concentration operations, the cell was changed back to be operated at room temperature with 1 M methanol; the corresponding performance is represented by curve B in Fig. 1. A comparison between curves A and B in Fig. 1 shows a drastic decline in both the OCV and the polarization curve after the cell was operated with higher concentrations of methanol at high temperature. It is seen from Fig. 1 that at the current density of 40 mA cm⁻², the voltage in curve A dropped from 0.26 to 0.15 V in curve B (around 40% decrease) after the higher methanol concentration and higher temperature operation. The reason for this huge decline in voltage is found to be due to severe poisoning of the cathode.

3. Results and discussion

The cell was first tested at room temperature with 1 M methanol; the corresponding polarization curve is represented by curve A in Fig. 1. The OCV value is found to be slightly lower (0.43 V) and this might be due to the presence of lower amount of catalyst loadings both on the anode and cathode of the MEA used in this work. To study the methanol crossover phenomenon for the Pd–Cu (6:4) alloy sputtered Nafion 115 membrane, the cell was subjected to operation at 70 °C using higher concentrations of methanol (first 2 M and then 4 M). After carrying out the high temperature and high concentration operations, the cell was changed back to be operated at room temperature with 1 M methanol; the corresponding performance is represented by curve B in Fig. 1. A comparison between curves A and B in Fig. 1 shows a drastic decline in both the OCV and the polarization curve after the cell was operated with higher concentrations of methanol at high temperature. It is seen from Fig. 1 that at the current density of 40 mA cm⁻², the voltage in curve A dropped from 0.26 to 0.15 V in curve B (around 40% decrease) after the higher methanol concentration and higher temperature operation. The reason for this huge decline in voltage is found to be due to severe poisoning of the cathode.

![Fig. 1. Cell performance by feeding 1 M methanol at the flow rate of 1 ml min⁻¹ and oxygen at 50 ml min⁻¹ at room temperature: (A) before and (B) after operating the cell with 2 and 4 M methanol at 70 °C.](image-url)
of the cell by the methanol adsorbates, which had occurred during the previous operation with 2 and 4 M methanol at 70 °C.

Fig. 2 shows the LSV performed on the cathode at room temperature after the cell had been operated with 2 and 4 M methanol at 70 °C. When the voltage is applied between 0 and 1.0 V, a broad peak is observed with onset and peak potentials at 0.4 and 0.87 V, respectively. The formation of this broad peak in the above potentials provides a clear evidence for the oxidation of methanol adsorbates present in the cathode [21]. A small oxidation current is observed at voltages less than ca. 0.4 V, because oxidation of methanol adsorbates requires active oxygen atoms, which are produced only above 0.4 V on the Pt electrode. The observed methanol adsorbate oxidation peak suggests that the complete oxidation of permeated methanol on Pt sites of the cathode to CO$_2$ is unlikely to occur, during the operation of cell at high temperature. It can be due to the fact that the simultaneous occurrence of both the ORR and permeated methanol oxidation reaction on the Pt sites of the cathode in the potential range from 0.8 to 0.4 V [26] is likely to inhibit the complete oxidation of permeated methanol molecules to CO$_2$, which can lead to the accumulation of some of the methanol adsorbed species (methanol adsorbates) on the Pt sites of the cathode [27].

During the DMFC operation with higher concentrations of methanol (2 and 4 M) at 70 °C, severe methanol crossover still occurred, despite the presence of Pd–Cu (6:4) alloy barrier on the anode side of the Nafion 115 is to mitigate the crossover effect. In fact, the presence of Pd–Cu alloy barrier has offered the beneficial effect in reducing methanol crossover to the cathodic side. For example, in Fig. 3 the performance of the DMFC that employed Pd–Cu alloy sputtered Nafion 115 is compared with that of the bare Nafion 115 membranes at 70 °C with 4 M methanol, and it can be seen that the Pd–Cu sputtered membrane shows higher OCV and performance in the lower current density region (below 120 mA cm$^{-2}$) than the unmodified membrane. This is owing to the occurrence of relatively lower amount of methanol crossover for the Pd–Cu sputtered Nafion 115 than that of the unmodified Nafion 115 membrane [15,23]. In the high current density region (above 120 mA cm$^{-2}$), for the Pd–Cu sputtered Nafion 115, there is a sudden drop in voltage occurring from 0.29 to 0.1 V. This might be due to the mass transfer limitation of excess CO$_2$ produced by the possible higher amount of methanol oxidation reaction in the anode side of the Pd–Cu sputtered Nafion 115, where methanol crossover is relatively lower than Nafion 115. From these results, it can be deduced that though the Pd–Cu (6:4) alloy sputtered Nafion 115 has some positive effect in reducing methanol crossover to the cathode, but the crossover still remains to be a serious problem. Hence, alternative approaches have to be explored to find out a permanent solution to this vexed problem.

In order to quantitatively assess the methanol permeation rates through the thin layer of Pd–Cu alloy sputtered Nafion 115 and the unmodified Nafion 115 membranes, the current densities corresponding to the electro-oxidation of the permeated methanol on the Pt sites of the cathode in the permeation cells were measured for 4 M methanol at room temperature and at 70 °C; and the results are shown in Fig. 4. The permeation cell with the Pd–Cu sputtered Nafion 115 membrane exhibited lower LCD than that with the Nafion 115 membrane both in room temperature and at 70 °C (see Fig. 4a and b). For the Pd–Cu alloy sputtered Nafion 115 membrane, the methanol crossover current density was decreased nearly about 17% and 19% when compared with the Nafion 115 membrane at room temperature and at 70 °C, respectively. The lower methanol permeation rate through the Pd–Cu sputtered Nafion 115 membrane explains why it yielded the higher OCV.
and performance in the lower current density region (see Fig. 3).

In order to prove how the presence of methanol adsorbates on Pt of the cathode affects the ORRs, the LSV experiment was carried out for the 20 wt% Pt/C electrode in 0.1 M HClO₄ containing 2 M methanol in the potential region from 0 to 0.4 V, at the scan rate of 10 mV s⁻¹ (see curve B in Fig. 5). The electrolyte HClO₄ were chosen because it is a better match for the situation in DMFC and the influence of anions of the acid does not severely cause any overpotentials for the ORRs [28,29], which would be discussed in the following section. The potential sweep is terminated at 0.4 V because within this potential region, the methanol adsorbates can be formed on the Pt sites [30]. The formation of methanol adsorbates can be confirmed by the suppression of H-desorption peaks, which occurred in the potential region from 0 to 0.25 V in 0.1 M HClO₄ in the absence of methanol (compare the curves A and B in Fig. 5).

Furthermore, the Pt/C electrode with the methanol adsorbates (electrode that was subjected to linear sweep in the potential region from 0 to 0.4 V in 0.1 M HClO₄ contains 2 M methanol) is used to study the behavior of ORR in 0.1 M HClO₄ solution and compared with that of the clean Pt/C electrode in Fig. 6. On the clean Pt/C electrode, the onset of the ORR takes place at 0.8 V and flat limiting plateau is observed from ca. 0.67 to 0.1 V, indicating that the ORR follows the four-electron transfer mechanism which is predominant over the Pt/C electrode (see curve A) [28]. For the Pt/C electrode with methanol adsorbates, the ORR starts at ca. 0.67 V, which is 130 mV less compared to that of the clean Pt/C electrode (see curve B). The dramatic increase in over-potential for the ORR on the methanol adsorbed Pt/C electrode can be attributed to the fact that the ORR is accompanied by methanol adsorbates oxidation and causes a mixed potential in the potential region from 0.8 to 0.67 V. Schmidt et al. [29] and Millard et al. [31] investigated the ORRs on the Pt/C electrode in 0.5 M H₂SO₄ and in 0.1 M HClO₄ electrolytes in the presence of methanol and observed the formation of small anodic methanol oxidation peak centered at potential of ca. 0.7 V vs. RHE. Contrarily, in our study, such a type of anodic peak is not observed, instead a flat slanting region has been noticed in the potential range from 0.8 to 0.67 V, i.e., just before the onset of independent ORR for the methanol adsorbed Pt/C electrode. This might be due to the suppressed reaction rate of insufficient methanol adsorbates present on the Pt electrode when compared with predominant ORR in the O₂

![Fig. 4](image1.png)

**Fig. 4.** Comparison of methanol crossover current density between the Pd–Cu (6:4) alloy sputtered Nafion 115 and unmodified Nafion 115 membranes for 4 M methanol: (a) at room temperature and (b) at 70 °C.

![Fig. 5](image2.png)

**Fig. 5.** CV curves for: (A) Pt/C electrode in 0.1 M HClO₄ in the potential range 0–1.2 V and (B) Pt/C electrode in 0.1 M HClO₄ containing 2 M methanol in the potential range 0–0.4 V.

![Fig. 6](image3.png)

**Fig. 6.** LSV curves for the ORR for: (A) clean Pt/C electrode in O₂ saturated 0.1 M HClO₄ and (B) methanol adsorbed Pt/C electrode in O₂ saturated 0.1 M HClO₄.
saturated electrolyte. Interestingly, the higher ORR current is observed for the methanol adsorbed Pt/C electrode (see curve B) when compared with that of the clean Pt/C electrode (see curve A). This phenomenon can be interpreted in a way that after the oxidation of methanol adsorbates in the mixed potential region (0.8–0.67 V), free Pt sites could be created and there is a higher possibility for the adsorption of molecular oxygen (O–O) on the double site mode (Pt–Pt), resulting in faster kinetics [32,33]. However, the limiting current observed in the potential region from 0.35 to 0.1 V is almost similar to that of the clean Pt/C electrode. The detailed discussion of this phenomenon is beyond the scope of the present work and requires further investigations. The above results clearly illustrate that the presence of methanol adsorbates on Pt of cathode of the DMFC affects the ORRs by the way of causing a mixed potential and held responsible for low OCV and considerable loss in voltage (ca. 100–150 mV) during the operation of the DMFC.

To get rid of the methanol adsorbates from Pt of the cathode of the DMFC that had been previously operated with higher concentrations of methanol (2 and 4 M) at 70 °C, electrochemical cycling has been performed between the potential region from 0 to 1.0 V, for the cathode by using the CV technique (see Fig. 7). It can be seen from this figure that the oxidation current of the methanol adsorbates decreases over the cycles, suggesting the depletion of methanol adsorbates present on Pt sites of the cathode. After the 15th cycle, there is no further decrease in the oxidation current, indicating that the methanol adsorbates are completely consumed in the oxidation process. From the third cycle

![Fig. 7. Electrochemical cycling for the cathode of the DMFC by using CV.](image7)

![Fig. 8. Cell performance by feeding 0.5 M methanol at the flow rate of 1 ml min⁻¹ and oxygen at 50 ml min⁻¹ at room temperature: (A) original condition, (B) before removal of methanol adsorbates from the cathode and (C) after removal of methanol adsorbates from the cathode.](image8)

![Fig. 9. Cell performance by feeding 1 M methanol at the flow rate of 1 ml min⁻¹ and oxygen at 50 ml min⁻¹ at room temperature: (A) original condition, (B) before removal of methanol adsorbates from the cathode and (C) after removal of methanol adsorbates from the cathode.](image9)

![Fig. 10. Cell performance by feeding 2 M methanol at the flow rate of 1 ml min⁻¹ and oxygen at 50 ml min⁻¹ at room temperature: (A) original condition, (B) before removal of methanol adsorbates from the cathode and (C) after removal of methanol adsorbates from the cathode.](image10)
onwards, broad peaks with low intensity are observed in the potential region of 0–0.45 V, indicating the occurrence of oxidation of H atoms [34,35]. The oxidation of H atoms is possible only on the bare Pt sites, implying that subsequent electrochemical cycling makes the Pt sites free by oxidatively scavenging the methanol adsorbates present in it. Thus, the methanol intermediates present in the cathode catalyst layer (Pt/C) can be easily removed by the simple electrochemical cycling method using voltammetry. This step helps to clean the cathode of the DMFC and can restore the performance to its original condition.

Figs. 8–10 compare the cell performance before and after removing methanol adsorbates from the cathode with the cell being operated at room temperature with 0.5, 1 and 2 M methanol, respectively. It is seen from these figures that for all the tested concentrations of methanol, the OCV values in the cases before removing methanol adsorbates from the cathode are lower than the original cell OCV values (see Table 1). For the former case, the OCV values are almost the same (curve B), irrespective of the change in methanol concentrations (also see Table 1). This observation is contrary to the real situation, where the OCV decreases with increasing the concentration of methanol due to the crossover phenomenon [11,21,36]. This can be explained based on the fact that the potential of the cathode, as discussed in the preceding sections, was already depolarized by the methanol adsorbates and the concentration gradients created by different concentrations of methanol, which is regarded as the main factor for the crossover phenomenon in the open circuit condition is unlikely to have further effect on the potential of the cathode and in turn on the cell voltage [20]. On the other hand, for the cell, after the removal of the methanol intermediates from the cathode (curve C), the OCV values are found to be more or less similar to that of the original condition as shown in Table 1. This observation gives the preliminary confirmation that methanol adsorbates in the cathode are completely removed and the cell has recovered its original condition.

There is nearly 30–50% loss in the power density for the cell, before removing the methanol adsorbates from the cathode, when compared with the original condition in all concentrations of methanol (0.5, 1 and 2 M) as shown in Table 2. For the former case, there is no systematic trend seen with respect to power density values, i.e., for 0.5 and 1 M methanol, the power density values are almost equal (6.5 and 6.7 mW cm$^{-2}$) (see Figs. 8 and 9) whereas for 2 M methanol, the power density is almost double (12.0 mW cm$^{-2}$) to that of the lower concentrations of methanol (see Fig. 10). It has suggested that for the 2 M methanol, the anode potential can be more stable though the cathode potential is depolarized by methanol adsorbates [23]. In the case of the cell, where Pt sites of the cathode are cleaned from the methanol adsorbates, there is a substantial increase in the power density values for all the concentrations of methanol (0.5, 1 and 2 M) and these values are slightly higher than the original cell data (see Table 2). The slight increase in power densities can be attributed to the activation of the Pt–Ru/C in the anode by means of hydrogen evolution reaction (HER), which occurred during the course of oxidative removal of methanol adsorbates from the cathode of the cell.

4. Conclusions

A single DMFC was tested at room temperature with different methanol concentrations of 0.5, 1 and 2 M. The cell was subsequently operated at 70 °C with higher concentrations of methanol (2 and 4 M).

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**Table 1**

OCV values for the cell in original condition, before and after removal of methanol adsorbates from the cathode

<table>
<thead>
<tr>
<th>Methanol concentration (M)</th>
<th>OCV in the original condition (V)</th>
<th>OCV before removal of methanol adsorbates from the cathode (V)</th>
<th>OCV after removal of methanol adsorbates from the cathode (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.454</td>
<td>0.399</td>
<td>0.463</td>
</tr>
<tr>
<td>1.0</td>
<td>0.433</td>
<td>0.398</td>
<td>0.436</td>
</tr>
<tr>
<td>2.0</td>
<td>0.426</td>
<td>0.398</td>
<td>0.430</td>
</tr>
</tbody>
</table>

**Table 2**

Power density values for cell in original condition, before and after removal of methanol adsorbates from the cathode

<table>
<thead>
<tr>
<th>Methanol concentration (M)</th>
<th>Cell voltage (V)</th>
<th>Power density in the original condition (mW cm$^{-2}$)</th>
<th>Power density before removal of methanol adsorbates from the cathode (mW cm$^{-2}$)</th>
<th>Power density after removal of methanol adsorbates from the cathode (mW cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.410</td>
<td>10.0</td>
<td>6.5</td>
<td>10.2</td>
</tr>
<tr>
<td>1.0</td>
<td>0.450</td>
<td>12.1</td>
<td>6.7</td>
<td>13.0</td>
</tr>
<tr>
<td>2.0</td>
<td>0.420</td>
<td>16.0</td>
<td>12.0</td>
<td>16.8</td>
</tr>
</tbody>
</table>
Afterwards, when the operating condition was changed back to room temperature and lower methanol concentrations, nearly 30–50% decline in power density has been found as compared with the original performance. The experimental results show that although the presence of Pd–Cu (6:4) alloy barrier (thickness 0.3 μm) on the anode side of the Nafion 115 membrane is effective in reducing methanol crossover as compared to the bare Nafion 115, methanol permeation to the cathodic side has still occurred when the cell was operated with higher concentrations of methanol at 70 °C. This finding indicates that the presence of methanol adsorbates on Pt sites of the cathode is likely responsible for the drastic decline in the cell performance, which has been confirmed by the LSV investigations carried out on the cathodic part of the cell. Subsequently, the CV experiments have also shown the presence of methanol adsorbates on Pt sites of the cathode, which caused a mixed potential and thereby shifting the ORR to 130 mV negative to that of the clean Pt/C cathode. In a further step to remove the methanol adsorbates from Pt sites of the cathode, a simple electrochemical cycling method has been performed by sweeping from 0 to 1.0 V. After performing 15 cycles, the oxidation current of the methanol adsorbates is likely responsible for the dramatic decline in the cell performance, which has been confirmed by the LSV investigations carried out on the cathodic part of the cell. Subsequently, the CV experiments have also shown the presence of methanol adsorbates on Pt sites of the cathode, which caused a mixed potential and thereby shifting the ORR to 130 mV negative to that of the clean Pt/C cathode. In a further step to remove the methanol adsorbates from Pt sites of the cathode, a simple electrochemical cycling method has been performed by sweeping from 0 to 1.0 V. After performing 15 cycles, the oxidation current of the methanol adsorbates has come to the lowest level, indicating the complete removal of the methanol adsorbates from the cathode. Finally, the OCVs and performance of the DMFC operated with 0.5, 1 and 2 M methanol at room temperature are found to be substantially improved and slightly higher than that of the original cell performance.

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