Abrupt Decline in the Open-Circuit Voltage of Direct Methanol Fuel Cells at Critical Oxygen Feed Rate

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The open-circuit voltage (OCV) of a direct methanol fuel cell (DMFC) was measured by varying the cathode oxygen flow rate (OFR) while keeping the methanol concentration and operating temperature at different values. It was found that at high OFRs, the OCV was almost independent of the OFR. When the OFR was reduced to a critical value, however, the OCV exhibited an abrupt decline. It was further found that the abrupt decline in the OCV at this critical oxygen flow rate (COFR) coincided with the onset of the electrolytic hydrogen evolution in the DMFC. Theoretically, it is shown that the mass flux of oxygen furnished at the COFR balances the oxidation rate of methanol that permeates from the anode to the cathode. Therefore, the COFR is a measure of the methanol permeation rate through the membrane. The equivalent methanol permeation current density determined from the COFR was found to be in reasonable agreement with that measured from the permeation cell for different methanol concentrations and at different temperatures.

The objective of this work was to investigate how the OCV varied as the cathode oxygen flow rate (OFR) was reduced step by step from high to rather low values. The unique phenomenon found in this work was that there existed a critical oxygen flow rate (COFR) at which the OCV dropped abruptly and the hydrogen evolution was simultaneously observed in the anode transparent flow field. Moreover, for the given DMFC hardware, we show that the equivalent methanol crossover current density approximately balances the equivalent oxygen supply current density at the COFR. As such, a novel method for measuring the methanol permeation rate through the membrane under open-circuit conditions is proposed by measuring COFR.

Experimental

Membrane-electrode assembly (MEA).— An MEA having an active area of 4.0 × 4.0 cm was fabricated in-house employing two single-side ELAT electrodes from E-TEK and a Nafion 115 membrane. Both the anode and cathode electrodes used carbon cloth (E-TEK, type A) as the backing support layer with 30% polytetrafluoroethylene (PTFE) wet-proofing treatment. The catalyst loading on the anode side was 4.0 mg cm−2 with unsupported [Pt:Ru] Ox (1:1 a/o), while the catalyst loading on the cathode side was 2.0 mg cm−2 using 40% Pt on Vulcan XC-72. The membrane was pretreated following the standard procedure: (i) boiling membrane in 5 wt % H2O2 solution at 80°C for 1 h; (ii) rinsing with deionized (DI) water at 80°C for 1 h; (iii) boiling membrane in 0.5 M H2SO4 solution at 80°C for 1 h; and (iv) rinsing with DI water at 80°C for 1 h. The final MEA was formed by hot pressing at 135°C and 5 MPa for 3 min.

Single cell assembly and anode flow field visualization.— The MEA was sandwiched between two fixture plates. For the purpose of the anode flow field visualization, the anode fixture plate was made of transparent poly(methyl methacrylate) (PMMA). For convenience of temperature control, the cathode fixture plate was made of an aluminum block. Both the anode and cathode flow fields (which also served as current collectors) were made of 316L stainless steel. A single serpentine channel, having 1.3 mm channel width, 1.0 mm rib width, and 1.0 mm depth, was formed on both the anode and cathode sides by wire-cut technology. The structure of the finished cell was detailed elsewhere.

Experimental apparatus and test conditions.— The cell voltage was measured and recorded using an Arbin BT2000 potentiostat-galvanostat electrochemical testing system. High-purity oxygen of 99.999% as oxidant was delivered to the cathode side at ambient pressure without humidification. The flow rate of oxygen was controlled and measured by mass flow controllers (Omega FMA-7105E...
and FMA-7101E) combined with a multiple channel indicator (Omega FMA-5876A), which can control the oxygen flow rate from 5 to 500 standard cubic centimeters per minute (sccm) and 0.2–20 sccm, respectively, with an accuracy of 1% of full scale and a repeatability of 0.25% of reading. Methanol solutions, with 0.125, 0.25, 0.5, 1.0, 2.0, and 4.0 M concentrations, were pumped through the DMFC anode flow field at 4.0 mL min\(^{-1}\) by a digital micropump (Laballiance, HPLC, Series III). During the limiting current measurement, degassed DI water was pumped through the DMFC cathode flow field at 4.0 mL min\(^{-1}\) by another digital micropump (Laballiance, HPLC, Series II). The cell temperature as well as the temperatures of methanol solution and oxygen feed were maintained at 30, 40, 50, 60, or 70°C.

Results and Discussion

The variation in the open-circuit voltage with the oxygen flow rate.— Since the OCV of a DMFC is inherently linked to the mass transport behavior of oxygen and water on the cathode, any fluctuations in the oxygen supply may cause a variation in the OCV. During the experiments, we noticed that once the oxygen supply was started, the OCV increased rapidly to a peak value and then decreased gradually to a steady-state value. This observation was consistent with that reported by Qi and Kaufman.\(^1\) All the OCV data reported in this work are stabilized values. The experiments were conducted by decreasing the oxygen flow rate (OFR) in the staircase manner, as illustrated in Fig. 1. Each OFR was maintained with a sufficient duration (from 3 to 60 min, depending on the OFR region) to ensure the corresponding OCV to be stabilized before collecting. A typical transient variation in the OCV with the controlled OFR is shown in Fig. 1.

We found that when the OFR was sufficiently high, the OCV for a given methanol concentration at a fixed temperature was independent of the OFR. We refer to the OCV that is independent of the OFR as the normal OCV. Figure 2 presents the variation in the normal OCV with temperature for various methanol concentrations ranging from 0.125 to 4.0 M. It is seen that the normal OCV increased almost linearly with temperature but decreased with methanol concentration. This behavior is consistent with the data reported in the literature.\(^1,16,19,20\)

At relatively lower OFRs, the OCV became more dependent on the change in the OFR. The variation in the measured OCV with the OFR at different operating temperatures is shown in Fig. 3. The experiments were performed at the same methanol solution flow rate (4 mL min\(^{-1}\)) but with different concentrations: 0.125 M (Fig. 3a), 0.25 M (Fig. 3b), 0.5 M (Fig. 3c), 1.0 M (Fig. 3d), 2.0 M (Fig. 3e), and 4.0 M (Fig. 3f). We now focus our attention on the variation in the OCV with the OFR shown in Fig. 3a for 0.125 M methanol solution. It is seen that when the OFR was sufficiently high, the OCV corresponding to each temperature was almost independent of the OFR and close to the normal OCV. However, it is interesting to notice from Fig. 3a that when the OFR was reduced to a critical value, the OCV dropped abruptly. Below this critical oxygen flow rate (COFR), the OCV decreased gradually. It is also noticed from Fig. 3a that a higher temperature yielded a higher normal OCV (at high OFR) and a higher COFR but lower OCVs below the COFR. In the cases with higher methanol concentrations shown in Fig. 3b–f, the OCVs varied with the OFR in a manner similar to the case with the lowest methanol concentration shown in Fig. 2a. By comparing Fig. 3a–f, we notice that at each temperature with an increase in methanol concentration the normal OCV decreased but the COFR increased. For instance, at 70°C, when methanol concentration increased from 0.125 M (Fig. 3a) to 4.0 M (Fig. 3f), the normal OCV was reduced from 751 to 641 mV, whereas the COFR was increased from 0.98 to 41.5 sccm. It is also worth mentioning that to highlight the OCV variation in the low OFR region, the plateau region of the normal OCV at high OFR is not completely shown in Fig. 3.

The mechanism leading to the abrupt decline in the OCV at the COFR.— During the experiments, we found that at the COFR the abrupt decline in the OCV coincided with the hydrogen evolution observed in the anode transparent flow field. This leads us to believe that the parasitic electrochemical reactions\(^2\) took place in the DMFC under the open-circuit conditions at lower OFRs. As schematically illustrated in Fig. 4, methanol, along with water, permeates through the membrane from the anode to cathode and is oxidized to CO\(_2\) on the cathodic catalyst sites as follows:

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \quad \text{(on the DMFC cathode)}
\]  \[1\]

where the produced protons and electrons react with oxygen immediately to form water

\[
\frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{(on the DMFC cathode)}
\]  \[2\]

Reaction 2 indicates that oxygen is continuously consumed, although no electric load is applied to the DMFC (the open-circuit condition). When the OFR would be sufficiently high, Reaction 2 would be maintained everywhere across the MEA. However, as shown in Fig. 5, at sufficiently low OFR (lower than COFR), an oxygen-lean region would be formed in the channel downstream, although oxygen still would remain relatively richer in the channel.

Figure 1. Staircase-varied OFRs and the corresponding variation in the OCV with time.

Figure 2. Variations in the normal OCVs with temperature for different methanol concentrations.
upstream region. Although the oxygen-rich and -lean regions are connected by both the electrodes and the same electrolyte (membrane), the lateral proton conduction in the electrolyte is so low that the oxygen-lean and -rich sections of the cell act as if they were two independent cells that are connected electrically but not ionically.\textsuperscript{24} The oxygen-lean region acts as an electrolytic cell, whereas the oxygen-rich region still acts as a galvanic cell (the normal DMFC operation) that maintains a voltage between the two electrodes. In the oxygen-lean region, in addition to Reaction 1, the following electrolytic reaction also takes place

$$6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2 \uparrow$$  \textit{(on the DMFC anode)}  \textsuperscript{3}

Reactions 1 and 3 are powered by the following galvanic cell reactions taking place in the oxygen-rich region

\textbf{Figure 3.} Variations in the steady-state OCVs with the OFR at different temperatures and for different methanol concentrations.
\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2^+ + 6\text{H}^+ + 6\text{e}^- \quad \text{(on the DMFC anode)} \]  
\[ \frac{3}{2}\text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} \quad \text{(on the DMFC cathode)} \]

Reactions 3 and 4 explain why the gas evolution occurred in the anode flow field of the DMFC under open-circuit conditions, as illustrated in Fig. 5. The above discussion also indicates that at sufficiently low OFR (lower than COFR), the galvanic and electrolytic reactions take place simultaneously at both sides of the MEA, creating a self-discharging current between the galvanic and electrolytic regions. This explains why the OCV dropped abruptly when the OFR reached the COFR.

The correlation between the methanol permeation rate and the COFR—The discussion in the preceding paragraph indicates that a critically low OFR (COFR) will lead to a localized shortage of oxygen in the catalyst layer on the cathode, which in turn results in an abrupt decline in the OCV as a result of the self-discharging current between the galvanic and electrolytic regions. As indicated in Reactions 1 and 2, the onset of the localized shortage of oxygen depends not only on the OFR but also on the methanol permeation rate. Therefore, the COFR is related to the permeation rate. To find the correlation between the methanol permeation rate and the COFR, we assume that the permeated methanol through the membrane is completely oxidized to CO\(_2\) on the cathode. This assumption is more realistic at high cathode potentials and for the cathode with high Pt catalyst loading. As such, under the condition that the DMFC generates the normal OCV, the mass flux of oxygen furnished at high OFR balances the oxidation rate of methanol that permeates from the anode. As illustrated in Fig. 4, expressing the methanol permeation flux and the mass flux of oxygen, respectively, as the equivalent methanol permeation current density \(J_{\text{crossover}}\) and the equivalent oxygen transport current density \(J_{\text{oxygen}}\), we have

\[ J_{\text{crossover}} = J_{\text{oxygen}} = \frac{4F}{A} \left( \text{OFR} - \text{ETFR} \times C_{\text{O}_2,\text{exit}} \right) \]

where \(F\) is the Faraday constant, \(A\) is the MEA area, and ETFR represents the total flow rate of effluent at the exit of the cathode flow channel, consisting of CO\(_2\), water vapor, and oxygen with \(C_{\text{O}_2,\text{exit}}\) representing the oxygen concentration at the exit. When the OFR is reduced to the COFR, the oxygen concentration in the flow-field channel downstream becomes too low to maintain the mass flux of oxygen required by Reaction 2, leading to the above-mentioned short-circuit reactions. The corresponding abrupt drop in the OCV indicates the shortage of oxygen somewhere in the flow channel. Because of the oxygen consumption along the flow channel, the shortage of the oxygen most likely occurs at the downstream of the flow channel. Thus, in such a case, the oxygen concentration at the exit of the cathode flow channel can be assumed to be zero \((C_{\text{O}_2,\text{exit}} = 0)\). Accordingly, Eq. 6 reduces to

\[ J_{\text{crossover},\text{COFR}} = \frac{4F \times \text{COFR}}{A} \]

where \(J_{\text{crossover},\text{COFR}}\) represents the equivalent methanol permeation current density at the COFR. Equation 7 indicates that for a given MEA, the methanol permeation rate can be determined by measuring the COFR. Figure 6 presents the variation in \(J_{\text{crossover},\text{COFR}}\) with methanol concentration at different temperatures, which are calculated from Eq. 7 with the COFR determined from the abrupt decline in the OCV as shown in Fig. 3. As shown in Fig. 6, \(J_{\text{crossover},\text{COFR}}\) increases almost linearly with methanol concentration, in particular at low temperatures and for low concentrations.
The methanol permeation flux is determined from the limiting current density for low methanol concentrations. In this method, the methanol permeation flux is determined from the transport-controlled methanol electro-oxidation at the Nafion membrane/Pt catalyst interface of the permeation cell. A potentiostat (EG&G 273 with the maximum current of 1 A) was used to supply the methanol concentration at different temperatures. Figure 6. Variations in the equivalent methanol permeation current density determined by the COFR with methanol concentration at different temperatures.

We now compare the equivalent methanol permeation current density calculated from Eq. 7 with that measured using the permeation cell, which was first developed by Ren and co-workers. In this method, the methanol permeation flux is determined from the limiting current density \( J_{\text{lim}} \) resulting from the transport-controlled methanol electro-oxidation at the Nafion membrane/Pt catalyst interface of the permeation cell. A potentiostat (EG&G 273 with the maximum current of 1 A) was used to supply the methanol concentration at different temperatures. Figure 7. Variations in the limiting current density measured from the permeation cell with methanol concentration at different temperatures.

The methanol permeation current density \( J_{\text{crossover}} \) obtained from Eq. 8 and that determined from the COFR \( J_{\text{crossover,COFR}} \) (given by Eq. 7) are compared in Fig. 8. For various methanol concentrations ranging from 0.125 to 4 M. It is seen from Fig. 8 that \( J_{\text{crossover,COFR}} \) agrees well with \( J_{\text{crossover}} \) at high temperatures with a maximum relative error of 4.8%. For 2 M methanol shown in Fig. 8e, \( J_{\text{crossover,COFR}} \) still agrees well with \( J_{\text{crossover}} \) at low temperatures but with a maximum error of 5.6% at 70°C. As shown in Fig. 8f, when the methanol concentration was further increased to 4 M, \( J_{\text{crossover,COFR}} \) agrees well with \( J_{\text{crossover}} \) at temperatures below 40°C and \( J_{\text{crossover,COFR}} \) apparently overestimates the methanol crossover current density \( J_{\text{crossover}} \) at high temperatures with a maximum error of 28.9% at 70°C. According to Eq. 6, this means that a higher oxygen flux is required to sustain the normal OCV. Because the oxygen concentration in the cathode catalyst layer is close to zero, a higher oxygen flux requires a higher oxygen concentration in the channel downstream or higher oxygen concentration at the exit of the flow channel \( C_{O_2,\text{exit}} \). In such a situation, assuming \( C_{O_2,\text{exit}} = 0 \) and using Eq. 7 would lead to a large error in determining the methanol permeation rate.

The above discussion indicates that an alternative method for determining the methanol permeation rate through the membrane is created based on Eq. 7 by measuring the COFR. According to Reaction 1 and 2, this new method actually determines the methanol permeation rate by determining the oxygen consumption rate required for electro-oxidizing the permeated methanol on the cathode, which can be approximated by the COFR when the oxygen flow rate at the exit of the cathode flow field is negligibly small. Instead of quantifying the oxygen consumption rate, according to Reaction 1, measuring \( CO_2 \) generation rate can also determine the methanol permeation rate. For instance, the methanol permeation rate can be determined by measuring \( CO_2 \) flow rate at the exit of the cathode flow channel using an infrared gas analyzer (e.g., Horiba gas analyzer). Apparently, a gas analyzer, which is usually expensive,
is needed in this IR method. Another disadvantage of the IR method is that the CO₂ gas permeated from the anode must be compensated, particularly at high discharge current densities. However, the COFR method proposed in this work is simpler, cheaper, and more convenient because no special apparatus (such as a potentiostat or a gas analyzer) and additional reactant (such as humidified nitrogen) are needed during the test. The accuracy is satisfactory, particularly for low methanol concentrations and at low temperatures.

In addition to using oxygen as oxidant, we also measured the OCV of the fuel cell fed by air at different flow rates. It was found that the variation in the OCV with the air flow rate (AFR) was similar to the OCV behavior when the cell was fed with oxygen. The
agreement with which is obtained from Eq. 7 with the COFR replaced by the CAFR. The normal OCV, a minimum oxygen concentration at the channel methanol concentrations and at high temperatures is due to the much higher air flow rate, which is, however, neglected in deriving Eq. 9 from Eq. 6. In summary, using air and Eq. 9 would usually lead to a larger error than using oxygen and Eq. 7 in determining the methanol crossover rate.

Conclusions
The oxygen flow rate (OFR) dependence of the open-circuit voltage (OCV) has been systematically investigated for different methanol concentrations and at different temperatures. The experimental results showed that there existed a critical oxygen flow rate, at which the OCV dropped abruptly and the hydrogen evolution simultaneously occurred in the anode flow field. This unique phenomenon in DMFCs under open-circuit conditions was caused by the local shortage of oxygen on the cathode, which created a self-discharging current between the galvanic and electrolytic reactions taking place in the single MEA. Moreover, we have shown that for the given DMFC hardware, the equivalent methanol permeation current density approximately balances the equivalent oxygen supply current density at the COFR. As such, a novel method for measuring the methanol permeation rate through the membrane under open-circuit conditions has been proposed by measuring COFR. As compared with the methods for measuring methanol crossover reported in the literature, this present method is simple, cheap, and convenient.

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