Current Oscillations in Direct Methanol Fuel Cells (DMFC)

Pyoungho Choi, Alexandre Hacquard, and Ravindra Datta

Fuel Cell Center, Department of Chemical Engineering,
Worcester Polytechnic Institute, Worcester, MA 01609, USA.

Introduction

Direct methanol fuel cell (DMFC) is considered as a highly promising power source for cellular phones and laptop computers.[1-3] The great advantage of DMFC is that it is a relatively simple system that uses methanol directly as a fuel. Methanol is much easier than hydrogen in terms of energy density, handing, storing, and using the infrastructure for its distribution. One of the challenging areas in DMFC is the development of effective electrocatalysts for methanol oxidation reaction. In the last few years, significant research efforts were expended to characterize and improve Pt based electrodes. The kinetics of methanol electro-oxidation over Pt based electrodes involves several steps of reaction including many carbon-containing intermediates that make further reaction difficult because of their strong affinity for the catalyst surface.

Here, we report sustained current oscillations in DMFC under constant voltage modes. These oscillations depend on the types of anode and operating conditions of the fuel cells.

Experiment

Electrodes were prepared using Pt and PtRu catalyst (Johnson Matthey) and spread on carbon cloth (E-Tek). MEAs were prepared by placing electrodes either side of a pretreated Nafion® 117 and hot pressing. Methanol solution was fed continuously into the anode, diffused through the diffusion layer and was electrochemically reduced on the anode surface to produce protons and electrons. An oxidant, *e.g.*, oxygen or air, was fed continuously into the cathode and reacts upon dissociation with the electrons traveling through an external wire and protons diffusing through the membrane to produce water. The DMFC experiments were carried out in different temperatures and pressures. The catalyst loadings used were 4 mg PtRu/cm^2 and 4 mg Pt/cm^2 for the anode and cathode, respectively. The concentration of methanol feed solution used was 1 M and the anode flow rate was 0.5 – 2 ml/min. Pure oxygen was used for the cathode feed and its flow rate was 40 ml/min.

Results and Discussions

The anode reaction of DMFC is the oxidation of methanol by electrochemical reaction. It may be assumed that a surface carbon species are responsible for the slow kinetics at the anode. Figure 1 shows the experimental data of current density as a function of time at different potentials from 0.1 V to 0.5 V. For the DMFC potential of 0.1 V, current oscillates from 0.6 to 1.4 A per 5 cm^2 MEA. Figure 2 shows the amplitude and period of the oscillations. At low potential, the current oscillates over wide ranges with irregular manner. This may be due to the many carbon-containing surface species react competitively. However, the amplitude of the oscillation decreases with the increase of potentials due to the one or two surface species determine the overall reaction and, thus, the current generations are rather regular. However, the periods of the oscillation remain the same at about 7.5 minutes for all the different potentials. The oscillatory behavior of electrochemical reactions has been reported for many systems,[3-8] although current oscillations are less common than potential oscillations. Current oscillations under potentiostatic conditions and potential oscillation under galvanostatic systems of HCOOH on Pt were reported.[9] Potential oscillations of methanol[10] and ethanol oxidation[11] in acid solutions have also been observed, although the mechanistic details are not well understood. The oscillations of current have not been reported yet under DMFC conditions. The reason for the current oscillation in DMFC can be attributed to the transition of the electrode surface from a poisoned to an active state. The electrochemical oxidation of methanol at anode is a multi-step reaction involving six electrons. The oxidation of methanol on Pt is inhibited by the adsorbed CO and hydrogenated residues such as COH, HCOH, CH$_2$OH.

The anode reactions would be methanol adsorption as the first step and successive stripping of hydrogen atoms.[12] The oscillation may be quantitatively understood based on the kinetics of methanol decomposition on the surface of anode, mass balances, and charge conservations.

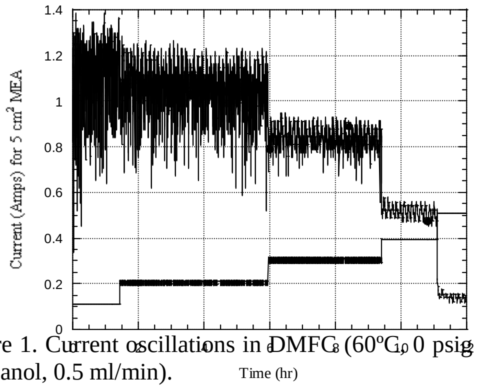

Figure 1. Current oscillations in DMFC (60ºC, 0 psig O$_2$, 1 M Methanol, 0.5 ml/min).

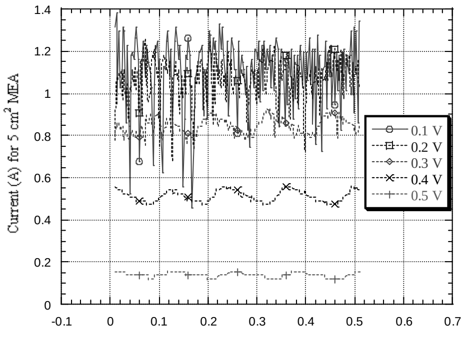

Figure 2. Period and amplitude of the oscillations.

References

1. X. Ren, P. Zelenay, S. Thomas, J. Davey and S. Gottesfeld, *J. Power Sources*, **86**, 111 (2000).
2 Dillon, S. Srinivasan, A. S. Arico and V. Antonucci, *J. Power Sources*, **127**, 112 (2004).
3. W. Bohannan, L. Y. Huang, F. S. Miller, M. G. Shumsky, and J. A. Switzer, *Langmuir*, **15**, 813 (1999).
4 D. T. Bowlin, A. Scheeline, and A. Pearlstein, *Electrochim. Acta*, **43**, 417 (1998).
5 J. Lee, P. Strasser, M. Eiswirth, and G. Ertl, *Electrochim. Acta*, **47**, 501 (2001).
6 M. Krausa and W. Vielstich, *J. Electroanal. Chem.*, **339**, 7 (1995).
7 S. Sriramulu, T. D. Jarvi, and E. M. Stuve, *J. Electroanal. Chem.*, **467**, 132 (1999).
8. F. Berthier, J. P. Diard, and S. Nugues, *J. Electroanal. Chem.*, **436**, 35 (1997).
9 J. Lee, J. Christoph, P. Strasser, M. Eiswirth, and G. Etrl, *J. Chem. Phys.*, **115**, 1485 (2001).
10 J. Lee, J. Christoph, M. Eiswirth, and G. Etrl, *Electrochim. Acta*, **47**, 2297 (2002).
11 S. Chen and M. Schell, *Electrochim. Acta*, **44**, 4773 (1999).
12. A. Hamnett, *Catalysis Today* **38**, 445 (1997).