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Simultaneous oxygen-reduction and methanol-oxidation reactions at the cathode of a DMFC: A model-based electrochemical impedance spectroscopy study

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Abstract

A model-based electrochemical impedance spectroscopy (EIS) approach that combines an equivalent electrical circuit (EEC) method and a mathematical model derived from the reaction kinetics is proposed to investigate the simultaneous oxygen-reduction reaction (ORR) and methanol-oxidation reaction (MOR) at the cathode of a DMFC. Good agreements between the calculated results and the experimental data validated the proposed method. Detailed kinetic parameters and state variables of the cathode were conveniently extracted and the concerned reaction processes were further analyzed, which demonstrated the comprehensive applicability of this method. The results showed a significant poisoning effect on the ORR by the presence of methanol at the cathode. The results also indicated that whether the methanol permeated from the anode can be completely oxidized by electrochemical reaction at the DMFC cathode depends on the electrode design and operating conditions, even at high potentials.

Keywords: DMFC; Cathode; Methanol crossover; EIS; Model

1. Introduction

Methanol crossover, the permeation of methanol through the ionomer membrane from the anode to the cathode, results in simultaneous cathodic oxygen-reduction reaction (ORR) and anodic methanol-oxidation reaction (MOR) at the cathode of a direct methanol fuel cell (DMFC). The simultaneous MOR and ORR lead to not only a fuel loss, but also a decrease in the cathode potential, which is one of major problems for DMFC performance [1–3]. To suppress the effect of the permeated methanol, it is essential to gain better understanding of the mechanism of how the MOR interacts with the ORR and how this interaction lowers the cathode potential. Recently, to understand the mechanism of the simultaneous MOR and ORR, extensive investigations have been reported by using traditional electrochemical and spectroscopic methods [1–8]. Despite a significant progress made, the kinetics of simultaneous MOR and ORR at the DMFC cathode is still not well understood, mainly due to the complicated nature of the reactions involving multi-step kinetics, and hence further studies are needed.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for elucidating reaction mechanisms involving multi-step kinetics, because it has the advantage of separating different rate processes in the frequency domain, and therefore provides a better insight on the interfacial processes and species in electrochemical systems. Up to now, however, only little attention has been paid to the application of EIS to the investigation of the DMFC cathode behavior [9–13]. Müller and Urban [9] firstly introduced a method of obtaining DMFC cathode impedance spectra based on recording individually the impedance data for the entire DMFC and the anode only, followed by the calculation of the DMFC cathode impedance. Using the same procedure, Piela et al. [10] measured and gave some further interpretation of the cathode impedance spectra. Also, aiming to examine transport and reaction kinetics, some reference electrode methods were adopted to measure the cathode impedance spectra individually [11–13]. These pioneering EIS investigations are greatly helpful in understanding the cathode behavior. However, partly because of the complexity of the impedance data, all these investigations used the equivalent electrical circuit (EEC) method, in

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which the obtained parameters may not have physical equivalents, and therefore, it is difficult to extract detailed information about the electrode reaction mechanism [14]. In addition, for a given impedance spectra, there may be several EECs that can all provide a good fitting, making it difficult to select the proper EEC model for the studied electrode system.

In this work, we propose a model-based EIS approach, which combines the EEC method and a mathematical model established from the detailed reaction mechanism, and apply this approach to investigate the simultaneous MOR and ORR at the DMFC cathode. This method can avoid the problems of the only EEC method, and more importantly, provide very detailed reaction information, e.g. the kinetic parameters and state variables. To the best of our knowledge, this is the first attempt to study the DMFC cathode by a model-based EIS method. We started with a mathematical derivation of the Faradaic impedance, based on a simplified reaction mechanism for the simultaneous MOR and ORR, and established a relationship between the Faradaic impedance and a general EEC. Then, the experimental impedance data were measured by a half-cell method. Finally, from the established relationship and the measured experimental data, the specific kinetic parameters and state variables for the simultaneous MOR and ORR were extracted and the results were analyzed based on the extracted parameters.

2. Theoretical

As discussed below, simultaneous MOR and ORR that occur at the cathode of a DMFC involve two adsorbed species. Based on the state variable theory [15,16], the Faradaic impedance (Z_F) for such an electrode process can be expressed as [17,18]:

$$Z_F = \frac{1}{(1/R_t) + (A + j\omega B)/(D - \omega^2 + j\omega T)} \quad (1)$$

where ω is the radial frequency,

$$\frac{1}{R_t} = \frac{\partial I_F}{\partial E} \quad (2)$$

with I_F and E representing the Faradaic current density and the electrode potential, respectively,

$$A = m_1 J_{12} n_2 + m_2 J_{21} n_1 - m_1 J_{22} n_1 - m_2 J_{11} n_2 \quad (3)$$

$$B = m_1 n_1 + m_2 n_2 \quad (4)$$

$$D = J_{11} J_{22} - J_{12} J_{21} \quad (5)$$

$$T = -J_{11} - J_{22} \quad (6)$$

with

$$m_i = \frac{\partial I_F}{\partial \theta_i} \quad i = 1, 2 \quad (7)$$

$$n_i = \frac{\partial \dot{\theta}_i}{\partial E} \quad i = 1, 2 \quad (8)$$

$$J_{ik} = \frac{\partial \dot{\theta}_i}{\partial \theta_k} \quad i, k = 1, 2 \quad (9)$$

where θ_i and $\dot{\theta}_i$ are respective adsorbate coverage and its change rate with time.

Apparently, to determine Z_F as a function of ω at a fixed potential E, the relationship between I_F, θ_i, $\dot{\theta}_i$, and E has to be identified to extract the parameter values for impedance calculation. To this end, a simple reaction mechanism for simultaneous MOR and ORR is employed:

$$\mathrm{Pt + CH_3OH} \xrightarrow{k_1} \mathrm{Pt - CO_{ads} + 4H^+ + 4e^-} \quad (10)$$

$$\mathrm{Pt - CO_{ads} + H_2O} \xrightarrow{k_2} \mathrm{Pt + CO_2 + 2H^+ + 2e^-} \quad (11)$$

$$\mathrm{Pt + O_2 + H^+ + e^-} \xrightarrow{k_3} \mathrm{Pt - O_2H_{ads}} \quad (12)$$

$$\mathrm{Pt - O_2H_{ads} + 3H^+ + 3e^-} \underset{k_{-4}}{\overset{k_{+4}}{\rightleftharpoons}} \mathrm{Pt + 2H_2O} \quad (13)$$

The electro-catalytic oxidation of methanol involves two series steps [19,20]. The first step is the adsorption and dehydration of methanol to form the absorbed CO species. The second step represents the irreversible oxidation of the CO species, leading to CO_2 evolution. Oxygen reduction on Pt under acidic media is usually characterized by the two-step Damjanovic mechanism [21,22]. The first step is an electrochemical step corresponding to the protonation of the O_2, which is the rate-determining step. Then the formed adsorption species, O_2H, is further reduced to water. The reaction rates v_i (i = 1, 2, 3, 4) corresponding to the Eqs. (10)–(13) can be expressed as:

$$v_1 = k_1 c_1 (1 - \theta_1 - \theta_2) \exp\left(\frac{E}{b_1}\right) \quad (14)$$

$$v_2 = k_2 \theta_1 \exp\left(\frac{E}{b_2}\right) \quad (15)$$

$$v_3 = k_3 c_2 (1 - \theta_1 - \theta_2) \exp\left(-\frac{E}{b_3}\right) \quad (16)$$

$$v_4 = k_{+4} \theta_2 \exp\left(-\frac{E}{b_4}\right) - k_{-4} (1 - \theta_1 - \theta_2) \exp\left(\frac{E}{b_4}\right) \quad (17)$$

where k_i (i = 1, 2, 3, +4, −4) are rate constants, b_i (i = 1, 2, 3, 4) the Tafel slopes, θ_1 and θ_2 the coverage of CO and O_2H, c_1 and c_2 the concentrations of methanol and oxygen. Based on the proposed reaction mechanism (Eqs. (10)–(13)), the Faradaic current density (I_F) can be written as:

$$I_F = F(4v_1 + 2v_2 - v_3 - 3v_4) \quad (18)$$

where F is the Faradaic constant. According to mass balance, the change rates of absorbate coverage ($\dot{\theta}_i$) is the net result of production and consumption of the absorbates, and can be expressed as:

$$\dot{\theta}_1 = \frac{d\theta_1}{dt} = \frac{F}{q_1}(v_1 - v_2) \quad (19)$$

$$\dot{\theta}_2 = \frac{d\theta_2}{dt} = \frac{F}{q_2}(v_3 - v_4) \quad (20)$$

where q_1 (420 $\mu C\,cm^{-2}$ [14]) and q_2 (assumed 420 $\mu C\,cm^{-2}$) are the charges required for complete CO and O_2H adsorption on unit Pt surface.