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In situ measurement of the oxygen diffusion coefficient in the cathode catalyst layer of a direct methanol fuel cell

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ABSTRACT

We report an *in situ* measurement of the oxygen diffusion coefficient D_{ox} in the cathode catalyst layer (CCL) of a direct methanol fuel cell (DMFC). The method is based on measuring two DMFC impedance spectra for the same cell current, but different oxygen concentrations in the cathode channel. The spectra are fitted using a transmission line model to extract the CCL resistivity. The difference of two CCL resistivities for different oxygen concentrations determines D_{ox}. We found $D_{ox} = 0.838 \times 10^{-4} \cdot \exp\left(-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{303}\right)\right)$ cm^2 s^{-1} in the temperature range from 30 °C to 90 °C, with $E_a \simeq 20.1$ kJ mol^{-1}. The activation energy is not far from that of the oxygen diffusion in Nafion; the value of this parameter is discussed.

1. Introduction

Direct methanol fuel cells (DMFCs) are compact sources of electricity based on direct electrochemical conversion of methanol combustion energy into electric current. Interest in this type of cells has been growing since the discovery of proton–conducting polymer Nafion in the late sixties of the XX century. A great advantage of DMFC over hydrogen cell is high volumetric energy density of liquid methanol, which makes DMFC an ideal power source for mobile gadgets.

However, well–known drawbacks of DMFCs retard wide commercialization of these cells. These are sluggish kinetics of methanol oxidation and large crossover of methanol from the anode to the cathode. Methanol permeated through the membrane is oxidized on the cathode side into protons and electrons. As a result, the total proton current that has to be converted in the cathode catalyst layer (CCL) greatly exceeds the useful current in the external load. Conversion of the parasitic current requires an extra flux of oxygen that needs to be transported through the cathode GDL and CCL. Both effects (higher proton current in the CCL and extra oxygen flux) dramatically lower the cell potential, especially in the range of small cell currents.

To understand the effect of crossover, a lot of modeling studies have been done (we refer reader to reviews of Wang [1], Yao et al. [2] and Bahrami and Faghri [3]). One of the key parameters governing the DMFC cathode operation is the oxygen diffusion coefficient in the CCL [4–8].

Typically, the CCL oxygen diffusivity is calculated using the Bruggemann correction for the CCL porosity/tortuosity to the oxygen diffusivity in free air [4,5,9,8]. The latter depends on temperature according to the power law $D_{ox} \sim T^{1.75}$ [10]. This correction, however, takes into account nor the contribution of the Knudsen diffusion, neither a Nafion film, which surrounds agglomerates of Pt/C particles, where the ORR takes place [11].

To the best of our knowledge, direct *in situ* measurements of D_{ox} in a working DMFC has not been published yet. Below, we report such measurements based on a recent model [12]. The model shows that the difference of CCL resistivities measured at the same cell current density but different oxygen concentrations in the cathode channel is inversely proportional to D_{ox}. To measure CCL resistivities we use electrochemical impedance spectroscopy (EIS).

2. Model equation

Oxygen transport in the CCL contributes to the total overpotential and to the differential CCL resistivity R_{CCL}. Recently, an analytical expression for the respective transport overpotential η_{ox} has been derived [13].

The model has been developed for the CCL with polymer electrolyte as a proton conductor and hence it works in the temperature

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range between zero and ≃90 °C. From the expression derived in [13] it follows, that R_{CCL} is given by

$$R_{CCL} = R_F(j_c) + R_{ox}(j_c, c_{ox}) \tag{1}$$

where R_F is the faradaic resistivity, and

$$R_{ox} = \frac{2(\sigma_p b + j_c l_t) b l_t}{3(2\sigma_p b + j_c l_t) 4 F D_{ox} c_{ox}} \tag{2}$$

is the resistivity due to the oxygen transport in the CCL. Here j_c is the total current density converted in the CCL (see below), c_{ox} is the oxygen concentration in the CCL, b is the Tafel slope of the oxygen reduction reaction, σ_p is the CCL proton conductivity, l_t is the CCL thickness, D_{ox} is the oxygen diffusion coefficient in the CCL.

It is difficult to separate experimentally the contribution of R_{ox} to the total CCL resistivity R_{CCL}. The most accurate technique for determining partial cell resistivities is electrochemical impedance spectroscopy (EIS). Unfortunately, the characteristic time of oxygen transport in the CCL $\tau_{ox} \simeq l_t^2/D_{ox}$ is very close to the characteristic time of faradaic processes $\tau_F \simeq C_{dl} l_t \eta_0 / j_c$, where C_{dl} is the double layer volumetric capacitance (F cm^{-3}) and η_0 is the total overpotential. Processes with close time scales cannot be resolved by impedance spectroscopy.

Nonetheless, the fact that R_F is independent of the oxygen concentration, while R_{ox} is inversely proportional to c_{ox} suggests an alternative method for R_{ox} determination [12]. Suppose that two impedance spectra have been measured for the same current densities, but *different* oxygen concentrations in the cell. Let the oxygen concentrations used be $c_{ox,1}$ and $c_{ox,2}$ and let $c_{ox,2} = k_c c_{ox,1}$, where $k_c > 1$. Writing down Eq. (1) for $c_{ox,1}$ and $c_{ox,2}$ and subtracting the resulting equations, we see that the faradaic terms cancel out and we get

$$\delta R_{CCL} = R_{ox,2} - R_{ox,1} = \frac{2(k_c - 1)(\sigma_p b + j_c l_t) b l_t}{3 k_c (2\sigma_p b + j_c l_t) 4 F D_{ox} c_{ox,1}} \tag{3}$$

From Eq. (3) we find the oxygen diffusion coefficient in the CCL

$$D_{ox} = \frac{2(k_c - 1)(\sigma_p b + j_c l_t) b l_t}{3 k_c (2\sigma_p b + j_c l_t) 4 F (\delta R_{CCL}) c_{ox,1}} \tag{4}$$

An important feature of DMFC's is large rate of methanol crossover through the membrane. Methanol permeated through the membrane is oxidized to protons and electrons in the CCL, and the resulting proton current density is then converted to the flux of water in the ORR [7]. Thus, the total current converted in the CCL is a sum of the useful j_0 and equivalent crossover j_{cross} current densities:

$$j_c = j_0 + j_{cross} \tag{5}$$

The value of j_c is related to the faradaic CCL resistivity. For the cell operating in the low–current regime (see below), the following relation holds [14]

$$R_F \simeq \frac{b}{j_c} \tag{6}$$

This equation allows us to calculate j_c, which then can be used in Eq. (4).

3. Experimental

3.1. MEA preparation

AvCarb 1071 HCB carbon cloth supplied by Ballard Material Products was used as a substrate for the anodes and cathodes. First, the carbon cloth was impregnated with PTFE dispersion TF 5032 (Dyneon) and subsequently dried and sintered at 350 °C. A microporous layer of carbon particles (VULCAN XC72 from Cabot) and PTFE (TF 5032 from Dyneon) was then prepared on the cloth by knife-coating to obtain gas diffusion layers (GDL). In a second coating step, the catalyst layers were prepared on the GDLs by knife-coating, too. Both catalyst layers consisted of catalyst material from Johnson Matthey and Nafion. In the case of the cathode catalyst layer, PTFE was added. The starting materials of PTFE and Nafion are the PTFE dispersion TF 5032 from Dyneon and the Nafion dispersion LQ1115 from Ion Power. HiSPEC 12100 catalyst (≃75 wt.% PtRu/C) with a loading of 2.6 mg cm^{-2} was used for the preparation of the anode. On the cathode side, HiSPEC 13100 catalyst (≃71 wt.% Pt/C) was applied with a loading of 2.0 mg cm^{-2}. Finally, the electrodes were cut to a size of 42 mm × 42 mm corresponding to a cell area of 17.64 cm^2 and hot-pressed on a Nafion® 115 membrane at 130 °C for 3 min.

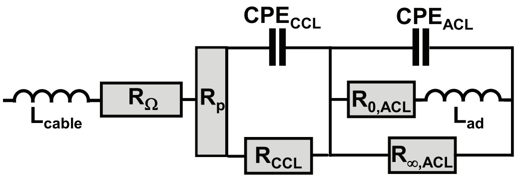

Fig. 1. Transmission line model used for the DMFC impedance fitting. For explanation of the elements see text.

3.2. Electrochemical impedance spectroscopy (EIS)

The impedance spectra were recorded by a ZAHNER-Elektrik "Zennium electrochemical workstation". The impedance measurements were always performed with a 10 mV input signal amplitude in a frequency range of 20 mHz - 20 kHz and the temperatures of 30, 40, 50, 60, 70, 80 and 90 °C under ambient pressure. DC current of −0.2 A was applied, corresponding to the current density through the cell of −11.34 mA cm^{-2}. The flow fields were made of graphite and had a grid design (ribs: 1 mm×1 mm×1 mm, channels: 1 mm width and depth). The anode was always fed with 1 M aqueous methanol solution with a flow rate of 1.1 ml min^{-1}, equivalent to stoichiometric λ–factor of 53. The cathode was fed by either pure oxygen (oxygen molar fraction 1.0), or by a mixture of oxygen and nitrogen with the oxygen molar fractions of 0.1 and 0.3. The gas flow rate at the cathode was 192 ml min^{-1}, corresponding to λ–factors greater than 10, depending on the oxygen fraction. The methanol solution was pre-heated to operating temperature. From these experiments, full cell impedances were obtained.

The impedance measurements were also carried out purging the cathode with hydrogen instead of air (V_{H2} = 192 ml min^{-1}). By applying a galvanostatic current, the cathode turns into a dynamic hydrogen evolving electrode (DHE), which performs as a quasi–reference electrode. As the impedance of the hydrogen cathode can be neglected, the cell impedance measured under these conditions is approximately equal to the anode impedance. By subtracting the anode impedance from the corresponding full cell impedances, the cathode impedances are obtained. These experiments demonstrate that the high frequency arc of the full cell impedance spectra can be undoubtedly attributed to the cathode impedance (see below).

The impedance spectra were fitted with the Zahner THALES Z 2.0 fit software using the equivalent circuit shown in Fig. 1. The equivalent circuit is based on a transmission line model of the cell discussed in [15]. It includes the following elements (i) L_{cable}, the cable inductance, (ii) R_Ω, the ohmic resistivity, (iii) R_p, the proton resistivity of both the catalyst layers, (iv) R_{CCL}, the kinetic resistivity of the cathode catalyst layer, (v) CPE_{CCL}, the constant phase element representing the pseudo double layer capacitance of the CCL, (vi) $R_{\infty,ACL}$, the resistivity associated with the charge-transfer part without change in CO surface coverage in the anode catalyst layer (ACL), (vii) R_0, the resistivity associated with relaxation of the