



Short Communication

Electrochemical impedance study on estimating the mass transport resistance in the polymer electrolyte fuel cell cathode catalyst layer



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ARTICLE INFO

Article history:

Received 6 March 2013

Received in revised form 6 May 2013

Accepted 8 May 2013

Available online 18 May 2013

Keywords:

PEFC

EIS

Mass transport resistance

Cathode catalyst layer

Impedance model

ABSTRACT

In this study the mass transport resistance in the cathode catalyst layer (CCL) of a polymer electrolyte fuel cell (PEFC) is estimated using electrochemical impedance spectroscopy (EIS) measurements. Experimental impedance measurements were carried out in a 6 cm² PEFC operated with two different relative humidity (RH) values in the cathode and different partial pressures of oxygen in He/O₂ and N₂/O₂ gas mixtures. A mathematical model predicting the CCL impedance response, derived in the authors' previous study, is applied to EIS measurements to calculate the CCL mass transport resistance. The experimental results show the presence of an overlapped second semicircle at low frequencies which is attributed to an increase in the time constant to diffuse oxygen through the CCL when the PEFC is operated at low oxygen partial pressures, $p(\text{O}_2) \leq 20\%$, in He/O₂ or N₂/O₂ gas mixtures. The results also show that oxygen diluted with nitrogen can reduce the steady state oxygen concentration in the CCL-gas diffusion layer (GDL) interface and can increase CCL mass transport resistance. It is possible, as such, to harness capabilities from both modelling and real-world EIS data in a complementary manner.

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1. Introduction

Polymer Electrolyte Fuel Cells (PEFCs) are the best candidates to be considered as the future source of propulsion for automobiles because they are able to produce high power densities at low temperatures and are not bound by the Carnot cycle. A PEFC converts the chemical energy of a fuel such as hydrogen gas into electrical energy. The study of mass transport resistance in the PEFC is of crucial interest, because the electrochemical reaction during hydrogen oxidation and oxygen reduction (redox) is affected by concentration gradients in the reactants supplied across the gas diffusion layer (GDL) and catalyst layer (CL); GDLs and CLs contain a tortuous pore network for the supply and removal of reactant gases and product water, respectively. External gas humidification is desirable to ensure appropriate humidification of the ionomer in the CL and the polymer electrolyte membrane (PEM). A high relative humidity (RH) enhances the ionic conductivity in the PEM and improves catalyst utilization and overall performance. Nevertheless, a high RH can result in pore saturation in the GDL and CL which will impede reactant transport. Electrochemical Impedance Spectroscopy (EIS) is an experimental technique that can be applied in-situ to separate the physical processes in the PEFC that occur at different rates through a frequency response plot. One of the challenges in EIS research is to quantify the mass transport limita-

tions between the CCL and the GDL. The Randles circuit [1] has been broadly used in impedance plots to estimate mass transport limitations in PEFC EIS measurements. However, it has not been clear how to determine whether this effect of oxygen transport limitation is dominated by the CCL or the GDL. In the authors' previous study [2], a mathematical model based on electrochemistry theory was developed to simulate the impedance spectrum of the cathodic side of a PEFC. The objective of the current study is to estimate the mass transport resistance in the cathode catalyst layer (CCL) using EIS measurements and the mathematical model developed in a previous study. To validate this work, experimental impedance measurements for a 6 cm² PEFC operated with two different relative humidity (RH) values in the cathode and different partial pressures of oxygen in He/O₂ and N₂/O₂ gas mixtures were considered.

2. Experimental

A 6 cm² PEFC was operated at 500 mA cm², 80 °C, 20 psig anode and cathode inlet pressures, 100% RH for the anode and 100/30% RH for the cathode. The flow rates were kept constant throughout the experiment at 125.5 sccm on the anode and 313 sccm on the cathode. The flow rates were controlled by computer controlled mass flow controllers (Bronkhorst®). The cell was allowed to sit at the required current on pure oxygen for 5 minutes and then the AC responses were measured. The gas was then switched to 80% O₂ in helium, held for a few minutes and then switched to

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80% O₂ in nitrogen. The concentrations were then stepped down to 60, 40, 20, and 10% O₂ in helium followed by nitrogen with impedance measurements taken at each point. The MEA was a developmental sample from Johnson Matthey Fuel Cells with 0.4 mg Pt/cm² on both anode and cathode. The thickness of the CLs was 10 μm. The membrane was a commercial 30 μm perfluorinated sulphonic acid membrane. The gas diffusion layers were based on wetproofed Toray TGP-H-060.

3. Model description

In the authors' previous study [2], a mathematical model was developed based on fundamental electrochemical and diffusion theory to simulate the impedance spectrum of the cathodic side of a PEFC operated for any zone of the polarisation curve, as such:

$$Z_{\text{Cathode}} = L_H(i\omega) + R_e + \frac{[R_C + Z_W]\gamma_1 \coth(\gamma_1 x)}{1 + Y(i\omega)^P [R_C + Z_W]} \quad (1)$$

With

$$\gamma_1 = \sqrt{R_p \left[\frac{1}{R_C + Z_W} + Y(i\omega)^P \right]}$$

R_p is the resistance to the flow of ions in the electrolytic phase of the CCL; R_C represents the charge transfer resistance during the oxygen reduction reaction (ORR) and is defined as $R_C = b/j_0 \exp(\eta_{ss}/b)$, where b is the Tafel slope, η_{ss} represents the activation overpotential, and j_0 is the exchange current; $Z_W = R_W \tanh(i\omega T_W)^{0.5} / (i\omega T_W)^{0.5}$ is defined as the Warburg impedance and describes diffusion across a finite dimension in the frequency domain, with $R_W = RT\delta / (z^2 F^2 c_0^* D)$ defined as resistance for the diffusion process and $T_W = \delta^2 / D$ defined as the time constant to diffuse oxygen through the CCL; Y represents a parameter related to capacitance, superscript P represents a parameter to correct the inhomogeneity in the distribution of charge between the electrode–electrolyte interface; ω is the angular frequency; i is the imaginary component in impedance; x represents the thickness of the CCL (dimensions) and for EIS measurements is equal to 1; L_H represents the inductance in the electrical cables in the measurement system; and R_e represents the total ohmic resistance to flow electrons and ions in the bipolar plate, GDL and PEM. In the authors' previous study [3] a reference electrode inserted in a PEFC operated with 100% RH in the anode and a multichannel frequency response analyser allowed the separation of the impedance response of the cell and cathode. The results showed that anode mechanisms (hydrogen oxidation reaction) have no contribution in EIS measurements at low frequencies where oxygen transport limitations are commonly manifested [3,4]. Springer et al. [5] reported that there is a negligible difference in impedance response when measuring the cathode impedance relative to the anode or relative to a reference electrode placed on the side of the anode. The anode contribution, neglecting any contaminant within the hydrogen supplied such as CO which affects the PEFC performance [6], can be considered negligible in these EIS measurements. Therefore Eq. (1) will be used to estimate the mass transport resistance in the CCL. The use of Eq. (1) with EIS measurements has already been demonstrated in previous studies [2–4]. The modelling predictions of Eq. (1) can be compared with the experimental impedance curves for a PEFC operated with different partial pressures of oxygen in He/O₂ and N₂/O₂ gas mixtures and two different RH values (100%, 30%) in the cathode. The simulated data from Eq. (1) were compared with the measured EIS data using a Graphic User Interface (GUI) developed in Matlab®. The use of the GUI with Eq. (1) for EIS analysis has already been demonstrated in the authors' previous study [2]. The parameters of Eq. (1) were manually adjusted with experimental EIS measurements using the GUI

to achieve a good agreement between the experimental and simulated data. In Eq. (1) there are some parameters that can also be estimated through a graphical interpretation of the Nyquist plot, as reported in a previous study [3]. This allows the reduction of the number of parameters to be fitted in the measured EIS spectra. The least-squares fitting method was used in order to find the best fit between the model and the measured data.

4. Results and discussion

The aim of this section is to estimate the mass transport resistance in the CCL when using O₂ diluted in He and N₂. For partial pressures of oxygen $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixtures, the kinetic and diffusion processes masked one another in the impedance plot. In EIS measurements carried out with $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixtures an overlapped second semicircle at low frequencies which can be attributed to oxygen diffusion effect was apparent, as shown in Fig. 1. In this study only EIS measurements with $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixtures were considered, as shown in Fig. 1, as it was possible to quantify accurately the charge transfer and mass transport resistances using Eq. (1).

4.1. Diffusion time constant

The presence of the overlapped semicircle at low frequencies is attributed to an increase in the time constant $T_W = \delta^2 / D$ to diffuse oxygen through the CCL [3]. The diffusion time constant is related to the three principal modes of transport of oxygen in the CCL: gas-phase diffusion in the CCL pore, diffusion in the liquid-water film surrounding a catalytic agglomerate, and diffusion in the ionomer of the agglomerate. The diffusion time constant calculated through Eq. (1) for EIS measurements at $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixtures and 100% and 30% RH values resulted in 0.003 s. For EIS measurements carried out at $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixtures an average value was calculated for 100% and 30% RH conditions. The average diffusion time constants for 100% RH and 30% RH were 0.08 s and 0.14 s respectively. Springer et al. [5] concluded that it is not possible to visualize the charge transfer and mass transport effects in PEFC EIS measurements with time constants of 10^{-4} and 10^{-3} orders of magnitude, and with either air or oxygen as a gas reactant. The finite diffusion distance δ for oxygen to reach the reaction sites in the CCL forms a complicated network of multi-phase parallel and serial paths and changes in dimension for different CCL composition (e.g. nafion loading, porosity, tortuosity) and at different fuel cell operating conditions (current density, temperature, relative humidity, etc.) [7]. Assuming that the finite diffusion distance is the thickness of the CCL to simplify the analysis, the effective diffusion coefficient D for EIS measurements at $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixtures at 100% RH and 30% RH was calculated to be 3.33×10^{-8} m²/s. For $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixtures at 100% RH the effective diffusion coefficient was calculated to be 1.25×10^{-9} m²/s and at 30% RH was 7.143×10^{-10} m²/s. These values present the same order of magnitude as the diffusion coefficients for diffusivity of oxygen in gas phase 2.68×10^{-8} m²/s, liquid-water phase 2.00×10^{-9} m²/s and ionomer phase 2.83×10^{-10} m²/s as reported by Malevich et al. [1]. It can be concluded that the main contribution to oxygen transport in the CCL for $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixtures at 100% RH and 30% RH is through the porous media. For $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixtures at 100% RH the main contribution to oxygen transport is through the water film surrounding a catalytic agglomerate and at 30% RH the main contribution is through the ionomer surrounding the agglomerate in the CCL.

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