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Electrochemical Impedance Study on Estimating the Mass Transport Resistance in the Polymer Electrolyte Fuel Cell Cathode Catalyst Layer.

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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 for a 6 cm² PEFC operated with two different relative humidity (RH) values in the cathode and different partial pressure of oxygen in He/O₂ and N₂/O₂ gas mixture were carried out. 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 pressure, $p(\text{O}_2) \leq 20\%$, in He/O₂ or N₂/O₂ gas mixture. 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.

Keywords: PEFC, EIS, mass transport resistance, cathode catalyst layer, impedance model

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 density at low temperature 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), for example. 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 an 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 limitations 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 define 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 pressure of oxygen in He/O₂ and N₂/O₂ gas mixture were considered. It is possible as such to harness capabilities from both modelling and EIS in a complementary manner.

2. Experimental

A 6 cm² PEFC was operated at 500 mAcm², 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 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 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.

How were the flow rates controlled?

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:

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

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

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 $R_w = RT\delta / (z^2 F^2 c_o^* D)$ 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; L_H represents the inductance in the electrical cables in the measurement system; and Re 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 not 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 place 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 have already been demonstrated in previous studies [2,3,4]. The modelling predictions of Eq.1 can be compared with the experimental impedance curves for a PEFC operated with different partial pressure of oxygen in He/O₂ and N₂/O₂ gas mixture and two RH (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 pressure of oxygen $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixture, 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 mixture 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 mixture 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 O₂ 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 for EIS measurements at $p(\text{O}_2) > 20\%$ in He/O₂ or N₂/O₂ gas mixture and 100 % and 30 % RH and calculated through Eq. 1 resulted in 0.003 s. For EIS measurements carried out at $p(\text{O}_2) \leq 20\%$ in He/O₂ or N₂/O₂ gas mixture an average value was calculated for 100 % and 30 % RH conditions. The average diffusion time constants for 100 % 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 change 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/O_2 or N_2/O_2 gas mixture at 100 % and 30 % RH was calculated to be $3.33 \times 10^{-8} \text{ m}^2/\text{s}$. For $p(\text{O}_2) \leq 20\%$ in He/O_2 or N_2/O_2 gas mixture at 100 % RH the effective diffusion coefficient was calculated to be $1.25 \times 10^{-9} \text{ m}^2/\text{s}$ and at 30 % RH was $7.143 \times 10^{-10} \text{ m}^2/\text{s}$. These values present the same order of magnitude as the diffusion coefficients for diffusivity of oxygen in gas phase $2.68 \times 10^{-8} \text{ m}^2/\text{s}$, liquid-water phase $2.00 \times 10^{-9} \text{ m}^2/\text{s}$ and ionomer phase $2.83 \times 10^{-10} \text{ m}^2/\text{s}$ 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/O_2 or N_2/O_2 gas mixture at 100 % and 30 % RH is through the porous media. For $p(\text{O}_2) \leq 20\%$ in He/O_2 or N_2/O_2 gas mixture 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.

4.2 Mass transport resistance in Cathode 100 % RH

The mass transport resistance R_w in the CCL expressed in Eq. 1 relates the change in oxygen concentration during the ORR from the GDL-CCL interface at steady state to the CCL-PEM interface at the frequency domain. R_w is a function of the steady state oxygen concentration c_o^* at the CCL-GDL interface. The steady state oxygen concentration can depend upon the conditions of the reactant supply to the cell and the physical properties of adjacent porous transport layers such as the GDL and microporous layer (MPL). Tab. 1 shows that CCL mass transport resistance calculated from EIS and Eq. 1 is reduced by using He/O_2 gas mixture, and increases with a decrease in $p(\text{O}_2)$. The diffusivity of O_2 diluted in N_2 at 80°C has been reported [8] to be $2.8 \times 10^{-5} \text{ m}^2/\text{sec}$ and the diffusion coefficient of water vapour in N_2 is $3.9 \times 10^{-5} \text{ m}^2/\text{sec}$; the oxygen diffusivity in He is $1.13 \times 10^{-4} \text{ m}^2/\text{sec}$ and the diffusion coefficient of water vapour in He is $3.14 \times 10^{-4} \text{ m}^2/\text{sec}$ under the same conditions. So, when the background gas in the cathode is switched to N_2 from He , an increase in mass transport limitations can be expected. The steady state oxygen concentrations c_o^* calculated from Eq. 1 are shown in Tab.1. The increase of CCL mass transport resistance R_w when O_2 is diluted with N_2 is due to a decrease in the steady state oxygen concentration c_o^* , as shown in Tab.1. The low diffusivity of O_2 diluted in N_2 in the GDL can decrease the steady state oxygen concentration c_o^* at the CCL-GDL interface and

increase the mass transport resistance in the CCL. It is well known that the EIS technique can separate the charge transfer resistance from mass transport losses. This effect can be noticeable when EIS measurements in PEFCs reflect two semicircles. The one at high-medium frequencies is related to the charge transfer resistance during the ORR and decreases with increasing current density. The other one, at low frequencies, is related to oxygen transport limitations and increases with increasing current density [3,9]. The charge transfer resistance R_C calculated from EIS measurements and using Eq. 1 is similar at the same $p(O_2)$ in He/O_2 or N_2/O_2 gas mixture. This effect can be observed in the spectra shown in Fig. 1a at frequencies from 2 kHz to 40 Hz. The charge transfer resistance increased with decreasing $p(O_2)$ in He/O_2 or N_2/O_2 gas mixture because the charge transfer during the ORR also depends on the distribution and amount of chemical species (oxygen, ions, and electrons) in the CCL electrode-electrolyte interface. Figure 1a shows that EIS spectra increase by using O_2 diluted in N_2 and also by reducing O_2 .

Figure 1 Comparison between experimental and simulated. Experimental $\diamond$ 20% O_2 -80% He ; $\square$ 20% O_2 -80% N_2 ; $\circ$ 10% O_2 -90% He ; Δ 10% O_2 -90% N_2 ; - Simulated; a) Cathode 100% RH, b) Cathode 30% RH

4.3 Mass transport resistance in Cathode 30 % RH

In the same way as the preceding subsection for 100% RH, the parameters that account for the mass transport resistance R_W and charge transfer resistance R_C were estimated through Eq. 1. Figure 1b shows the comparison between the simulated spectra from Eq.1 and the measured data at 30 % RH. At 30 % RH the mass transport resistance in the CCL is less than that accounting for the 100 % RH case as shown in Tab. 1. This can be attributed to the low water content in the GDL which increases the steady state oxygen concentration c_o^* in the CCL-GDL interface, as shown in Tab.1. The charge transfer resistance R_C is higher at 30 % RH than for the 100 % RH case. Similar results were reported by Xu *et al.* [10]; the authors carried out EIS measurements at different cathode RH (20, 35, 50, and

72%) in a 5 cm² PEFC. The CCL comprises Pt/C/ionomer agglomerates. Each agglomerate is considered to be surrounded by a film of water. At high RH the water film that surrounds the agglomerate increases and consequently improves catalyst utilisation in the CCL. This argument is supported by the superscript P from Eq. 1 and shown in Tab. 1. When $P=1$, a pure capacitive effect is present in the CCL [11] and therefore there is a homogeneous charge distribution between the electrode-electrolyte interface. At 100 % RH there is an increase in P when compared with the 30% RH condition. A homogenous charge distribution between dissimilar materials improves the charge transfer during the ORR reaction.

Cathode 100% RH	R_C $\Omega.cm^2$	P	R_w $\Omega.cm^2$	c_O^* mol/cm ³	Cathode 30% RH	R_C $\Omega.cm^2$	P	R_w $\Omega.cm^2$	c_O^* mol/cm ³
20% O ₂ -80%He	0.7944	0.9444	0.1018	1.549x10 ⁻⁵	20% O ₂ -80%He	0.9571	0.7546	0.0982	2.810x10 ⁻⁵
20% O ₂ -80%N ₂	0.7944	0.9693	0.1963	8.033x10 ⁻⁶	20% O ₂ -80%N ₂	0.9571	0.7669	0.1227	2.249x10 ⁻⁵
10% O ₂ -90%He	0.9518	0.9632	0.4172	3.779x10 ⁻⁶	10% O ₂ -90%He	0.9815	0.8896	0.2454	1.343x10 ⁻⁵
10% O ₂ -90%N ₂	0.9518	0.9528	1.2025	1.311x10 ⁻⁶	10% O ₂ -90%N ₂	0.9815	0.8896	0.5153	5.355x10 ⁻⁶

Table 1 Parameters estimated using Eq. 1 and EIS measurements

5 Conclusions

This study demonstrates that it is possible to attain a deeper understanding of the internal phenomenological processes in the PEFC by coupling the experimental EIS technique with the fundamental electrochemical theory. Experimental tests were carried out on a 6 cm² single cell operated at 80°C and RH of 100 % for anode and RH of 100/30 % for cathode. Different partial pressure of oxygen in He/O₂ and N₂/O₂ gas mixture was considered as background gases. A mathematical model predicting the CCL impedance response, derived in the authors' previous study, was applied to EIS measurements to quantify the mass transport resistance of the CCL. The results showed that it is possible to separate the CCL mass transport resistance and charge transfer resistance in EIS measurements when a PEFC is operated with low oxygen partial pressure $p(O_2) \leq 20$ % in either He/O₂ or N₂/O₂ gas mixture. The results also showed that the low diffusivity of O₂ diluted in N₂ in the GDL can decrease the steady state oxygen concentration c_O^* at the CCL-GDL interface and

increase CCL mass transport resistance. This study can be applied when studying the effect of different GDL structures on equilibrium oxygen concentration at GDL-GDL interface. A further study has to be conducted to examine the effect of oxygen transportation in every single phase of the CCL on EIS measurements. This is the aim of a future work.

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