

Impedance Analysis of Molten Carbonate Fuel Cell Cathodes

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Introduction

Electrochemical Impedance Spectroscopy (EIS) is a convenient tool for analyzing the behavior of porous fuel cell electrodes. Using this technique, it is possible to delineate the effects of various processes and identify critical operating parameters. Since, the technique is *in-situ* in nature, it is invaluable for studying the performance of high temperature reactions such as the oxygen reduction in Molten Carbonate Fuel Cells (MCFCs). Yuh and Selman¹ developed an impedance model to simulate the operation of the MCFC cathode. It was seen that under normal operating conditions, ohmic and kinetic limitations dominate the performance of the MCFC cathode. Reducing the gas concentration was seen to induce mass transfer limitations. Similar results were observed by Prins-Jansen *et al.*², who used a three phase homogeneous model to simulate the impedance response of the MCFC cathode. Both the above models neglect variations in the melt concentration and do not consider changes in electrolyte conductivity across the length of the cell. This could be critical in cases where applied currents or cell dimensions are large. The goal of this work is to simulate the impedance spectrum of the MCFC cathode including the effects of electrolyte migration. Impedance data under various operating conditions has been gathered. Specifically, the effect of temperature and inlet gas concentration on the Nyquist response has been studied. Results have been obtained for both NiO and Co doped lithiated nickel oxide.

Impedance Analysis

Our analysis is based on the agglomerate model for fuel cell electrodes¹ in which the electrolyte and solid phases are treated as superposed continua. Applying a mass balance for the electrolyte species across the length of the electrode we obtain,

$$\frac{\partial(\epsilon c_i)}{\partial t} = \frac{2a}{R^2} \int_0^R j_{in} r dr - \nabla \cdot N_i \quad [1]$$

where N_i is the flux of the species in the pore solution and $a_{j_{in}}$ represents the transfer rate of species i from the solid phases to the pore solution per unit electrode volume. The current in the liquid phase, i_2 is given by,

$$i_2 = F \sum z_i N_i \quad [2]$$

The condition of electroneutrality for each phase gives,

$$\sum z_i c_i = 0 \quad [3]$$

The electrolyte melt in the MCFC cathode is a eutectic mixture of Li carbonate and potassium carbonate. Explicit relationships for the fluxes in terms of the thermodynamic potential driving forces for a three ion concentrated solution are give by Pollard and Newman.³ For the matrix Ohm's law applies,

$$i_1 = -\sigma \nabla \Phi_1 \quad [4]$$

where σ is the solid phase conductivity. Based on conservation of electroneutrality we know that the sum of the electronic current density and ionic current density equals the overall applied current density, I_T . Hence,

$$\nabla i_1 + \nabla i_2 = 0 \quad [5]$$

Mass balance for reactant in the agglomerate (across the

thickness of the pore) is given by,

$$\frac{\partial(\epsilon c_i)}{\partial t} = \frac{-s_i}{nF} a_{j_{in}} - \nabla \cdot N_i \quad [1]$$

The local reaction rate, i_j , is given by

$$i_j = i_{oj,ref} \left\{ \begin{array}{l} \prod_i \left(\frac{c_i}{c_i^o} \right) \exp \left[\frac{\alpha_{aj} F}{RT} (\Phi^2 - \Phi^1 - \Phi_j^o) \right] - \\ \prod_i \left(\frac{c_i}{c_i^o} \right) \exp \left[\frac{-\alpha_{cj} F}{RT} (\Phi^2 - \Phi^1 - \Phi_j^o) \right] \end{array} \right\}$$

The above set of equations are first linearized and subsequently converted into the frequency domain using Laplace transforms. The linearized set of ODEs is solved using Newman's Band. Figure 1 shows model predictions of the Nyquist response of a NiO cathode under the absence of concentration variations. For a porous electrode, the initial increase in impedance at high frequencies corresponds to the transfer of current into the pore electrolyte.⁴ Subsequently, kinetic limitations of the oxygen reduction reaction dominate the Nyquist plot. This is seen by the increase in impedance with decrease in reaction rate. Further studies are being done to understand the effects of electrolyte filling and bias potentials on the impedance response of MCFC cathodes. The effect of inlet gas concentration and operating temperature will also be studied.

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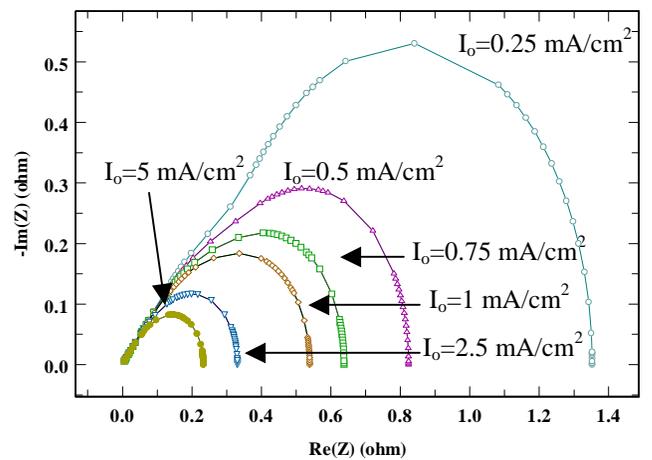


Figure 1. Nyquist Plots of MCFC Cathode – Effect of Reaction Kinetics