Transient Techniques for Investigating Mass-Transport Limitations in the PEFC cathode

Frédéric Jaouen, Göran Lindbergh, Katarina Wiezell
Dept of Chemical Engineering and Technology
Applied Electrochemistry, The Royal Institute of Technology (KTH)
SE-100 44 Stockholm, Sweden

Introduction

The efficiency of Polymer Electrolyte Fuel Cells is limited by the slow kinetics of the Oxygen Reduction Reaction. The knowledge of the mass-transports limiting the reaction rate of the cathode is therefore important. Extending our previous work on the steady-state behavior [1], the dynamic response to current-interrupts (CI) and electrochemical impedance spectroscopy (EIS) is investigated and the information obtainable from each technique is reviewed.

Modeling

The assumed geometry is that of the agglomerate model. We are concerned with the direction perpendicular to the electrode surface. Kinetics, diffusion in agglomerates and proton migration are taken into account. Diffusion in the gas phase and electron conduction are neglected. The systems of differential equations are solved for a given cathode current.. For presenting the EIS results, we define the Tafel impedance Z_t

$$Z_t = \frac{\tilde{E}}{\log(\tilde{j})} = \frac{\tilde{E}}{\tilde{j}} j_{st} \qquad / \text{V}$$

Where j_{st} is the steady-state current density. Z_t is thus simply equal to the usual impedance Z times the current density.

Results

Figure 1 is a predicted plot of the relaxation of the cathode potential after a CI. At large time, the potential relaxes at a pace equal to the Tafel slope (V/decade time). At medium times, the relaxation is faster owing to the relaxation of the O_2 concentration (see inset). Fig. 2 shows predicted Nyquist plots of Z_t for the same type of limitation and identical parameters. At low current, the semi-circle is characteristic for kinetic and its diameter is related to the Tafel slope. At high current, kinetic and diffusion limitations yield a doubled semi-circle. Surprisingly, the latter is completely independent on the diffusion coefficient and diffusion length for galvanostatic control. The doubled diameter corresponds to the double Tafel slope simulated at steady-state. The same type of study was performed for limitation by kinetics and migration, and for simultaneous limitation by kinetics, diffusion and migration. Impedance in inert gas was also simulated. The effect of a change in the O_2 concentration and electrode thickness were investigated for all cases. Examples of experimental results and of the fitting of the model to these results will be presented. The model also

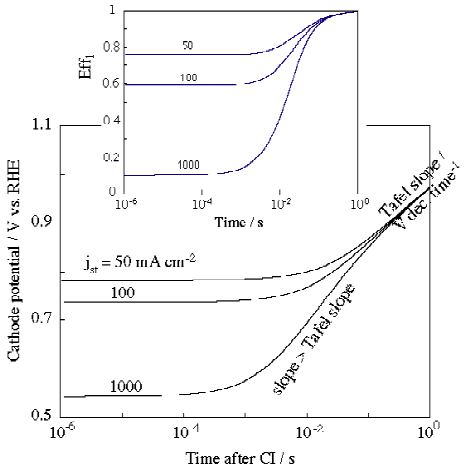

Figure 1: Predicted relaxation of the potential after CI for kinetic and diffusion control. Inset: relaxation of the effectiveness factor for O_2 diffusion in agglomerates

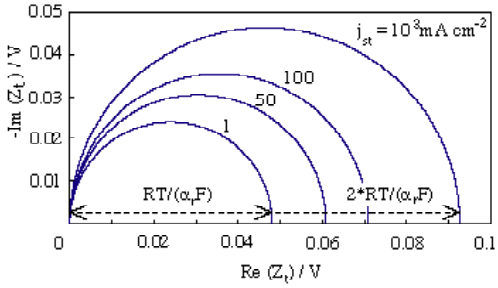

Figure 2: Predicted Nyquist plots for kinetic and diffusion control, α_r is the transfer coefficient for the oxygen reduction.

Conclusions

Transient techniques are powerful methods in order to separate processes occurring simultaneously at steady-state. Here, an innovative impedance is defined, allowing simple presentation of the data and straightforward coupling between the diameter of the semi-circle and the slope of the Tafel plots of steady-state polarization curves. The advantage of EIS against CI is that it results in faster computation due to the linerization of the equations.

[1] F. Jaouen, G. Lindbergh, G. Sundholm, J. of The Electrochem. Soc. 149, A437 (2002)