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Diagnostics of PEM Fuel Cell Degradation

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1. Introduction

Performance of PEM fuel cells degrades over time. Significant research efforts are devoted to better understanding of degradation causes [1,2] and mechanisms, and early detection of the symptoms. Diagnostics of fuel cell degradation should not only detect the symptoms as early as possible, but also, if possible, identify the causes and/or mechanisms so that corrective actions could be taken. The loss of potential is the most obvious symptom of degradation. By comparing the polarization curves at the beginning of life and after degradation it is relatively easy to determine which type of polarization, i.e., voltage loss, has increased over period of time [3].

2. Accelerated Stress Test

In order to study degradation in a controlled manner, a 50 cm^2 single cell was subjected to an accelerated stress test in accordance with the U.S. Department of Energy (DOE) Accelerated Stress Test (AST) protocol for electrocatalyst degradation. The cell was exposed to voltage cycling between 0.6 V and 0.9 V in a non-operating mode, i.e. nitrogen was used on the cathode and hydrogen on the anode side, while the potential was externally imposed. Usual diagnostic tests, such as polarization curve, electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and linear sweep voltammetry (LSV), were performed at the beginning of life (BOL) and then after 1000, 3000 and 5000 cycles. From the resulting polarization curves (Fig. 1) and EIS plots (Fig.2) it was obvious that the cell degraded. The analysis of the polarization curves and diagnostic tests confirmed that the voltage loss was caused by the loss of the electrochemical active area (ECSA) and by the increased resistance in the catalyst layer.
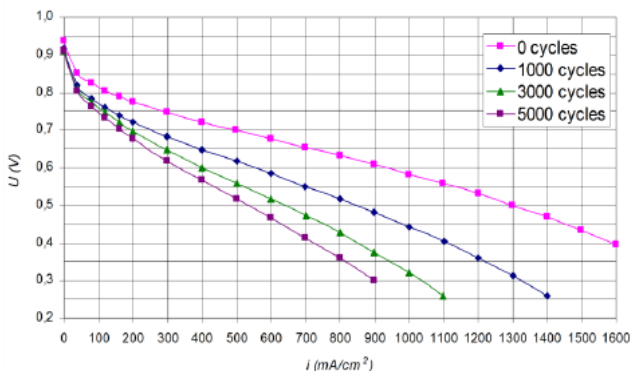

Fig. 1 Polarization curves taken during the accelerated stress test
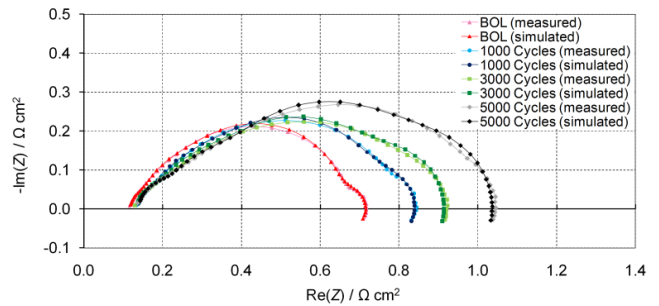

Fig. 2. EIS results of the accelerated stress test

The diagram clearly shows performance deterioration with time (i.e. number of cycles): the semicircles are distorted at high-frequencies, indicating an increase in the catalyst layer ionic resistance, while the low-frequency loops, representing mass transport losses, are getting bigger and in the end it is difficult to tell the two semicircles apart. As a result, the total resistance of the cell increased dramatically (the low frequency intercept). At the same time the high-frequency intercept, indicating ohmic losses, increased only in the first 1000 cycles (by ~20%), while it remained unchanged for the remainder of the degradation test. This concurs with the findings of the other diagnostic tests (polarization curves and cyclic voltammetry), which also indicated a significant loss of the ECSA. This loss of the ECSA apparently resulted in big structural changes within the catalyst layer, which resulted in increased catalyst layer resistance and increased mass transport losses.

3. Equivalent Circuit Model

Because standard representation of the fuel cell processes by equivalent circuits, involving resistance/capacitance loops, representing charge transfer resistance and double layer capacitance in series with a resistance, could not explain the inductive loops at low frequencies [4] (whose beginnings are visible in Fig. 2), a novel equivalent circuit model was proposed (Fig. 3) [5].
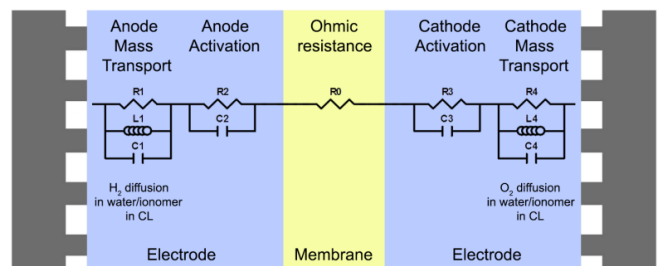

Fig. 3 Proposed equivalent circuit model

This model has additional loops, one for the cathode and one for the anode, comprising of a resistance, capacitance and inductance in parallel (the so called resonant loop). These resonant loops represent the mass transport and resistive losses within the catalyst layer. In this case, the physical processes preceding the catalytic reaction that take place in a complex structure of the fuel cell catalyst layer are represented by their electrical equivalents. Namely, inductance represents inertia of reactant gas (oxygen on the cathode and hydrogen on the anode) to dissolve in water, capacitance represents stored (dissolved) quantity of gas within the water/ionomer in the catalyst layer, and resistance represents protonic resistance through ionomer within the catalyst layer.

After being validated at different current densities and a variety of operating conditions [6], the previously described model was fitted to the obtained EIS spectra, using Z Fit numerical tool from Bio-Logic EC-Lab® software, in order to give more insight into cell's degradation. As shown in Fig. 2, a very good agreement between simulation and measured data was achieved. This enabled quantification of individual model components and the change of their values during the degradation experiment.

4. Results and Discussion

Fig. 4 shows the resulting changes in the equivalent circuit model elements during the accelerated stress test.
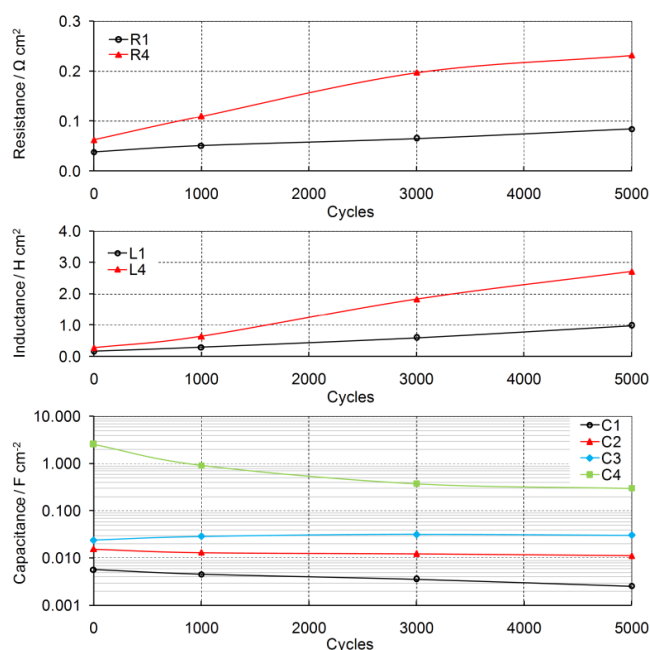

Figure 4 Changes of equivalent circuit model elements during the accelerated stress test; resistances (upper), inductances (middle), capacitances (lower)

The only parameters changing during the accelerated stress test are those within the cathode resonant loop, namely cathode catalyst layer resistance (R4), inductance (L4) and capacitance (C4). This is not surprising because the accelerated stress test targeted the cathode catalyst. These results, at least qualitatively, correspond to the findings of other analysis (polarization change curves) and tests (CV).

5. Conclusions

A novel equivalent circuit model, that attempts to include the processes in the catalyst layers, represented by the two resonant loops, was applied as a tool for diagnostic of PEM fuel cell degradation. A fuel cell exposed to an accelerated stress test degraded very fast. The periodic diagnostic tests confirmed that it was the cathode catalyst layer that degraded, as intended by frequent voltage cycling. The proposed model also indicated that the cathode catalyst layer significantly degraded. The cathode catalyst layer resistance and the cathode inductance both increased several times during the accelerated degradation test, while the catalyst layer capacitance decreased by an order of magnitude. This coincides with almost 80% of the electrochemical surface area loss during the accelerated stress test, confirmed by the polarization change curves analysis and by cyclic voltammetry. The loss of electrochemical surface area caused by the accelerated stress test was probably the result of morphological changes within the catalyst layer, which in turn resulted in increase in catalyst layer resistance and capacitance and decrease of catalyst layer capacitance. It appears that electrochemical impedance spectroscopy accompanied by the presented novel equivalent circuit model may be used for diagnostics of PEM fuel cell degradation.

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