Catalyst degradation diagnostics of proton exchange membrane fuel cells using electrochemical impedance spectroscopy

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ABSTRACT

A previously validated equivalent circuit model, in which two resonant circuits were inserted to represent the processes in the catalyst layers, is applied to fit the electrochemical impedance spectroscopy results of a single proton exchange membrane fuel cell exposed to accelerated stress test targeting catalyst degradation. The simulation results of the applied equivalent circuit model show very good agreement with the experimental data. The applied model is able to extract contributions of each of the model elements to the cell degradation. The obtained results indicate that the cathode catalyst layer resonant loop parameters, together with the cathode charge transfer resistance and cathode double-layer capacitance, change the most during the accelerated stress test. If each of the elements of the cathode resonant loop can be associated with physical processes inside the catalyst layer, the model may be used to give more insight into the degradation effects on functioning of the catalyst layer. From the conducted electrochemical impedance spectroscopy analysis, it seems that the low-frequency intercept in Nyquist plot shows the most significant change with degradation, so it may be used directly as a sufficient indicator of fuel cell performance degradation due to catalyst layer degradation.

Introduction

Durability is one of the main shortcomings in state-of-the-art automotive fuel cell systems, because performance of proton exchange membrane (PEM) fuel cells degrades over time, which limits a faster commercialization of this zero-emission power technology. Many researchers worldwide are devoted to find a better understanding of degradation causes and mechanisms, with early detection of the degradation symptoms [1—4]. However, diagnostics of fuel cell degradation should not only detect the symptoms, as early as possible, but also identify the causes and/or mechanisms, if it is possible, so that corrective actions could be taken [5]. There are several degradation mechanisms, typical for automotive applications, such as: degradation of the catalyst layer (CL) caused by carbon corrosion due to frequent starts and stops (air fuel front), loss of catalyst active area caused by platinum (Pt) dissolution and sintering due to frequent voltage cycling, loss of catalyst active area due to adsorption of contaminants from the inlet gases, mechanical degradation due to thermal and humidity cycling induced by the load profile as well as by the

environment in which the vehicle operates. However, the loss of catalyst active area caused by Pt dissolution and sintering due to frequent voltage cycling was selected here as the target for the laboratory experiments as the most relevant for the fuel cell systems in automotive application. Furthermore, application of the electrochemical impedance spectroscopy (EIS), as a well-known and already established diagnostic method for various diagnostic purposes [6—12], which enables *in situ* identification and quantification of physical phenomena that influence fuel cell performance, seems to be an adequate method also for degradation tracking to identify the main unhealthy behaviors and their causes in order to define and improve suited control strategies. However, only a handful of studies in literature have already used EIS primarily for catalyst degradation diagnostics of PEM fuel cells [13—17].

Nara et al. [13] developed a novel transmission line (TML) model for the impedance analysis in a low current region to evaluate cathode CL on a PEM fuel cell degraded by an accelerated start-stop degradation method, which involved a potential step cycle of 1.3 V for 30 s and 0.9 V for 30 s at 80 °C, while feeding nitrogen and oxygen to the anode and cathode, respectively. However, the impedances were measured in the frequency range of 10 kHz to 10 mHz, but the lower frequency limit was restricted to 0.5 Hz in the further analysis, because of the TML model limitations in the low-frequency region with an inductive phenomena [18].

Saleh and Easton [14] developed a simple but effective diagnostic protocol for testing the CL degradation. It is based on EIS periodical measurements combined with electrochemical active surface area (ECSA) monitoring using cyclic voltammetry (CV) during an accelerated aging by potential cycling for 4000 cycles (between −0.2 V and 1.2 V in a N_2-purged 0.5 M H_2SO_4 solution at 25 °C). The identification of the CL degradation mechanism(s) for two different carbon catalyst materials and structures was done by tracking the changes in the capacitance plots during the test. In their following paper [15], they have advanced their previous study by investigating the durability of CLs with three different amounts of Pt loading (under triangle sweep cycles between −0.25 V and 1.1 V with 50 mV s^{-1}), which led to a different level of interaction between Pt and the carbon support. However, EIS measurements were conducted at DC bias potential of 0.2 V and between 100 kHz and 0.1 Hz. Together with Reid [16], they have extended previous methodology by varying five different DC bias potentials at which the impedance spectra were recorded during the cycling between 0.056 V and 1.32 V. By doing so, they have derived an expression relating faradaic pseudo-capacitance associated with H_2 adsorption determined by EIS over time and the ECSA determined by CV.

Zhang et al. [17] have conducted an accelerated aging by potential cycling of the cathode (between 0.06 V and 1.2 V for 20 h with 10 mV s^{-1} at 40 °C) of a single PEM fuel cell containing a reference electrode (i.e. dynamic hydrogen electrode), which enabled independent EIS measurements of the anode and cathode to clarify the degradation mechanism(s). An inductive loop was also obtained in the low-frequency region of the impedance spectra, and it was fitted by the second model inductance, but they did not give an explanation for any of the model elements in the equivalent circuit

used for the fitting procedure. Furthermore, two different equivalent circuits were used to obtain the best fits of the EIS spectra before and after the potential cycling, because the inductive behavior was captured before the potential cycling but disappeared after the potential cycling (probably because the lower frequency limit was too high, i.e., 0.1 Hz).

Bezmalinovic et al. [5] have investigated the applicability of the polarization change curves on the accelerated aging of a single cell exposed to potential cycling (between 0.6 V and 0.9 V) with the aim to degrade the Pt catalyst. In order to compare the obtained results with polarization change curves analysis, the other diagnostic tests were also performed periodically during the conducted accelerated stress test, such as EIS, CV and linear sweep voltammetry (LSV). However, the deeper analysis of the EIS measurements was not done, primarily due to lack of a suitable impedance model at the time and because that was not the main focus of this work, but the potential of this method in the diagnosis of CL degradation was noted, which opened up space for further research in the present paper.

On the other hand, based on our recently published review paper [18], the inductive phenomena present in the low-frequency region in form of the inductive loop in the Nyquist diagram at all operating conditions, should certainly be captured in the EIS measurements and modeling of the impedance spectra. As our novel, previously validated impedance model [19] was capable of yielding experimentally obtained low-frequency inductive behavior in the impedance spectra of PEM fuel cells, and as each of the model elements were related to different properties and phenomena in the cell, it should be possible to quantify each model element and monitor their changes over time, i.e., during an accelerated stress test. Therefore, the applicability of the EIS and an already developed impedance model will be investigated here during an accelerated durability test performed on a single cell, in order to develop an effective diagnostic tool for condition monitoring and health assessment of PEM fuel cells.

Experimental

An accelerated stress test (AST) has been performed on a 50 cm^2 active area MEA, produced by BASF (12E-W MEA), within a single PEM fuel cell hardware from Fuel Cell Technologies with graphite four-channel serpentine cathode flow field and single-channel anode flow field. This air-cooled single cell was tested in co-flow configuration. It was exposed to an accelerated stress test for catalyst degradation during which several standard laboratory diagnostic procedures were periodically performed in order to monitor degradation. These diagnostic methods include polarization curves, EIS, CV, and LSV.

The AST, designed to target electrocatalyst degradation, involves 40 s long potential cycling profile (Fig. 1) between voltages of 0.6 V for 10 s and 0.9 V for 30 s, which is slightly modified version of the U.S. Department of Energy (DoE) recommended AST protocol for electrocatalyst degradation [20]. Instead of DoE's cycling between 0.7 V and 0.9 V, cycling was conducted here between 0.6 V and 0.9 V, in order to speed-up the degradation process, and it was stopped after 5000 cycles