

Modelling-Based Diagnostic Method for *Ex situ* Characterization of Pt Degradation

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The cathode catalyst layer in an automotive polymer electrolyte fuel cell is susceptible to degradation during its operational lifetime. The net result of cathode degradation is a decay in operational cell voltage which has been linked to a gradual loss in electrochemically active surface-area of the catalyst. The surface-area loss can be further linked with changes in the size distribution of Pt nanoparticles in the CCL.[1] Though these effects are observed in an operational fuel cell (*in situ*), many studies have focused on degradation of supported Pt nanoparticles in electrochemical cells (*ex situ*) to gain a clearer understanding of the conditions that may influence the rate of surface-area loss as well as the mechanisms that cause it. Potential cycling has been shown to be one of the main accelerating factors of catalyst degradation. The potential cycle wave-form ϕ_{wav} as well as the upper ϕ_{upl} and lower ϕ_{lp1} potential limits of the cycling window have been shown to influence the rates of surface-area loss.[2, 3] Other influencing factors involve the pH and temperature.

The main mechanisms of surface-area loss are (i) dissolution and re-deposition or Ostwald ripening, (ii) coagulation or coalescence, sintering, agglomeration and (iii) particle detachment.[4] Discerning mechanisms as a function of operational conditions is of tremendous value for materials scientists as different mechanisms can be related to different material properties. For example, a coagulation or detachment mechanism may be more related to support properties whereas a dissolution mechanism would be more related to the properties of the catalyst. In Refs. 5, 6 and 7 we developed a theory of Pt mass balance that accounts for the 3 main mechanisms of surface-area loss.

In pursuing diagnostic applications of the model jointly with experimentalists we present here an extensive set of electrochemical surface-area loss experiments probing the impact of ϕ_{wav} , ϕ_{upl} and temperature. With their high temporal density these experiments serve as the primary source for diagnostic analyses. Transmission electron microscopy (TEM) coupled with particle image analyses software is used for the extraction of initial conditions and inductively coupled mass spectrometry (ICP-MS) is used for secondary diagnostic evaluation. Our Pt mass balance model unifies the aforementioned approaches and accordingly discriminates the predominant degradation mechanisms. We find that dissolution and re-deposition seems to be the most reasonable mechanism for describing surface-area loss in these experiments and that ϕ_{upl} has the largest influence on model parameters. The model parameters are relatively insensitive to temperature and potential wave-form. The effect of ϕ_{upl} on the model parameters are consistent with Pt dissolution studies. More specifically, there is an increase in 2 orders of magnitude of the Pt dissolution rate when ϕ_{upl} is increased from 900 mV to 1200 mV. Fig. 1 shows the experimental data and model-based analysis performed

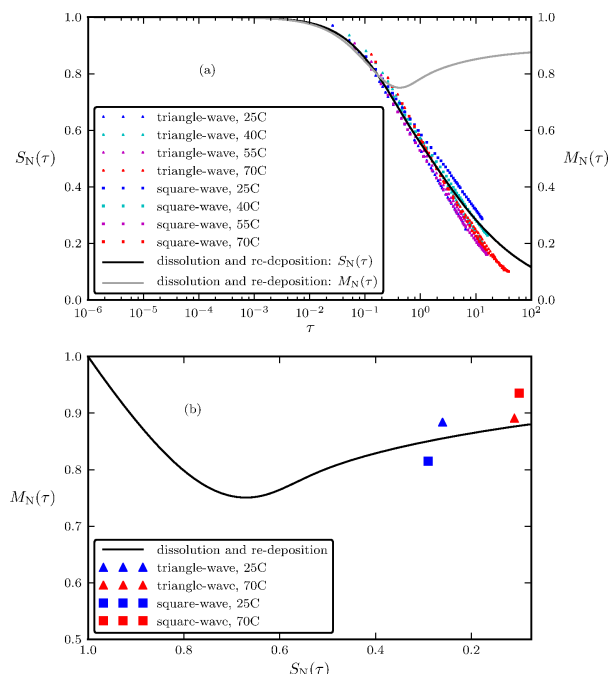


Figure 1: In (a) we show plot of model calculated catalyst surface-area $S_N(\tau)$ (black solid line) and mass $M_N(\tau)$ (gray solid line) as a function of dissolution rate-scaled dimensionless time τ and corresponding electrochemical surface-area measurements (points). The corresponding moment-comparison (black solid line) showing $M_N(\tau)$ plotted against decreasing $S_N(\tau)$ is given in (b) with the experimentally determined comparison between end-of-test catalyst mass (ICP-MS) and surface-area (electrochemical).

for the 1200 mV study. Some initial results regarding the effects of pH on surface-area loss are also discussed.

References

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