Platinum Durability in Cathode Catalyst Layers of PEM Fuel Cells: An Ex situ Diagnostics Approach

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Proton Exchange Membrane Fuel Cells (PEMFCs) are deemed a viable alternative to the Internal Combustion Engine (ICE) currently used today in automotive propulsion. The impending future depletion of fossil resources and the need to reduce greenhouse gas emissions has motivated tremendous interest in the development of PEMFCs during the past 30 years. PEMFC generates electrical power by direct conversion of chemical energy (H_2 and O_2), with water as the only reaction product. The efficiency of PEMFC stacks is significantly higher than ICE (Carnot limitations). [1]

However, automotive PEMFC technology development is still hampered by sever issues such as the price of components (catalytic layers and membrane). The low durability of the electrocatalyst in the cathode catalytic layer is another challenge. Indeed, under automotive operation conditions, the Cathode Catalytic Layer (CCL) is subject to high potential changes during idle-to-peak cycles (typically from almost 1.2 to 0.6 V) and the potential in the CCL can reach 1.5 V during the PEMFC shutdown and startup. Additionally, other severe conditions observed in catalytic layers (ie. very low pH, relative humidity cycling from dry layer to fully hydrated and temperature fluctuations) result in more pronounced degradation of both Platinum (Pt) catalyst and carbon support. The combination of these different effects leads to PEMFC performances loss due to a decrease in electrochemically active surface area (ECSA) and a concurrent drop in the activity of the Oxygen Reduction Reaction (ORR). Today, the understanding of the degradation mechanisms in the CCL is a key objective in efforts to create improved electrocatalysts while keeping a sufficient catalytic activity toward ORR. [2]

In order to study these degradation mechanisms, a systematic diagnostic approach has been developed. Defined Accelerated Stress Tests (ASTs) were applied consisting in fast potential perturbations from 0.6 V to different upper potential limits using a thin film catalyst on glassy carbon in liquid electrolyte. All tests were performed in the absence of ionomer. During this work, multiple parameters have been investigated: the shape of the potential perturbation profile (triangular versus square waves), the effect of the upper potential limit (0.9 V for idle operation or 1.2 V to emulate fuel cell shutdown), the effect of temperature ranging from 25 to 70°C and the influence of pH in order to study the importance of dry to hydrated cycles encountered during a fuel cell operation.

The ASTs consisted in a total of 25,000 perturbation cycles to have a global idea on the degradation behavior under each of the aforementioned variations. At the end of

each experiment, the remaining thin catalyst film was recovered to determine the morphological changes in terms of particle size distribution, particle density and carbon corrosion by using transmission electron microscope (TEM). The Pt mass balance was assessed by analyzing a sample of electrolyte using Inductively Coupled Plasma/Mass Spectroscopy (ICP/MS) allowing us to determine the total dissolved platinum content combined with TEM and ECSA.
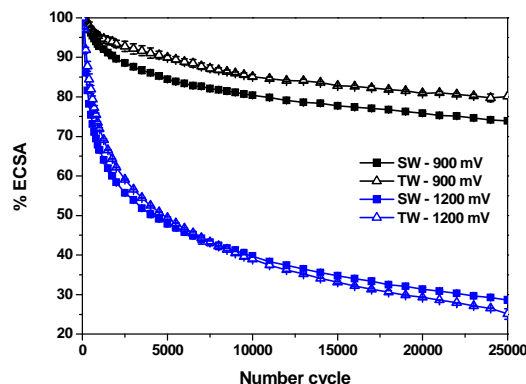
Figure 1: ECSA loss profile during AST, effect of the potential perturbation profile and the upper potential limit
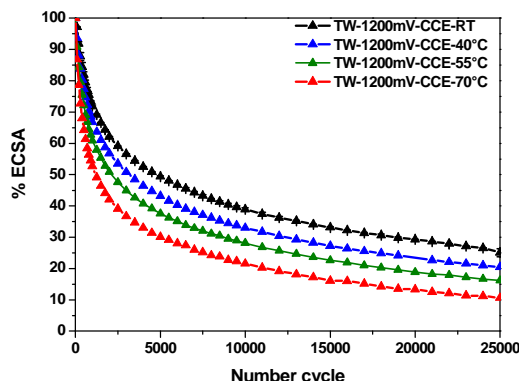
Figure 2: Effect of the temperature on the ECSA loss rate during triangular wave with an UPL of 1.2 V

The results presented in Figure 1 indicate a low effect of the potential perturbation profile (particularly when the UPL was fixed at 1.2 V) on the final ECSA loss. As expected, the UPL has a strong effect on the degradation rate and it clearly indicates that most of the catalytic layer degradation occurs during simulated startup/shutdown cycles with a total loss of 70% of ECSA after 25,000 cycles at room temperature. Moreover, the temperature is also drastically affecting the rate of ECSA loss (Figure 2). Showing an increase in the degradation as the temperature was raised for both UPLs and perturbation profiles studied. Finally preliminary results show that decreasing the pH leads to a high platinum dissolution rate and also to pronounced carbon corrosion. In addition, the TEM analysis of the aged catalyst layers will be presented in order to provide a global understanding on the effect of operational conditions on the degradation mechanisms of supported Pt-based catalysts used in CCL of PEMFCs.

References:

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