

Non-equilibrium interfacial electrochemical phenomena in aging PEM Fuel Cells: a new theory for multi-scale simulation of nano-structured catalysts degradation and durability prediction

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Activity, selectivity and stability of PEMFC nano-structured catalysts are strongly linked properties, highly dependent on composition and nano-morphology (e.g. structural changes produced by an alloy). Deep theoretical understanding of electro-catalysis is crucial to provide rigorous physical-based interpretation of experimental observables, and thus to open new guidelines for engineering breakthroughs on PEMFC MEA performance and durability improvement research. Nano-structured catalysts degradation in state-of-the-art PEMFC is one of the main shortcomings limiting the large-scale development and commercialization of this zero-emission power technology. It is largely observed that the nano/micro-structural properties of Pt and Pt-alloy electrodes evolve during the MEA operation, limiting the PEMFC lifetime [1-5]. These spatiotemporal nano/micro-structural changes are strongly dependent on the PEMFC operating conditions and translate into the cell potential degradation. Elementary mechanisms behind PEMFC nano-structured catalysts aging are however difficult to understand. Water splitting and hydroxyl adsorption are speculated to modify the surface Pt-alloys dissolution thermodynamics [6]: thus, the stability properties of nano-structured catalysts (e.g. facility to oxidize) can be strongly affected by the electrochemical reactions of interest in PEMFC environments, such as the HOR or the ORR. Structure and interatomic distance can also change during reactant (H_2 or O_2) exposure [7] or liquid adsorption. For example, surface segregation of Pt-Rh nano-clusters is dramatically altered by hydrogen chemisorption [8]: in the absence of hydrogen, the cluster surfaces are Pt-rich, but in the presence of hydrogen, the cluster surfaces can be Rh-rich (“reversing segregation” or “reconstruction” phenomena). Some mathematical models have been proposed to describe PEMFC catalysts degradation [9]. Despite that these models provide useful information, they are, in our opinion, supported on small physical basis, in particular regarding the electrochemical processes: the main drawbacks of these models are that they 1) don't provide connection with first-principles and surface science data: global electrochemical reactions (e.g. catalyst oxidation) are fitted with ex-situ experimental data at specific operating conditions not necessary representative of realistic PEMFC operating conditions; 2) don't provide prediction of materials durability and cell potential degradation: the models are steady-state and local operating conditions are assumed to be invariant during the PEMFC operation (the impact of the modeled degradation phenomenon on the structural and physico-chemical properties of the MEA materials - e.g. variation of the specific electrode activity, variation of porosity...- appears to be unexplored); 3) use the classical Butler-Volmer theory to describe the degradation kinetics and global HOR and ORR (e.g. Pt oxidation/dissolution or carbon support corrosion): the

electrochemical double layer capacity is usually assumed to be constant (i.e. the double layer structure is assumed to be uncoupled from the electrochemical reactions). In our opinion the use of Butler-Volmer theory cannot be justified for describing electron transfer reactions on nano-materials with an evolving structure (in fact, standard Butler-Volmer transition-state theory assumes that the “catalyst” properties, by definition of “catalyst”, are time-invariant).

In this paper we discuss a new extended first-principles-based transition-state theory proposed by us allowing describing non-equilibrium electrochemical processes (such as HOR and ORR) on aging bi-metallic nano-structured catalysts with evolving activity and stability properties. The theory accounts for the 1) feedback between the electrochemical double layer structure evolution and the detailed elementary kinetics of degradation and electrochemical reactions related to the PEMFC demanded current; 2) the impact of the instantaneous intermediate reaction specie coverages on induced-reconstruction phenomena and intrinsic stability properties. In this paper, the practical theory application is illustrated through simulation results of PEMFC cathode Pt_x-M_y catalysts oxidation, dissolution and electrochemical ripening (with M being a transition metal element) in comparison with experiments. These results are obtained by coupling Monte Carlo simulation method for catalyst nanostructure prediction during its degradation [1-2] and non-equilibrium thermodynamics/mean field kinetic simulations for the calculation of the PEMFC electrodes potential degradation: this methodology allows predicting nano-structured catalysts durability and provides new and useful mechanistic insights on degradation physicochemical phenomena at the nano-scale (Fig.1).

References

- [1] A. A. Franco, S. Passot, P. Fugier, C. Anglade, E. Billy, L. Guetaz, N. Guillet, S. Mailley, *ECS Trans.*, **13** (17), 29 (2008).
- [2] A.A. Franco, S. Passot, P. Fugier, C. Anglade, E. Billy, L. Guetaz, N. Guillet, S. Mailley, *J. Electrochem. Soc.*, in press (2008).
- [3] A. A. Franco, M. Gerard, *J. Electrochem. Soc.*, **155** (4) B367 (2008).
- [4] A. A. Franco and M. Tembely, *J. Electrochem. Soc.*, **154** (7) B712 (2007).
- [5] A. A. Franco, *ECS Trans.*, **6** (10) 1 (2007).
- [6] J. Greeley, J. K. Norskov, *Electrochim. Acta*, **52**, 5829 (2007).
- [7] R. Choukroun, D. de Caro, B. Chaudret, P. Lecante, E. Snoeck, *New J. Chem.*, **25**, 525 (2001).
- [8] L. Zhu, R. Wang, T. S. King, A. E. DePristo, *J. Catalysis*, **167**, 408 (1997).
- [9] R.M. Darling, J.P. Meyers, *J. Electrochem. Soc.*, **150**, A1523 (2003).

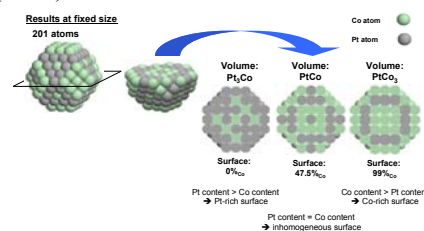


Fig.1: cut views of nanoparticles of 201 atoms (1.6 nm) after Monte Carlo simulations for three different atomic compositions. $PtCo_3$ is expected to be more unstable (towards both chemical leaching and polarization) because instantaneously contains more Co atoms at the surface [2].