

Fundamental Studies at Electrochemical Interfaces using in situ Synchrotron Spectroscopy: Case study on Electrocatalysts for the Next Generation of Low and Medium Temperature Fuel Cells

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Abstract

This presentation will provide an introduction to materials considerations as it pertains to design of electrocatalysts for Polymer Electrolyte Fuel Cells (PEMFCs). New insights on structure property correlation for electrocatalysts and their interactions with the solid polymer electrolyte will be presented in the context of the unique environment afforded by these nano-phase composite structures. The relatively high overpotential for cathodic oxygen reduction will be discussed in terms of interplay of molecular oxygen adsorption and water activation pathways on Pt and Pt alloys^{1,2} as well as the more complex reaction environment in chalcogenides³ and enzymatic mimics. Some new insight on the effect of electrocatalyst morphology and kinetics of direct methanol oxidation will be presented⁴, together with the effect of Ru dissolution and migration⁵. In these systems the role of the reaction center will be presented in light of new data from synchrotron based *in situ* X-ray absorption spectroscopy measurements which are more specifically tailored towards elucidation of surface adsorption modes. This new methodology referred to as the Delta μ -Technique uses recently developed code (FEFF-8) to simulate multi-electron scattering from XAS to simulate the near edge part of the spectra called x-ray absorption near edge structure (XANES)⁶⁻⁸. This in conjunction with the extended part of the spectra, referred to as extended x-ray absorption fine structure (EXAFS) is used to generate a complete map of the electronic and structural changes on the transition metal reaction center as a function of reactant composition, interfacial water activity as well as electrode potentials. A combination of theory and experiment (classical electrochemistry and synchrotron based *in situ* x-ray absorption spectroscopy), will show specific pathways for electrocatalysis as a function of overpotential. Besides this, free radical initiated chemical attack at the electrocatalyst-electrode interface will also be shown, wherein the degradation mode of the surrounding ionomer will be discussed in the context of peroxide generation. The theoretical contribution will be based on an ab-initio charge self-consistent method for predicting redox reaction energies and electron transfer activation energies for reactant and products solvated in bulk solution.

References

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