Size and composition distribution dynamics of Pt alloy nanoparticle electrocatalysts probed by Anomalous Small Angle X-ray Scattering (ASAXS)

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Introduction

Probing and understanding of structure-property relationships of high surface area Pt and Pt alloy nanoparticle electrocatalysts represents one of the biggest challenges in the field of energy-related electrocatalysis. What is needed are methods to study the size, the bulk composition as well the surface composition of alloy particle ensembles during reaction conditions.

Synchrotron-based Small Angle X-ray scattering (SAXS) is a reciprocal-space method that is suited for the investigation of particles in the 1-100 nm diameter range. SAXS can be used ex-situ and in-situ and is therefore a powerful technique to study changes of the size distribution of nanoparticles during the catalytic reaction. Element specificity is introduced by varying the incident X-ray energy (Anomalous SAXS, ASAXS)[1]. Using ASAXS, one can measure the particle size distributions of Pt and one or more transition metals independently. Hence, on top of size distribution information, in-situ ASAXS allows to probe the dynamics of composition distributions and metal enrichments due to corrosion, leaching, or dissolution.

In this contribution, we highlight and illustrate the benefits of ASAXS analytics when applied to nanoparticle electrocatalysts for the electroreduction of oxygen inside gas-diffusion layers. In particular, we address carbon supported Pt-Co and Pt-Cu alloy nanoparticles cast in thin Nafion® containing layers and discuss their size and composition dynamics under various electrochemical conditions.

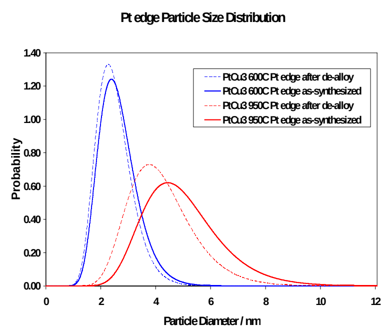
Materials and Methods

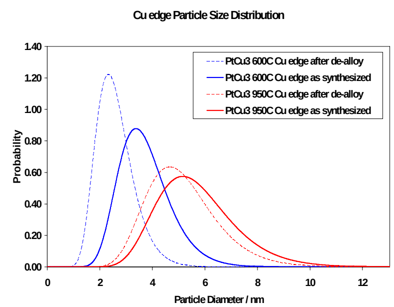
Anomalous small angle X-ray scattering (ASAXS), a better way to remove background scattering, is by making measurements at two different X-ray energies near the absorption edge of the metal in the catalyst. The difference in the scattering at the two wavelengths should consist essentially of the scattering of the metal. In this study, we used synchrotron-based anomalous small angle x-ray scattering (ASAXS) at Stanford Synchrotron Radiation laboratory. The alloy catalysts used in this study were prepared from commercially available Pt/C catalyst (TKK, 28.2 wt % of Pt), by adding proper amount of De-ionized water containing appropriate amounts of solid Cu precursor ($Cu(NO_3)_2 \cdot 6H_2O$, Sigma Aldrich #239267), then, the mixture was ultrasonicated to form a thick slurry. The catalyst synthesis mixture was subsequently frozen in liquid nitrogen, and then freeze-dried in vacuum (50 mTorr) overnight at room temperature. The resulting powders were annealed in a flow furnace with a constant gas mixture flow containing 4% hydrogen. for 7 hours at specific temperature.

Results and Discussion

Size distribution of the platinum particles was obtained by fitting the ASAXS data using a log-normal distribution. Preliminary results showed a general decrease in particle size upon undergoing electrochemical testing. Also, the results showed that the particle size increase with the annealing temperature increase. The ability of ASAXS to probe specific element within the catalyst nanoparticles also allowed us to track the changes in each elements present in the catalysts and hence compare the differences in the effect of treatment in each element. The result indicated that Cu particle size normally bigger than the Pt particle size for the same catalyst. Also, for Pt and Cu edge measurement, "the particle size changing after electrochemical testing" is different. A comparison of different distribution curves of the same catalyst after different leaching conditions showed size changes, which in turn indicated implications to the catalyst's stability and durability during fuel cell operation.

Significance





References

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