Segregation is an important physical phenomenon in alloy materials and has significant influences on the physical and chemical properties. In particular, segregation at the surface or subsurface can drastically change the molecular adsorption properties of alloy surfaces and thus becomes a promising way to design highly active catalysts. Atomic understanding of segregation effect in nanoscale alloy catalyst particles is therefore crucial yet still challenging for future catalyst designs.

In this talk, we will highlight some of our recent works on understanding and controlling nano segregation effect in advanced Pt alloy catalysts for fuel cell technologies. We demonstrate how alloy composition (Fig. 1), particle size (Fig. 2), and particle shape (Fig. 3) can result in different segregation behaviors in Pt alloy nanoparticles and thus drastically influence their catalytic activity and stability. Focus will be placed on the atomic imaging of nano segregation by using state-of-the-art aberration-corrected scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) and in situ experiments. In particular, by using STEM-EELS elemental profile/mapping, we revealed novel compositional segregation patterns in Pt$_{x}$Ni$_{1-x}$ core-shell nanoparticles, showing an unexpected Ni-segregated inner shells depending on the bulk alloy composition (Fig. 1). Furthermore, we discovered a distinctly different compositional segregation in octahedral Pt$_{x}$Ni$_{1-x}$ nanoparticles, which featured a surprising Pt segregation at the edges/corners and Ni segregation at the facets (Fig. 3). We explored the physical origin for these distinct segregation behaviors and their impact on the catalytic activities and stability for fuel cell reactions. This will be further complemented by in-situ STEM-EELS experiments to study the structural and compositional evolution of Pt alloy nanoparticles during nanoparticle synthesis, post thermal annealing, and solution-phase electrocatalysis, shedding important light for catalyst designs with desired segregation patterns and chemical properties.

References:

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Fig. 1: Aberration-corrected STEM-EELS elemental profiles of dealloyed PtNi (a, d), PtNi3 (b, e) and PtNi5 (c, f) core-shell NPs, showing near-surface Ni-rich inner shells.

Fig. 2: STEM images and EELS line profiles of size-selected spherical PtNi3 catalyst after stability test. Nanoporous particles formed at larger sizes (ca. 10 nm) and, consequently, lower near-surface Ni content as well as larger Pt shell thickness.

Fig. 3: EELS elemental mapping of octahedral PtNi1.5 nanoparticles along (a) <110> direction and (b) <100> direction, showing that Pt segregated at the edges and corners whereas Ni segregated at the facets. (c) The revealed structural model.