

## Atomic Imaging and Spectroscopy of Size- and Shape-Dependent Degradation of Pt Bimetallic Fuel Cell Catalysts

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Over the past two decades, Pt bimetallic alloys have been considered promising candidates as oxygen reduction reaction (ORR) catalysts for polymer electrolyte membrane fuel cell (PEMFC) cathodes. It is only since recent years that innovative surface and subsurface alloy structures and morphologies, such as Pt skins, Pt monolayers, Pt core-shell particles, size and shape-controlled Pt particles, and Pt nanostructured thin films are being explored and uncovered with activity enhancements approaching, meeting, or exceeding PEMFC commercialization targets.<sup>1</sup> However, for viable PEMFCs, not only initial sufficient beginning of life activity but also long-term durability is needed, which has remained an unachieved goal.

Here, we present our recent works on and atomic insight in the development of active and stable Pt-Ni catalysts based on aberration-corrected scanning transmission electron microscopy (STEM) and spectroscopic (EELS) studies.<sup>2-4</sup> We demonstrate that how atomic core-shell fine structure,<sup>2</sup> size-related nanoporosity,<sup>3</sup> and nanoparticle shape<sup>4</sup> can influence the activity and, more importantly, the stability of Pt-Ni bimetallic nanoparticles for ORR electrocatalysis. The key point is to control the particle size below a critical value (ca. 10 nm) to avoid nanoporosity formation (Figure 1), i.e., retain a solid core-shell structure, which is critical for retaining a high Ni content at subsurface layers leading to high surface reactivity.<sup>3</sup> Shaped Pt nanoparticles exhibited exceptional high initial activity yet suffered from severe degradation. Specifically, we uncovered an unique intraparticle compositional segregation in pristine octahedral Pt-Ni nanoparticles, showing the Ni segregation at the facets and Pt segregation at the edges/corners (Figure 2).<sup>4</sup> Such segregation led to drastic Ni dissolution from the facets and hence severe activity degradation. Our results provide important insights for designing new generation Pt fuel cell catalyst with both high activity and high stability.

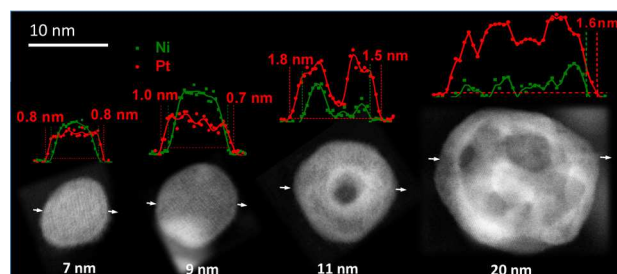


Figure 1. Aberration-corrected STEM images and EELS line profiles of size-selected spherical PtNi<sub>3</sub> catalyst after stability test. Nanoporous particles formed at larger sizes (ca. 10 nm) and, consequently, lower Ni content as well as larger Pt shell thickness, which became one of the major reasons for activity degradation.<sup>3</sup>

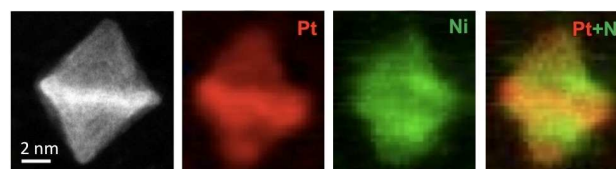


Figure 2. Aberration-corrected STEM images and EELS mapping of octahedral PtNi<sub>1.5</sub> nanoparticles, showing the segregation of Ni at facets that played a critical role in their activity degradation.<sup>4</sup>

### References

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