

Au-Ni@Pt Electrocatalysts for the Oxygen Reduction Reaction: Structural Effects of Cores

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The commercialization of the proton exchange membrane fuel cell (PEMFC) is impeded by high price of catalysts caused by the sluggish kinetics of the oxygen reduction reaction (ORR) occurring at the fuel cell cathode even on platinum the most efficient monometallic catalyst.¹ One promising way of resolving this impasse involves using electrocatalysts comprising of a Pt monolayer (one atom thick layer) on the substrates of a second metal or metal alloy. This improves the electrocatalyst performance, and also reduces the Pt content. The synthesis of active, durable and cheap substrate for the Pt monolayer is one of the urgent needs for developing ORR catalysts. It is generally accepted that the substrates induced lattice strain in Pt monolayer plays an important role in determining the catalysts' properties^{2,3}.

Here we report on a new class of these electrocatalysts consisting of Pt-monolayer shell on Au-Ni core nanoparticle. Pt monolayer deposition is based on displacement of the underpotential deposited Cu monolayer.⁴ To understand the effect of substrates on the Pt monolayer we prepared an AuNi alloy and Ni@Au core-shell nanoparticle substrates using various synthetic techniques.

The synchrotron x-ray diffraction patterns from AuNi alloy and Ni@Au core-shell nanoparticles showed distinct features. The AuNi alloy nanoparticles exhibited four pronounced peaks between Au and Ni reflection peaks, indicating the formation of a solid solution structure. On the other hand, additional peaks were observed on the pattern from the Ni@Au core-shell nanoparticles, which may be due to the formation of Ni-rich cores. The formation of AuNi alloy and Ni@Au core-shell nanoparticles has also been verified by scanning transmission electron microscopy (STEM) coupled with electron energy-loss spectroscopy (EELS) and x-ray absorption spectroscopy (XAS). The Pt mass activities for the Pt_{ML}/AuNi/C electrocatalyst are higher than Pt_{ML}/Ni@Au/C and commercial Pt/C electrocatalysts. The high activity observed can be ascribed to the structural- and electronic interaction between the Pt monolayer and the Au-Ni nanoparticles. The results demonstrate that using Pt monolayers on alloy nanoparticles can resolve key ORR problems while minimizing the Pt loading.

Further discussion of these results will be presented at meeting.

References

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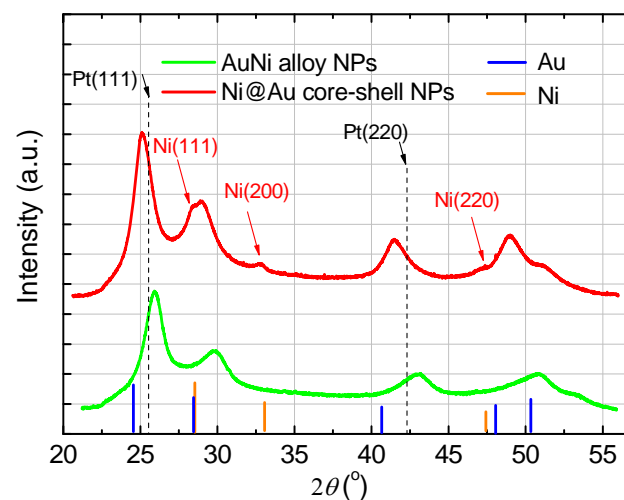


Fig.1. X-ray powder diffractions from AuNi alloy and Ni@Au core-shell nanoparticles (the wavelength = 1.0 Å).

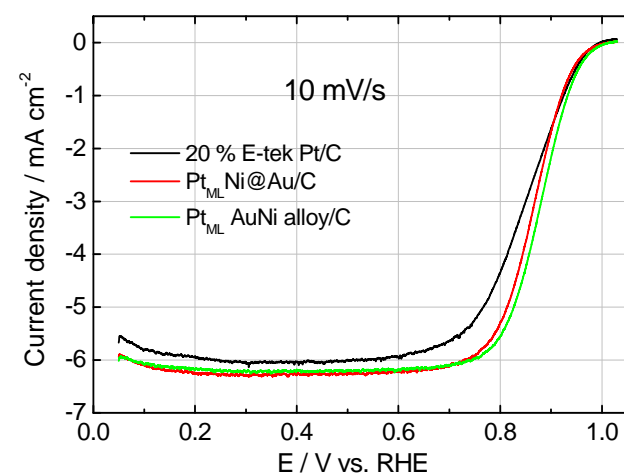


Fig.2. ORR curves with different samples in O₂-saturated 0.1 M HClO₄.