

Understanding the Durability and ORR Reactivity of Four Different Dealloyed PtNi_x Cathodic Catalysts

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Recently[1] we reported the activity and durability of a wide range of de-alloyed PtNi catalysts (4 different catalysts at 3 different stages of life) tested in PEM fuel cells. The factors include, as summarized in Table 1, the PtNi₃ precursor (A or B), the acid used for leaching the Ni (HNO₃ or H₂SO₄ denoted NA or SA), the time and dealloying temperature (time [hrs]/ temp[°C]), and the use of a post-dealloying thermal anneal in 5% H₂/N₂ at 400 °C for 4hrs (denoted un-annealed or annealed). Initial (BOL) ORR mass activities (A/mg-PGM at 0.9 V RT) and that after 10k and 30k cycles (following DOE protocol [2]) are given. All catalysts exceed the DOE 2017 BOL mass activity target (0.44A/mg-PGM at 0.9 V_{IR free} [2]), but have widely varying durability. Understanding the durability and its dependence on particle morphology requires knowledge of many properties such as the final Pt/Ni atomic ratios, outer Pt skin thickness, and nature of Pt sites on the outer surface; properties difficult to experimentally obtain.

Table 1 Mass activity (A/mg-PGM) of the PtNi_x catalysts

Pre	Acid	t/T	An	BOL	10k	30k
A	NA	24/70	ua	.50	.25	.17
B	NA	24/70	ua	.75	.66	.47
B	SA	24/80	ua	.64	.61	.51
B	SA	24/80	a	.48	.57	.56

The PtNi de-alloyed catalysts were characterized structurally with HAADF/EELS [3] and by XAS using Pt L₃ and Ni K-edge EXAFS and Δμ XANES [4]. The Ni K-edge ΔμXANES provides unique information on the Pt skin porosity and/or thickness and the Pt L₃ Δμ XANES on the adsorbate coverage and binding site information for adsorbates such as O(H)* (adsorbed O or OH) and OO(H)* (undissociated O₂ or OOH) on the Pt [4]. It is possible to follow these adsorbate coverages on the cathode in either N₂ or O₂ saturated electrolyte (0.1 M HClO₄). The O(H)* coverage with N₂, arises just from water activation, with O₂ from water and O₂ activation.

Previously [4], we reported the first *in situ* measurement of OO(H)* and O(H)* coverage on the PtNi_x A-NA catalyst along with two PtCo catalysts in O₂ using the Pt Δμ XANES. The Sabatier principle [4] was confirmed, with the non-dissociative mechanism rate-determining on the Pt-O weak side, and the dissociative mechanism on the strong side of the volcano maximum. The lattice compression in the Pt skin appeared to dominate for the dealloyed PtM_x catalysts examined in that work, as indicated by the ordering with EXAFS Pt-Pt distances.

As illustrated in Fig. 1, the Ni Δμ XANES reveals the growing thickness of the Pt skin with cycling on the PtNi_x A-NA catalyst. HAADF data show that the A-NA catalyst at BOL has a multicore structure with a porous Pt skin [3]. This was confirmed by the Ni |Δμ| XANES showing Pt-O contact below 0.5 V, as the adsorbing O from water activation could easily gain access to the near

surface Ni. After cycling for 10k, the Pt skin is significantly enhanced, since penetration by the O is not evident until around 0.85 V. This is true in both N₂ and O₂, but the presence of a greater electronic ligand effect from the adsorbed molecular species in O₂ is clearly evident. After 30k cycles, penetration of the Pt skin is not evident until potentials well above 1.0 V, suggesting a much thicker Pt skin. Note the strong inhibition of water activation in the presence of O₂, as atomic O from the water must now compete for Pt sites with the molecularly adsorbed OO(H)* species.

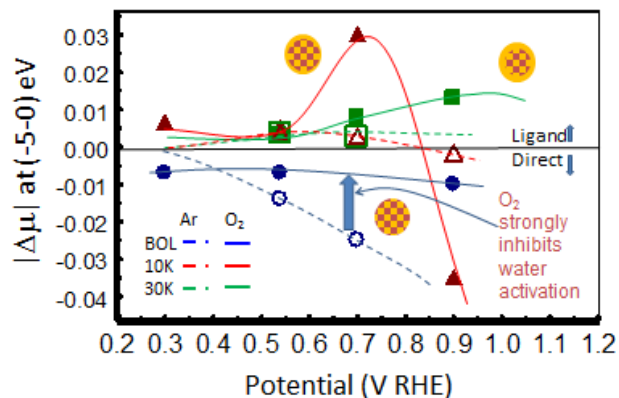


Fig. 1 The magnitude of Δμ (|Δμ|) in the range of -5 to 0 eV for the PtNi_x A-NA catalyst, reflecting an electronic ligand effect when positive and direct Ni-O contact when negative. The increasing relative Pt skin thickness with cycling is indicated schematically.

The Δμ results for the PtNi_x with B precursor and with greater durability clearly show that this arises from the initially thicker Pt skin. Further, this skin appears to thin with cycling, suggesting that the cycling produces a characteristic thickness; the Pt skin thickness is increased when it starts out thin in the A-NA catalyst, but it is reduced when it starts out thick in all of the B catalysts. The thickness of the Pt skin determines the rate of leaching of the Ni, and therefore has a profound effect on the durability of the catalysts, and the Pt skin thickness does not appear to strongly alter the ORR activity.

Post annealing is found to significantly reduce O(H)* and enhance OO(H)*, indicating the strong reduction of active Pt corner and edge sites by the anneal process, and their return and increase in ORR activity after 10k cycles.

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