

Electrochemical Properties and Electronic Structure of Ni₇₀Pt₃₀ Thin Films On High Surface Area Nstf Supports

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In an effort to reduce the platinum group metal (PGM) loading for the cathode in hydrogen-air fuel cells, recent reports have shown that Pt-deficient alloys in the Ni_{100-x}Pt_x binary series exhibit anomalously large oxygen reduction reaction (ORR) current densities at 0.9 V (vs. NHE), for x ~30% (At.%)¹. In this report, Ni₇₀Pt₃₀ thin films on 3M NSTF supports were prepared by sequential sputtering techniques, i.e., bi-layer synthesis, followed by surface treatments to promote alloy formation. To help elucidate the physical mechanisms responsible for this behavior, we have studied in depth, Ni₇₀Pt₃₀ films deposited onto NSTF supports by dc-magnetron co-sputtering. In general, NSTF surfaces exhibit an ~10-fold increase in surface area compared to a flat extended surface. In this presentation, we will present measurement results from microstructural (SEM and TEM), composition, and electrochemical property measurements [hydrogen-oxidation-reaction (HOR) & oxygen-reduction-reaction] conducted on co-evaporated research grade Ni₇₀Pt₃₀ NSTF-supported specimens. Our TEM results for co-sputtered Ni₇₀Pt₃₀ NSTF show that complete alloy formation takes place on nm length scales, with no evidence for short range chemical ordering or composition segregation. Hence, the co-sputtered alloys do not require any post deposition surface treatments. The Ni₇₀Pt₃₀ NSTF dendrites exhibit a strong (111) crystallographic orientation. Our TEM measurements conducted on 3M supplied sequentially sputtered NSTF supported Ni₇₀Pt₃₀ films, reveal that alloy formation is not fully complete, with remnant composition variations along individual whisker dendrites, and at the NSTF tip. The electrochemical properties of the films were measured using the rotating-disk-electrode techniques, in a 0.1 N perchloric acid electrolyte. Our cyclic voltammetry measurements reveal that the fresh alloy surfaces are not electrochemically stable in the 0.1 N perchloric acid electrolyte, with a significant charge loss occurring in the first few hundred potential cycles (1/2-CVs). Eventually, the rate of dissolution of Ni from the surface is reduced with continued potential cycling, as the surface compositions shifts towards a more Pt-rich composition (~50-50). After significant cycling, the loss of Ni still occurs, even though the CVs obtained, exhibit primarily a prototypical Pt character with HOR peaks manifest by normal potential dependent surface reconstructions, of Pt character. Our RDE obtained ORR results on JPL prepared Ni₇₀Pt₃₀-NSTF films, are in agreement with those presented by Debe *et al.*¹ In a companion presentation at these proceedings, we will present the results of ORR measurements in the Pt-Ag composition manifold, which shows that this phenomena, is a universal trend in properly designed and prepared; binary and multi-component alloys with Pt.

Based on our cumulative results in a wide range of Pt-based alloys, we will discuss how the electronic structure and the corresponding composition dependence for the ORR are well described by considering the variation in d-band filling, within the Pt 5d band, as the composition is varied in each alloy system.

References

[1] M. K. Debe M. K.; A. J. Steinbach A. J.; G. D. Vernstrom et al., J. Electrochemical Soc. 158, B910 (2011).

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