

Electrochemical Properties and Electronic Structure of Crystallographically Oriented Ag_{100-x}Pt_x Thin Films

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As in their acid electrolyte PEMFC counterparts, the electrocatalysts for alkaline-membrane fuel cells (AMFC) are required to exhibit high activity for the hydrogen oxidation reaction (HOR, anode) and oxygen reduction reaction (ORR, cathode). For PEMFCs, the platinum group metals (PGM) Pt, Pd, and Ru, and their alloys, e.g., with 3d transition metals like Co, Ni, and Fe, are the only materials to date that provide adequate activity. Fortunately, the greater stability of many metals in alkaline media, as compared with acidic media, means that a much greater range of materials may be available for use in AMFC electrodes; including some that are inexpensive and abundant. However, even though there exists a greater potential for chemical stability, the activity of these materials for use in AMFCs is still in question.

In this contribution, we will present detailed measurements of the microstructural, crystallographic, and electrochemical properties, for crystallographically oriented Ag_{100-x}Pt_x thin film alloys. This alloy system was selected as a model system in alkaline electrolytes, to determine if the anomalously large ORR current densities at 0.9 V (vs. NHE), observed for Pt-deficient alloys in the Ni_{100-x}Pt_x binary series, observed in perchloric acid solutions, translated to a similar alloy system, albeit with the electrochemical properties examined in a 1M KOH electrolyte.¹ The Ag-Pt alloys were prepared in the form of multi-electrode arrays using combinatorial film deposition methods; which enabled the simultaneous synthesis of a wide range of alloy compositions for evaluation.^{2,3} All multi-electrode arrays consisted of 18 thin film electrodes, which were deposited using a three-step physical masking method.

The results of x-ray energy dispersive analysis (EDAX) measurements on the Ag-Pt array reveal that the range of Pt content was 27 < x < 80 At. %. The results of scanning electron microscopy (SEM) measurements, collected at a magnification of 100 kX, reveal that the microstructures of the catalyst films were single phase, with an average grain size of 40-50 nm. X-ray diffraction measurements performed also reveal that the films were single phase. The linear trend of (111) plane lattice constant values, are characteristic of solid solution behavior (i.e., they obey Vegard's law).

Using the multi-electrode, high-throughput, electrochemical technique developed at JPL, we examined the electrochemical properties of the Ag_{100-x}Pt_x thin films. We will present the ORR polarization behavior, HOR electrochemically active surface area (ESA), and durability for multiple thin film specimens. RDE measurements were also conducted on pure Ag surfaces. The Ag surface does not exhibit any hydrogen underpotential adsorption (H_{upd}) or HOR currents over the potential range 0 – 0.4 V (vs. NHE). A small current wave observed between 0 – 0.4 V, is attributed to the adsorption of OH⁻ onto the surface. In the 1.0 M KOH solution, the dissolution of Ag is delayed to potentials V > 1.1 V (vs. NHE). However, when alloyed with Pt, our experimental results indicate that oriented Ag-Pt (111) thin films are not stable in the 1 M KOH electrolyte for Pt-deficient compositions, with the alloy surfaces only becoming stable for Pt contents of greater than 25 atomic percent.

Unlike Ag surfaces, the Ag_{100-x}Pt_x thin films exhibit both H_{upd} and HOR current waves over the potential range 0 – 0.4 V (vs. NHE). The Ag₅₅Pt₄₅ (At.%) surface demonstrates a strong H_{upd} region on cathodic sweeps towards 0 V (vs. NHE). The HOR ESA exhibits a strong dependence on the Ag content, with a maximum for Ag₅₅Pt₄₅ (At.%); ESA = 232.75 μC/cm². Surprisingly, even with 55% Ag, the ESA is commensurate with the ESA values observed on (111) Pt.⁴ The comparable magnitude of the ESA value obtained on Ag₅₅Pt₄₅, suggests that the surface is fully reconstructed to Pt. The CV for this composition exhibits all of the features normally associated with that of a (111) Pt crystal; in this case, the Pt-like CV is manifest by a catalytically active surface film, with n-type character, Pt²⁺(OH)₂ in KOH.

The multi-electrode cell measurements show that

alloys are electrochemically active for the ORR. In addition, the ORR was found to be very dependent on the scan direction (cathodic and anodic) for ORR scans conducted at nearly potentiostatic scan rates, 1 mV/sec, over the potential range 0.4 – 1.04 V (vs. NHE). This dependence on scan direction is related to the formation of a non-conductive blocking film at high potentials during cleaning CVs done prior to the ORR run. When the CVs are cycled to voltages above the double-layer capacitance region, a thin gelatinous Pt-Ag-oxyhydroxide film forms, with the film thickness increasing with the applied voltage value, ~20 Å/V. At a critical blocking-film thickness value, charge transfer is blocked, effectively killing the ORR activity. Conversely, when cleaning 1/2-CVs were conducted, along with an anodic scan from potentials just above zero, the blocking-film does not form until after the ORR takes place on the “nearly bare” metal surface. This procedure enabled large ORR currents to be observed. A full discussion is not presented here. The composition dependence for the ORR exhibited a bi-modal peak in the ORR current density: one at Ag₆₉Pt₃₁, J_{ORR} = -128 μA/cm²; and the other at Ag₃₀Pt₇₀, J_{ORR} = -258 μA/cm², each 1.25X and 2.5X greater respectively, than the ORR recorded for Pt via RDE measured in the same electrolyte. It is no surprise that the Pt-deficient compositions exhibit a behavior similar to that observed by Debe *et al* for the ORR dependence on composition observed for Ni₇₀Pt₃₀-NSTF films. The bimodal distribution with alloy composition is directly related to the intra-alloy electron transfer between the respective d-bands (Pt, Ag), as well as s-d scattering, with both atom types acting as scattering centers for the current carrying electrons in the electrode. This concept will be described fully in an upcoming article.

In companion presentations at these proceedings, and with 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 within a given 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).
- 2) J.F. Whitacre, T. I. Valdez, and S.R. Narayanan, Electrochimica Acta **53**, 3680 (2008).
- 3) C. C. Hays, J. G. Kulleck, B. E. Haines, and S.R. Narayan, ECS Transactions **25**, 619 (2009).
- 4) T. J. Schmidt, P. N. Ross, and N. M. Markovic, J. Phys. Chem. B **105**, 12082 (2001).

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