

Pt-M (M = Cu, Co, Ni) Alloy Catalysts for Oxygen Reduction in PEM Fuel Cell

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Introduction

Hydrogen fuelled proton exchange membrane (PEM) fuel cells have demonstrated great promise as future source of energy due to their high conversion efficiency, lower temperature of operation and lack of greenhouse emissions. Till now Pt has been found to be the best electrocatalyst for the oxygen reduction reaction (ORR) due to higher electrocatalytic activity and stability. But the limitation is due to high costs incurred. In recent years lot of emphasis has been put on Pt alloy catalysts because of even higher activity and lower cost as compared to Pt catalysts only [1,2]

The mechanistic bases of the observed improvements in the catalytic ORR activity is still highly contentious: While some researchers base it on the Pt 5d band vacancy leading to stronger Pt-O₂ interaction[3], others report that pure Pt binds oxygen surface species too strongly, and thus, alloys are a way to lower the Pt-O chemisorption energy [4]¹. Ordering and disordering in the alloy bulk also plays a role in enhancement of the surface catalytic activity of oxygen reduction reaction [5]. Also the activity increase is attributed to decrease of coverage of surface oxides and enrichment of active Pt sites [6]. Further decrease in Pt-Pt distance and Pt-Pt coordination number causes the enhanced activity [7].

Materials and Methods

Catalyst precursors [M (NO₃)₂.xH₂O where M=Cu, Ni, Co] precursor were dissolved in deionized water by sonicating for 15min. Then 30 wt% Pt/C was added to the precursor solution and mixed with magnetic stirrer for 15min. Finally the mixture was sonicated for 45min. At the end of ultrasonication the sample is allowed to freeze for 15min in liq N₂ without allowing the mixture to settle. Then the frozen mixture is vacuum dried until the sample reaches 24 °C. The catalyst mixture was annealed in 4% H₂- 96% Ar gas mixture at 600 °C for 7h. The annealed catalyst was leached with H₂SO₄ and HClO₄ at 80 °C for 36h to see the effect of acid leaching on the activity of the catalyst. During leaching the container was open to atmosphere.

Membrane electrode assemblies were prepared from the catalyst inks obtained by ultrasonically dispersing catalyst with HPLC grade isopropyl alcohol (Aldrich) and blending with 5 wt% Nafion solution. Then the ink was coated on a pretreated Nafion® membrane (NRE212) with a robotic spray machine (PVA Inc.).

Results and Discussion

In this work carbon supported PtCu, PtCo and PtNi alloys were prepared by unique synthesis method and the catalyst activities were evaluated in an *in-situ* test condition. Initially screening of the alloys with rotating disk electrode (RDE) measurement shows 3X to >5X Pt mass based activities for the un-leached Pt alloys compared to 40 wt% Pt/C (E-tek Inc.).

However to suppress the *in-situ* leaching of base metal in the fuel cell environment and its reduction on proton conduction, the catalysts were leached before testing and the preliminary results were exhibited. To understand the structure based activity of the catalyst and the leaching condition on ORR kinetics, catalyst with several compositions of Pt/base metals were synthesized and tested. Initial result shows the activities are higher for the sulfuric acid leached Pt-Cu/C than perchloric acid. Further results backed up with extensive characterization (XRD, XPS) of the catalyst will be presented.

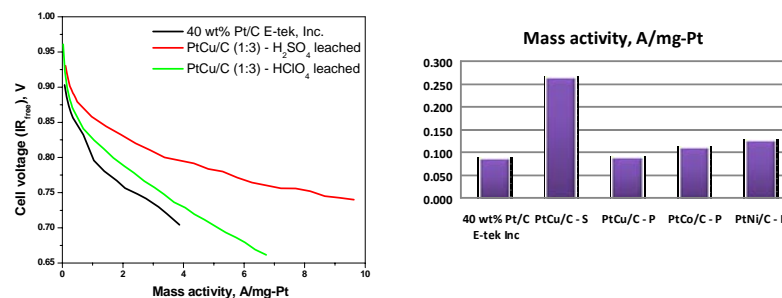


Figure (Right): Comparison of mass activity of the catalyst leached with sulfuric and perchloric acid. Cell/Anode/Cathode temperature = 80/75/65 °C, H₂/O₂ stoichiometry = 2/3. **Figure (Left):** Mass activities of the perchloric (-P) and sulfuric (-S) acid leached Pt alloy catalysts at 0.9V (IR-free). The un-leached composition of the alloy is 1:3 (Pt:M).

Significance

Pt Cu de-alloyed electrocatalysts are currently meeting and exceeding the mass based activities of the state-of-the-art PtCo electrocatalysts reported in literature (about 0.25 A/mg Pt). Based on the RDE activity, these materials show great promise to meet the required mass based activity of 0.45 A/mg-Pt set by DOE for 2010. Optimization of the base metal wash procedure will be necessary to closely mimic the RDE conditions.

References

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