Postdoc Journal
Vol. 1, No. 4, April 2013
Journal of Postdoctoral Research
www.postdocjournal.com

Tunable Hierarchical Metallic-Glass Nanostructures

Yiyi Yang
School of Engineering, Brown University, Providence, RI 02912
Email : yiyi_yang@brown.edu

Abstract A new multi-step synthesis method, including thermo-plastic forming and electro-chemical processing, is proposed to fabricating different nano-scale morphologies of $Ni_{60}Pd_{20}P_{17}B_3$ bulk metallic glass. Due to the large surface area and the enrichment of the active noble metal on the surface, these processed metallic glass morphologies show enhanced catalytic behavior during methanol oxidation. Also, these nanostructures show less accumulation of poisoning intermediates on the catalysis surface.

Keywords: *Metallic glass, nanostructure, catalysis, methanol oxidation*

In a recent paper published by a group from Yale University [1], the authors proposed a new multi-step synthesis method, including thermo-plastic forming and electro-chemical processing, for fabricating a wide range of morphologies and length-scales $Ni_{60}Pd_{20}P_{17}B_3$ metallic glass. Since these nanostructure metallic glasses can (1) provide large surface area and high dispersion of the active metal; (2) enrich the active noble metal on the surface; and (3) eliminate carbon substrate support, they will have a wide range of electro-catalytic applications.

A metallic glass is a solid metallic material, usually an alloy, with non-crystalline, and glass-like structure. Metallic glasses are usually produced by a variety of quick-cooling methods. In this paper, bulk $Ni_{60}Pd_{20}P_{17}B_3$ metallic glass were prepared by water quenching molten master alloys from a temperature of 1000°C. The bulk specimen was then thermo-plastically processed in the super-cooled liquid region above its glass transition temperature. An array of 200nm-diameter nano-rods was formed on the specimen surface by forcing bulk metallic glass onto an anodized alumina mold at a temperature of 390°C. The final step is to enrich the active noble metal (Pd, in this case) on these rods surface using electrochemical tuning. Two different methods were proposed in this paper for tuning. One is electrochemical dealloying, which pulls away non-noble metal atoms out of the rod surface, leaving nano-pores and Pd skeleton structure. The other is re-depositing noble metal atoms during reverse sweep of cyclic voltammetry, which results in dendritic structures of Pd on the surface. The two methods were both proved to be effective to largely increase the Pd atomic percentage in the rods.

A series of electrochemical characterization of the two nanostructures fabricated by the proposed method proved their better catalytic behavior compared to pure-Pd surface. Cyclic voltammetry for methanol oxidation (an important electro-chemical reaction in the fuel cell application) showed that both the nano-porous surface and the dendritic structure have over an order of magnitude higher peak current density, and about 200mV lower onset potential compared to pure-Pd surface. Also, the higher forward peak of these nanostructures compared to the reverse peak suggested lesser accumulation of poisoning intermediates.

For last few decades, materials scientist were mainly focused on the unique mechanical and magnetic properties of the bulk metallic glasses [2], while chemical engineers preferred to use nano-particles (*e.g.* pure metal and core-shell structures) and thin films as electro-catalysts. This is one of the few existing papers bringing bulk metallic glass and electro-catalysts together. These nanostructures provide a large electrochemical reaction surface area, similar to nano-particles. At the same time, these catalysts largely reduce the possibility of detach from carbon support or substrate, which often occurs in nano-particle systems, avoiding loss of catalytic activity over time. Also, using thermo-plastic forming, metallic glass can be easily fabricated into different shapes. However, one concern is that bulk metallic glasses might suffer reduction-oxidation reaction [3], commonly known as redox, when used in fuel cell systems, due to their brittle nature at room temperature region. Redox reactions could induce large mechanical stresses into the materials and eventually cause pre-mature failure. Nevertheless, this paper introduced a new possibility of applying metallic glass into electrochemical applications. As authors pointed out in their abstract, "…the approach may serve as a tool-box for fabricating complex hierarchical nanostructures for wide ranging applications."

References

[1] S. Mukherjee, *et al.*, Advanced Functional Materials, 23(21), 2708(2013).
[2] W. Wang, Nature Materials, 11, 275(2012).
[3] C.P. Andrieux, *et al.*, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry, 113(1), 19(1980).