PtRu nanotubes and PtRu coated CuNWs as catalysts for methanol oxidation reaction in direct methanol fuel cells

Jie Zheng and Yushan Yan*

Department of Chemical and Biomolecular Engineering
University of Delaware
150 Academy Street, Newark, DE 19716, USA
*yanys@udel.edu

Direct methanol fuel cells (DMFCs) are an attractive alternative to hydrogen-fueled proton exchange fuel cells for powering portable electronic devices because of their high energy density and ease of fuel transportation and storage. While nearly zero overpotential is observed for hydrogen oxidation reaction in acid, large overpotential exists even on the state-of-the-art PtRu/C MOR catalyst.[1] Therefore, developing catalysts with high MOR activity is of great importance.

MOR is known to be a structure sensitive reaction with Pt(110) facet showing the highest specific activity among low index surfaces.[2] One-dimensional (1D) nanostructures with 2D extended surfaces such as nanowires, nanotubes and nanorods often have the preferential exposure of certain facets which will enhance the MOR activity.[3] Studies have shown that platinum nanotubes (PtNTs) have higher MOR specific activity than platinum nanoparticles supported on carbon (Pt/C)[4], which might be attributed to the exposure of (110) facets of PtNTs. However, it remains unclear whether 1D PtRu nanostructures have higher MOR activity.

In our work, we synthesized PtRu nanotubes (PtRuNTs) and PtRu coated Cu nanowires (PtRu/CuNWs) via complete or partial galvanic displacement of CuNWs by Pt and Ru precursors. By varying the Pt and Ru precursor ratio, PtRuNTs and PtRu/CuNWs with different Pt:Ru ratio were obtained. Their MOR activities were evaluated by cyclic voltammetry using rotating disk electrodes and compared with the benchmark commercial catalysts PtRu/C (HiSPEC® 12100).

Our results show that the optimal Pt:Ru raito is about 4 for both PtRuNTs and PtRu/CuNWs. Enhanced specific MOR activities were observed on PtRuNTs and PtRu/CuNWs compared with the benchmark PtRu/C, with specific activity in the order of PtRu/CuNWs > PtRuNTs > PtRu/C. However, PtRuNTs showed smaller mass activity than PtRu/C due to their small electrochemical surface areas (ECSAs). PtRu/CuNWs showed comparable mass activity compared with PtRu/C, attributed to the improved specific activity as well as increased ECSA. X-ray photoelectron spectroscopy (XPS) reveals a stronger electron transfer from Ru to Pt on PtRu/CuNWs, which may have led to a stronger back-donation of electron from Pt to CO (the poisoning intermediate), and consequently a weaker Pt-CO bond and a higher MOR activity on PtRu/CuNWs.

References

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