Applications of Pd based catalysts in direct formic acid fuel cells
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INTRODUCTION

Direct formic acid fuel cells (DFAFC) are expected to be among the first commercial applications of fuel cells as a power supply for portable applications. It is established that palladium performs particularly well as an anode catalyst. The problem with palladium is that it becomes gradually deactivated. One of the ways to overcome this problem is periodical activation of the catalyst by anodic pulses, but it may lead to palladium losses. The addition of the second metal, such as Au, may increase the catalyst resistance to Pd dissolution stability during anodic activation.

The aim of the present series of works [1-5] was to: 1) Increase maximum power density of DFAFC and resistance of the Pd-based catalysts to regeneration with periodic anodic pulses by alloying with Pd with Au, 2) to develop preparation method yielding highly dispersed Pd nanocrystals with the surface free from contaminants by application of polyol method and selecting optimum post-treatment.

EXPERIMENTAL

Metal precursors were reduced by ethylene glycol (polyol process) at 170 °C. The small metal particles (4 - 5 nm) were well dispersed on CNTs surface. The various post-treatments were applied: 1) annealing in Ar at 250 °C - C250, 2) annealing in 5% H2/Ar at 200 °C - R200, 3) activation in 3M HOAc for 0.5 h. The catalysts were characterized by: TGA analysis, X-ray Diffraction Analysis, Field Emission Scanning Electron Microscopy, Field Emission Transmission Electron Microscopy, EDX-2D Mapping, XPS/XAES, Cyclic Voltammetry, Chronamperometry, and DFAFC tests.

CONCLUSIONS

1. Pd-Au/MWCNTs - C250 (Ar at 250 °C), synthesized by sequential deposition of Pd and Au on MWCNTs via a polyol method led to a material of a core-shell structure, with Pd in the core and Au in the shell. This catalyst was catalytically inactive, however, the catalyst can be re-activated by the posttreatment up to 20% FA for 20-30 cycles.

2. Lack of initial activity of C250 Pd-based catalysts is caused by: i) formation of carbon-PdOx layer which is poisoning the Pd surface, ii) poor electronic contact of metal crystallites with the MWCNTs support, iii) formation of larger Pd based crystallites.

3. Pd-Au/MWCNTs catalyst synthesized via polyol method after H2/Ar heat-treatment (R200) results in formation of well-dispersed Pd-Au solid solution nanoparticles. Initial activity towards formic acid electrooxidation is ranged in the order: Pd-Au/MWCNTs > Pd/MWCNTs > Pt-Ru/Vulcan.

4. CV cycling simulating reactivation of the catalysts by anodic impulses, showed that the Pd-Au catalyst is more viable than Pd catalyst.

5. The rate of the deactivation of MWCNTs supported Pd and Pd-Au catalysts rapidly increase with: (i) amounts of impurities (mainly sulfuric acid and methanol), (ii) loading current, (iii) flow rate of FA. The main reason of the deactivation of Pd based catalysts, in p.a. formic acid, is formation of passina from impurities of the formic acid.