Mechanistic Studies of Palladium Based Catalysts in the Reactions of Alcohols Electrooxidation

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Despite the significant investments in the research fuel cell technology, at the moment, fuel cell systems are still not on the market, primarily due to the high cost of the final device, due mostly to the use of Pt or Pt-based alloys as electrocatalysts. There are an increasing number of published works devoted to development of Pt-free catalysts for both the anode [1] and cathode [2] sides of membrane electrode assembly (MEA). Palladium based alloys possess reasonable activity and stability in alkaline media, and can be considered as possible substitutes of Pt for alcohol oxidation. Here we discuss the synthesis and characterization of palladium based materials for MeOH, EtOH, ethylene glycol and glycerol oxidation. To investigate the influence of the Pd:M (where M=Cu, Pb etc) ratio on catalytic activity towards alcohol oxidation, a series of catalysts with various Pd:M ratios were prepared and the reduction conditions were optimized.

All catalysts presented in this work were synthesized using a modified sacrificial silica support method which was developed in our research group [3]. Appropriate amounts of metal precursors (palladium nitrate, tin nitrate etc) were deposited on the surface of fumed silica Cab-O-Sil® EH-5 (surface area ~380 m^2 g^{-1}). The composite materials were chemically reduced using solution $NaBH_4$ or thermally reduced in H_2 atmosphere. After reduction, the fumed silica was removed by etching in KOH solution, and washed appropriately. The catalysts were comprehensively characterized by BET, SEM, TEM, XRD and XPS. Catalytic activity for alcohols oxidation was measured in alkaline media using the RDE method. The inks for RDE experiments were prepared by mixing the catalyst powder with an optimized amount of Nafion™ in an IPA/H_2O solution. Homogeneity of the inks was achieved by means of sonication using ultrasound probe.

Figure 1 represents XRD data for Pd-Cu catalysts prepared by thermal reduction method.

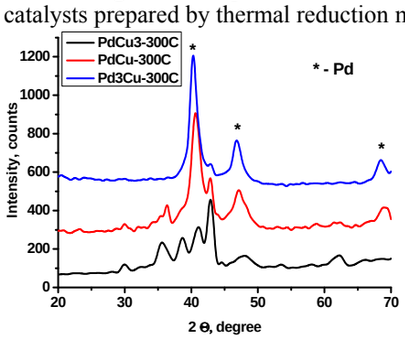

Figure 1. XRD of Pd-Cu catalysts prepared by the thermal decomposition of the precursors.

It was found that $PdCu_3$ and PdCu were mixture of Pd, PdCu and CuO_x phases.

Analysis of material morphology from SEM images reveals that Pd-Cu catalysts possesses highly developed porous structure with BET surface area ~40 m^2 g^{-1} (**Fig. 2**).

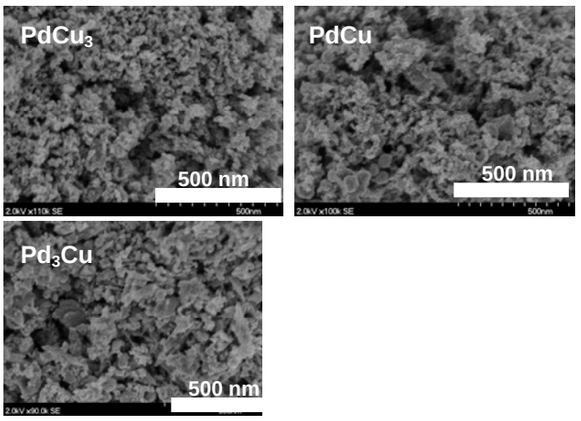

Figure 2. SEM images for a Pd-Cu catalysts (thermal reduction).

Comparison of catalytic activity of Pd-Cu catalysts to pure Pd metal in reaction of MeOH electrooxidation is shown on **Figure 3**.

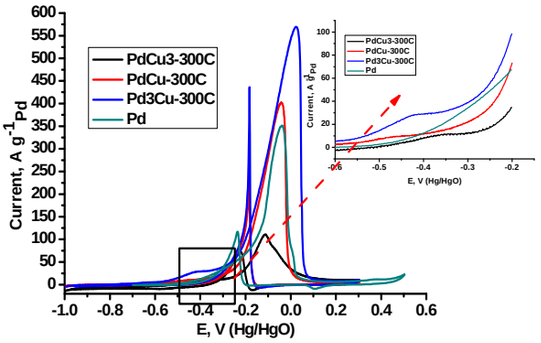

Figure 3. Electrochemical data for Pd-Cu and Pd catalysts in 1M KOH+1M MeOH (catalyst loading: 200 μg cm^{-2}, 1600RPM, scan rate 20 mV s^{-1}).

It was observed that Pd_3Cu catalyst possesses highest activity in series of thermally reduced samples and significantly higher activity compared to Pd: 570 vs 350 A g^{-1}_{Pd}, respectively. Addition of second metal improves onset potential of the prepared catalysts in comparison with palladium.

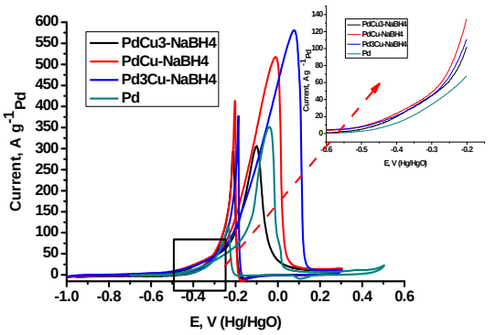

Figure 4. Electrochemical data for Pd-Cu and Pd catalysts in 1M KOH+1M MeOH (catalyst loading: 200 μg cm^{-2}, 1600RPM, scan rate 20 mV s^{-1}).

The same trend was observed in the case of Pd-Cu catalysts prepared by chemical reduction of the precursors with $NaBH_4$ (**Fig. 4**)

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References:

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3. S. Pylypenko, S. Mukherjee, T. Olson, P. Atanassov, *Electrochim. Acta* 53 (2008) 7875-7883