Pd-Bi Catalysts for Electrooxidation of Alcohols

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Palladium based nanoalloys possess high activity and stability in alkaline media, and can be considered as possible economical substitutes of Pt for alcohol oxidation. There is an increasing number of published works devoted to the development of Pt-free anode catalysts for direct alcohol fuel cells[1-3]. Here we discuss the synthesis and characterization of Pd-Bi materials for methanol, ethanol, ethylene glycol, isopropanol and glycerol oxidation. To investigate the influence of the Pd:Bi ratio on the catalytic activity towards alcohol oxidation, a series of catalysts with various Pd:Bi ratios were prepared by the sacrificial support method (SSM),which was developed by the research group of Prof. Atanassov[3-7]. Appropriate amounts of metal precursors (palladium nitrate) were deposited on the surface of fumed silica Cab-O-Sil® EH-5 (surface area ~ 380 m^{-2} g^{-1}). The composite materials were reduced using a hydrogen atmosphere. After reduction, the fumed silica was removed by etching in KOH solution, and washed appropriately. The catalysts were comprehensively characterized by SEM, TEM, XRD and cyclic voltammetry (CV). The inks for CV 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 SEM and TEM images for Pd-Bi unsupported catalysts with size of nanoparticles about 5 nm.

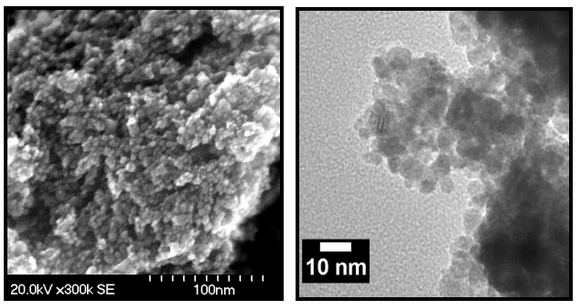

Figure 1. SEM and TEM images for Pd-Bi catalysts.

The activity of five catalysts Pd, Pd_3Bi, Pd_5Bi_2, PdBi and $PdBi_2$ was compared towards oxidation of different alcohols. The promotion effect of small amount of bismuth (Pd_3Bi catalyst composition) was found in the case of all alcohols, but the highest current density is observed in the case of ethylene glycol (Figure 2).

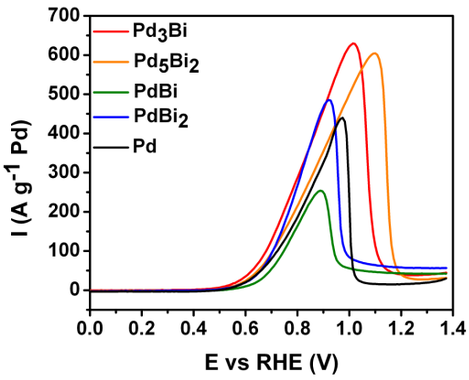

Figure 2. Electrochemical data for Pd-Bi catalysts in 1M KOH + 0.1M Ethylene glycol (scan rate 0.1 V s^{-1}).

Pd_3Bi catalyst possesses the highest activity in the series of prepared catalysts for electrooxidation of methanol, ethanol, ethylene glycol, isopropanol, but with the exception of glycerol.

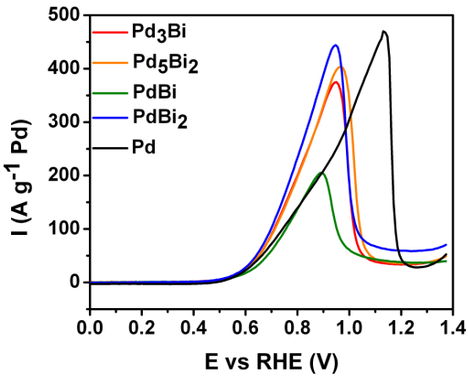

Figure 3. Electrochemical data for Pd-Bi catalysts in 1M KOH + 0.1M Glycerol (scan rate 0.1 V s^{-1}).

The modification of palladium with bismuth resulted in a shift of the peak potential for glycerol oxidation (Figure 3). This result clearly demonstrates an increase of the reaction rate of glycerol oxidation in the presence of bismuth.

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