Nanostructured platinum-copper electrocatalysts for the oxidation of borohydride

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This work is focused on the use and study of the nanostructured platinum-copper catalysts deposited on the titanium surface by a two-step process which involves electroless copper deposition followed by a spontaneous Pt displacement from the hexachloro-complex solution as electrocatalysts for the oxidation of BH_4^- ions in alkaline medium. The morphology and composition of prepared catalysts were characterized using field-emission scanning electron microscopy (FESEM) and energy dispersive X-ray spectroscopy (EDAX). The electrochemical behavior of the as-prepared nano-Pt(Cu)/Ti catalysts was examined by means of cyclic voltammetry and chrono-techniques. The electrocatalytic activity of the catalysts towards the oxidation of BH_4^- ions was compared with that of bare Pt and Cu/Ti electrodes.

Platinum-coated copper films (Pt/Cu), with particles of a few nanometers in size have been prepared on the titanium surface by immersion of Cu/Ti electrode into the platinum-containing solution for various time periods as testified in Fig. 1 (b-d). Electroless copper deposited on the titanium surface produced a layer of polycrystalline copper with the average size of crystallites ca. 1 μm (Fig. 1a). The thickness of the electroless copper layer was about 1.5 μm. The Pt particles appear as bright crystallites of cubic form of 10 up to 50 nm in size and are homogeneously dispersed on the copper surface (Fig. 1, b-d).

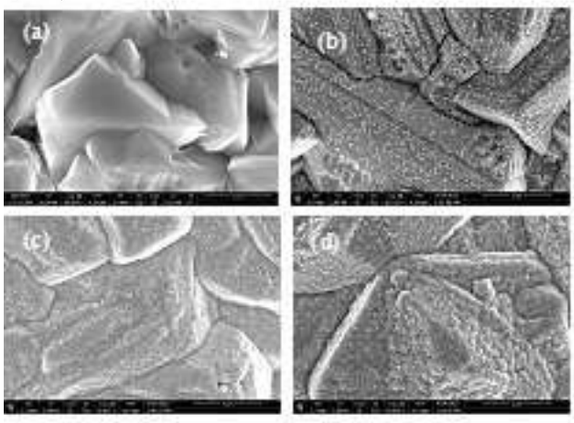

Figure 1. Top side views of as-prepared Cu/Ti (a) and nano-Pt(Cu)/Ti catalysts (b-d). The catalysts were prepared by immersion of Ti sheets in the electroless copper solution at 25 ^oC for 15 min, followed by their immersion in 1 mM H_2PtCl_6 + 0.1 M HCl at room temperature for 5 (b), 15 (c) and 30 (d) min.

The presence of Pt and Cu was confirmed by energy dispersive X-ray analysis. A significant amount of deposited copper and a much lower amount of platinum remaining on the electrode surface was determined. The Pt loadings were 2.14, 13.6 and 26.5 μg cm^{-2} in the as-prepared catalysts after immersion of the Cu/Ti surfaces in a hexaplatinum-containing solution for 5, 15 and 30 min, respectively.

Figure 2 shows positive-potential going CVs of the oxidation of BH_4^- ions recorded on bare Pt (*dotted line*), Cu/Ti (*dash-dotted line*) (x) and different nano-Pt(Cu)/Ti (y) catalysts at a potential scan rate of 10 mV s^{-1}. The shape of CVs determined for the nano-Pt(Cu)/Ti catalysts is similar to the CV onto bare Pt, except the enhanced anodic currents. During the anodic scan well-distinguished anodic peaks a and d, which are related with the oxidation of H_2 generated by catalytic hydrolysis of BH_4^- and direct oxidation of the BH_4^-, are seen in both CVs plot (Fig. 2x, *dotted line* and y). The peak b attributed to electrooxidation of BH_3OH^-, which is hardly discernible at -0.3 V on bare Pt (Fig. 1x, *dotted line*), is also enhanced on the nanostructured Pt(Cu)/Ti catalysts (Fig. 2y). The current densities of peaks a, b and d on the nano-Pt(Cu)/Ti catalysts are from ca. 4-to-10-fold higher as compared to that on bulk Pt.

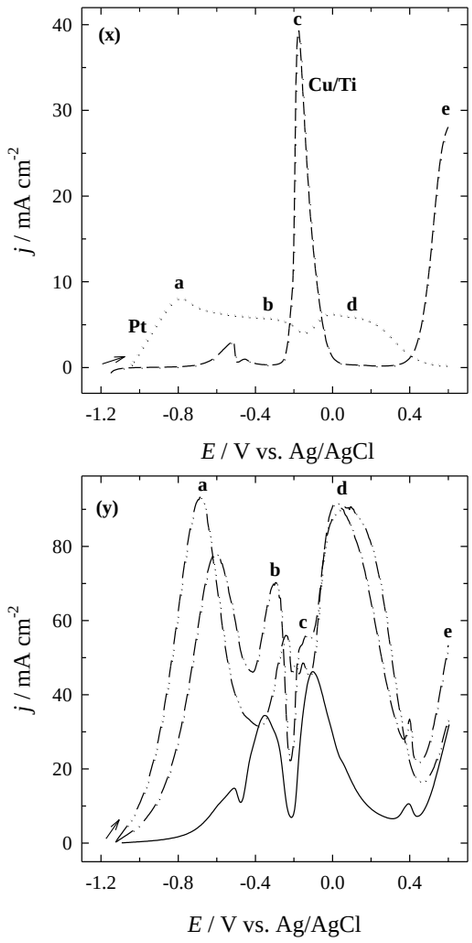

Figure 2. (x) Positive-potential going CVs recorded on bare Pt (*dotted line*), Cu/Ti (*dashed line*) and (y) nano-Pt(Cu)/Ti catalysts with Pt loadings of 2.14 (*solid line*), 13.6 (*dash-dotted line*) and 26.5 (*dash-dot-dotted line*) μg_{Pt} cm^{-2} in 0.05 M $NaBH_4$ + 1 M NaOH at 10 mV s^{-1}.

The as-prepared catalysts with different Pt loadings demonstrated their significantly higher electrocatalytic activity towards the oxidation of both H_2 (peak a) and BH_4^- ions (peak d) as compared to that of bulk Pt or Cu/Ti and seem to be a promising anodic material for direct borohydride fuel cells.

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