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Cu sub-monolayer decorated Pd/C and Pt/C as electrocatalyst for ethanol oxidation in alkaline solution

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Easy storage and handling, high energy density, wide availability, and low toxicity are features that make ethanol attractive fuel cell liquid combustibles and the most promising among alternative power sources [1,2]. Unfortunately, the slow and incomplete ethanol oxidation reaction (EOR) occurs at the anode even on the best available catalysts known to date. Pure Pt and Pd are not capable of catalyzing the oxidation of ethanol through the total oxidation pathway [2]. However, Pt and Pd are necessary catalyst constituents to provide efficient adsorption of ethanol, which is the first reaction step in ethanol oxidation. The activity of Pd and Pt for alcohol oxidation can be enhanced by adding a co-catalytic element, mainly oxophilic metal (either d- or p-metals), or compounds such as oxides [3]. Therefore, in the present work, the influence of Cu sub-monolayers decoration of carbon-supported Pd and Pt nanoparticles was investigated for ethanol oxidation reaction (EOR) in the alkaline solution.

Commercial Pt/C (E-TEK®) and Pd/C catalyst synthesized by borohydride reduction method [4] were electrochemically characterized by cyclic voltammetry and CO_{ads} stripping in acid and alkaline solutions. The onset potential and the peak potential of CO_{ads} oxidation on Pd/C were more positive than those for Pt/C in both solutions, indicating lower oxophilicity and/or stronger bonding with CO_{ads} in the case of Pd than Pt. Catalysts were decorated by underpotential deposition of Cu atoms (Cu_{upd}) in acid solution with various surface coverages (up to 0.5). Electrochemically active surface area (ECSA) of undecorated catalysts was calculated from the charge of desorption of CO and Cu_{upd} in acid solution, while ECSA of Cu_{upd} decorated catalyst was calculated from the charge of CO desorption in alkaline solution. Cyclic voltammetry showed that on the Cu_{upd} decorated surfaces the onset of CO desorption was negatively shifted. This indicates that Cu_{upd} atoms provide oxygen-containing species at adjacent Pt or Pd sites at a lower potential than that achieved on pure metals.

The influence of Cu_{upd} decoration of the Pt/C and Pd/C catalysts on activity for EOR in 0.1 M KOH was investigated under potentiodynamic conditions. Although the onset potential was the same, Pd/C was more active for EOR than Pt/C with the 1.5-fold enhancement of maximum current. Pd/C with Cu_{upd} coverage of 0.30 exhibited lower onset potential and up to 2.5-fold increase in EOR activity with respect to Pd/C (calculated per Pd ECSA). However, with further increase in coverage the positive effect of Cu_{upd} disappeared and activity even decreased. In the case of Pt/C the promotion effect of Cu_{upd} was negligible, because only the catalyst with coverage of 0.11 showed lower onset potential and slightly higher current at low potentials. The higher EOR activity of Pd/C compared to Pt/C can be attributed to the optimum oxophilicity of Pd which provides ample space for adsorption of ethanol and still provides oxygen containing species for its oxidation. Decoration of Pd/C by 0.3 monolayer of Cu_{upd} increases the amount of oxygen containing species that intensify ethanol oxidation rate on Pd.

References

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