

Electrocatalytic Properties $\text{Co}_3\text{O}_4\text{-CeO}_2$ Nanocomposites

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Catalytic systems based on nanostructures of carbon-supported platinum, Pt/C (catalytic centers), and metal oxides, MO_x (cocatalytic sites), namely nanocomposites of cobalt(III,II)-oxide and cerium(IV,III)-oxide, admixed in different proportions have been investigated under electrochemical conditions toward both reductions of such inert reactants as oxygen, carbon dioxide and nitrogen as well as oxidation of water (water splitting to oxygen). Evidence has been provided that the existence of specific interactions between MO_x and noble metal (Pt) nanoparticles should improve the stability and activity of the metal catalytic sites due to modification of the Pt electronic structure and diminishing of the oxo (OH) species adsorption on Pt surface, thus promoting centers for the adsorptive activation of oxygen and the cleavage of O=O bonds. Development of catalytic systems for oxygen reduction reaction, particularly with respect to potential applications in low-temperature fuel cells, is one of the most important areas of electrocatalysis. Considerable research efforts have centered on the development of low-Pt-content catalytic systems. In other words, there is a need of better utilization of catalytic sites and significant lowering of the noble metal loadings. The activating interactions mentioned above would also facilitate dispersion of Pt catalytic centers, inhibit their detachment and further aggregation, and, consequently, prevent or decrease their degradation during the practical operation (e.g., in low-temperature fuel cells). In the present study, we have demonstrate that Co_3O_4 -modified CeO_2 additive (to Pt/C) synthesized in a form of intermixed oxides with homogeneously dispersed cobalt ionic sites enhance activity of Pt centers during oxygen reduction in acid medium. Conventional cyclic voltammetry and rotating ring-disk electrode voltammetry were considered as diagnostic techniques permitting to comment on the dynamic of oxygen reduction and formation of the undesirable hydrogen peroxide intermediate. The CO_2 -reduction, which has also been considered here, is a much more inert process that requires breaking the double C=O bond in the stable CO_2 molecule. A common feature is the appearance of the poisoning or passivating CO-intermediate. Furthermore, when the CO_2 -reduction is performed in aqueous solutions, the competitive hydrogen evolution reaction is a complicating side-reaction. The Co_3O_4 -modified CeO_2 nanocomposite catalysts have been demonstrated to act as potent catalysts permitting reduction of carbon dioxide (predominantly to formate and carbon monoxide, selectively relative to hydrogen evolution). Among other inert small inorganic molecules, electroreduction of nitrogen has also been considered. Here, catalytic systems based on $\text{Co}_3\text{O}_4\text{-CeO}_2$ nanocomposites have exhibited electrocatalytic activity toward N_2 -reduction reaction in semi-neutral medium (phosphate buffer, pH=6.1). Our voltammetric experiments indicate that the nanocomposite catalysts facilitate conversion of N_2 to NH_3 , and the processes are fairly selective with respect to the competing hydrogen evolution. Finally, the $\text{Co}_3\text{O}_4\text{-CeO}_2$ nanocomposites have occurred to exhibit high stability and promising activity under anodic conditions, namely during electrooxidation of water (water splitting) in acid medium. In addition to promising results of experiments in $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$, the highest activities toward water oxidation have been observed in strongly acidic polytungstate solutions, presumably due to the formation of the highly active electrocatalytic interface formed by the oxidized $\text{CoO}_x/\text{CeO}_y$ catalytic nanocomposites activated and stabilized by tungsten-oxo-species.

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