

**ELECTRONICALLY CONDUCTIVE
POLYMER/MIXED VALENCE TRANSITION
METAL OXIDE COMPOSITE ELECTRODES FOR
ELECTROCATALYSIS**

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Mixed valence transition metal oxides (spinel, perovskites, pyrochlores essentially) exhibit electrocatalytic properties towards many electrochemical reactions of interest in industrial, environmental and analytical processes.

We are currently investigating [1-4] a new generation of electrodes in which the oxide (Ox) is dispersed into an electronically conductive polymer (ECP) matrix, forming the composite ECP(Ox) active layer of a multilayer composite electrode. For instance we have investigated the behavior of copper/manganese and nickel/cobalt spinel oxides (Ox) in a composite electrode GC/PPy/PPy(Ox)/PPy, in which GC is glassy carbon, PPy polypyrrole, and Ox = Cu_{1.4}Mn_{1.6}O₄ and Ni_{0.3}Co_{2.7}O₄. The latter oxides were selected on the basis of previous investigations of the series Cu_xMn_{3-x}O₄ and Ni_xCo_{3-x}O₄ in the authors laboratories, which demonstrated their electrocatalytic properties towards the oxygen reduction reaction (orr) either into water using 4e⁻ (Cu_{1.4}Mn_{1.6}O₄) or into hydrogen peroxide using 2e⁻ (Ni_{0.3}Co_{2.7}O₄) in alkaline media. Those properties had been correlated with the cationic distributions in the bulk and at the surface of the oxides, using XRD and XPS.

The composite electrode structure GC/PPy/PPy(Ox)/PPy was grown by electrodeposition of the successive PPy, PPy(Ox) and PPy layers onto GC. Ox was actually a nanosized powder of the oxide, prepared using low temperature techniques. It was dispersed and confined in the PPy(Ox) inner layer, sandwiched between two PPy layers. Typical thicknesses of the successive layers were 1.2, 9.0 and 2.2 μm. Figure 1 exemplifies the steady state electrocatalysis of the reduction of O₂ in a moderately alkaline solution (pH 11.4, Ox = Ni_{0.3}Co_{2.7}O₄), [2,3]. Perfectly constant O₂ reduction currents at fixed potentials below -0.1 V/SCE were sustained up to 16 hours (a time at which the electrolyses were arbitrarily interrupted) without losses.

The lecture will review recent advances in relation with the properties and with the structure of the mixed valence oxides and polymer in the composite electrodes GC/PPy/PPy(Ox)/PPy. Mixed valence oxides are usually unstable under cathodic conditions in acidic media, being reduced into lower valence oxides, and PPy is usually in an insulating state at cathodic potentials.

The major findings of this work were that in such a composite electrode i) the spinel structure and the electrocatalytic activity remained remarkably stable in

acidic media at pHs where normally, in free standing acid electrolytes, the oxide would be electrochemically reduced ii) PPy retained its electronic conductivity at cathodic potentials where it would be normally in its insulated reduced state. Those composite electrodes sustained the orr at cathodic potentials in acidic solutions as they do in alkaline solutions, for hours without signs of

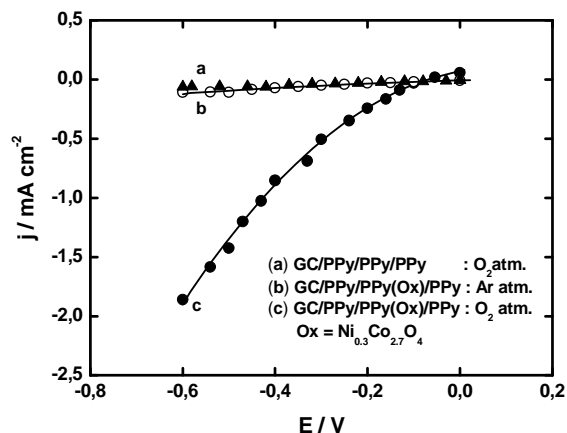


Figure 1 : Steady state *j*-E curves recorded in a 2.5 10⁻³M KOH + 0.8M KCl solution under Ar or O₂, [2].

deterioration [1]. The reasons for the unexpected stabilization of the oxide and for the conservation of the electrical conductivity of the polymer will be reviewed and discussed.

A particular emphasis will be given to the GC/PPy/PPy(Ni_{0.3}Co_{2.7}O₄/PPy composite electrode, which produces hydrogen peroxide. XRD data show that same diffraction lines than in the free oxide powder were maintained in the composite. XPS data show that cobalt is present in both divalent and trivalent states, according to the cation distribution Co_{0.43}²⁺Co_{0.57}³⁺[Co_{1.43}³⁺Co_{0.27}²⁺Ni_{0.30}²⁺], which had been determined elsewhere [5]. The oxide/PPy mass ratio and Cl/N atomic ratio were, respectively, 4.5% and 19%, the latter percentage representing the doping level of PPy. It shows that the electronic structure of PPy was not altered by the electropolymerization process in presence of the fine oxide nanoparticles [2]. The effect of the formation of hydrogen peroxide by the orr in the bulk of the composite electrode will be discussed. It will be shown that it does not alter the structure and properties of the polymer, despite its oxidative power.

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