

7. Phase Composition and Voltammetric Behavior of Doped and Nanostructured Manganese(IV) Oxides in Alkaline Saturated by Oxygen Medium

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Introduction. The modern systems of Li-ion batteries had the great effect on miniaturization of electronic device used (mobile phones, laptops, electric vehicle and etc.). The recently proposed Li-air battery technology combines advantages of Li-ion batteries with cheap and effective work of air-electrodes.

Manganese(IV) oxides are among the most effective O_2 electrocatalysts, therefore the objective of this paper is to study influence of induced by changes dopant ions in phase composition and disorder of surface states on ability of manganese(IV) oxides.

Materials and methods. The pristine fluorine-containing electrolyte consisted of 0.1 M HF + 0.7 M $MnSO_4$. The dopant additives in the electrolyte were: 0.01 M Cr^{3+} , 0.01 M Co^{2+} , 1.5 M NH_4^+ as an optimal concentration from the current yield and functionality point of view. Manganese(IV) oxide electrosynthesised on the platinum anode (with current density (j) of 10 A/dm²) using the glass-carbon plate as an auxiliary electrode.

The cyclic voltammetry (CVA) experiment was carried out in a standard three electrode cell using 0.3 M KOH electrolyte saturated with O_2 . The voltammograms were registered on IPC-PRO potentiostat-galvanostat with computer interface at the potential change rate of 0.001–0.5 V/s. Glass carbon plate was an auxiliary electrode. Carbon paste electrode (CPE) was a thoroughly grounded mixture of doped manganese oxide: graphite in the ratio of 70:30 and polytetrafluoroethylene (PTFE) emulsion loaded into PTFE-tube.

Results. CVAs of doped MnO_2 CPE in 0.30 M KOH solution saturated with ambient oxygen are shown in Figure 1. MnO_2 CPE 1 exhibit two reduction peaks (Fig.1) and two oxidation peaks with slightly resolved shoulder of the third one, whereas Co-doped CPE 2 displays additional reduction peak at more electropositive potentials (Fig.1). Oxygen reduction on Cr^{3+} -doped MnO_2 CPE is irreversible and oxidation peaks are absent. Graphite electrode has by the order of magnitude lower currents of the same processes that are shifted due to polarisation effects.

Peaks observed were ascribed to the successive two-electron reduction of O_2 with HO^{2-} as the intermediate. The first reduction peak of Co-doped CPE2 was attributed to the reduction of O_2 to HO^{2-} redox-mediated by the oxygen-containing groups and the second one was due to the reduction of HO^{2-} to OH^- . Three reduction peaks of Co-doped CPE2 are supposed to be the result of simultaneous action of Co and Mn interface species here the second reduction peak is common for both active sites.

Conclusions. The electrolytic doping procedure improves the perspectives of practical application of electrolytic manganese(IV) oxides as electrode material.

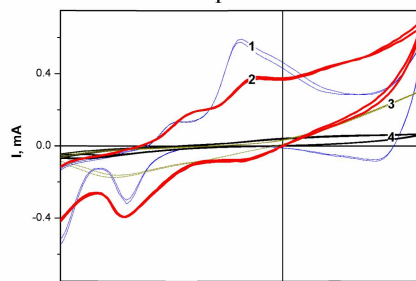


Fig. 1. CVA of NH_4^+ (1), Co^{2+} (2) Cr^{3+} (3)-doped manganese(IV) oxide and graphite(4) electrodes in the saturated by O_2 0.3 M KOH electrolyte solution ($V = 10 \text{ mV} \cdot \text{s}^{-1}$).