

## Oxygen Electrocatalysis by Electrolytically Doped Manganese (IV) Oxides

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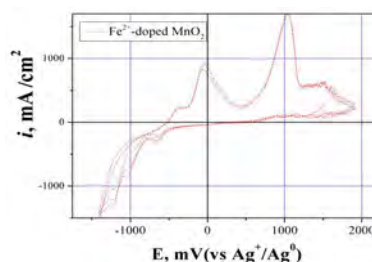
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Manganese (IV) oxides are among the most effective O<sub>2</sub> electrocatalysts. The phase composition and structure defects have profound influence on this material activity. The purpose of this work was to study influence of induced by dopant ions changes in phase composition and disorder of surface states on ability of manganese(IV) oxides to be oxygen electrocatalyst.

Manganese (IV) oxide obtained on the platinum anode (with current density,  $i$ , of 10 A/dm<sup>2</sup>) using the vitreous carbon plate as an auxiliary electrode. The pristine fluoride-containing electrolyte consisted of 0.1 M HF + 0.7 M MnSO<sub>4</sub> and the dopant additives in the electrolyte were: 0.01 M Fe<sup>2+</sup>, 1.5 M NH<sub>4</sub><sup>+</sup> [1]. XRD was performed on a DRON 4 instrument (CuK $\alpha$ -radiation). The cyclic voltammetry (CVA) experiment was carried out in a standard three electrode cell and 0.3 M LiOH electrolyte saturated with O<sub>2</sub> on IPC-PRO potentiostat-galvanostat at the potential scan rate to within 0.001–0.5 V/s. Carbon paste electrode (CPE) was a thoroughly grounded mixture of doped manganese oxide : graphite in the ratio 70:30 and polytetrafluoroethylene (PTFE) emulsion loaded into PTFE-tube.

The XRD phase analysis showed the following main phase components depending on dopants added:  $\alpha$ -MnO<sub>2</sub> (hollandite, I4/m) — NH<sub>4</sub><sup>+</sup>;  $\gamma$ -MnO<sub>2</sub> (ramsdellite, Pbam) — Fe<sup>2+</sup>. These results are in agreement with thermodynamics of hollandite phase since foreign ions like NH<sub>4</sub><sup>+</sup> in structure channels decrease its free energy significantly [2] as a result of influence of entropic factor. Both samples have nanorod shape of crystallites with diameter of about 10–20 nm as shown by TEM. The high activity in oxygen reduction(oxidation) reaction ORR (OOR) of  $\alpha$ -MnO<sub>2</sub> nanorods among other MnO<sub>2</sub> polymorphs [3] can be attributed to availability of structure tunnels to small O<sub>2</sub> and H<sub>2</sub>O molecules. The broadened nature of ORR (OOR) peaks on  $\alpha$ -MnO<sub>2</sub> unlike Fe-doped  $\gamma$ -MnO<sub>2</sub> sample confirms the latter hypothesis. The high activity of Fe<sup>2+</sup>-doped MnO<sub>2</sub> indicates the positive role of Fe<sup>3+</sup>/Fe<sup>2+</sup> redox pairs as active sites of surface states. The ORR (OOR) CVA effects in literature are uncertain. ORR electrode potential range based on rotating disk electrode (RDE) and RDE with ring electrode is too negative because thermodynamically the ORR starts at higher potentials as two weak waves. CVAs of doped MnO<sub>2</sub> CPE in 0.30 M LiOH solution saturated with ambient oxygen are demonstrated at V=20 mV·s<sup>-1</sup>, **Figure**. MnO<sub>2</sub> CPE 1 exhibit two reduction peaks (–0.75 V and –1.05 V) and two oxidation peaks (–0.35 V and –0.1 V) with slightly resolved shoulder of the third one (0.2 V) that were ascribed to manganese redox behaviour. Graphite electrode has by the order of magnitude lower currents of the same processes that are shifted due to polarisation effects. Peaks observed at higher electrode potentials were ascribed to the four-electron redox processes of O<sub>2</sub> with HO<sub>2</sub><sup>-</sup> as the intermediate, Fe<sup>3+</sup>/Fe<sup>2+</sup>.

The electrolytic doping procedure makes the number of available structure states of electrodeposited materials broader and improves the prospective of practical application of electrodeposited manganese(IV) oxides as electrocatalyst.



**Fig.** CVA of Fe<sup>2+</sup>-doped  $\gamma$ -MnO<sub>2</sub> sample CPE in O<sub>2</sub> saturated 0.3M LiOH (V = 20 mV·s<sup>-1</sup>)

[1] G.V. Sokolsky, S.V. Ivanov, E. I. Boldyrev et al., *Solid State Phenom.* **230** (2015) 85. [2] S. Fritsch, E. J. Post, A. Navrotsky, *Geochim. Cosmochim. Acta.* **61**(13) (1997) 2613. [3] P.-C. Li, C.-C. Hu, et al., *Journal of Power Sources* **298** (2015) 102-113.