NANO-2023

Doped by NH_4^+, Co^{2+}, Fe^{2+} Manganese(IV) Oxide Electrode Nanomaterial of OER Processes

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1.1. Introduction

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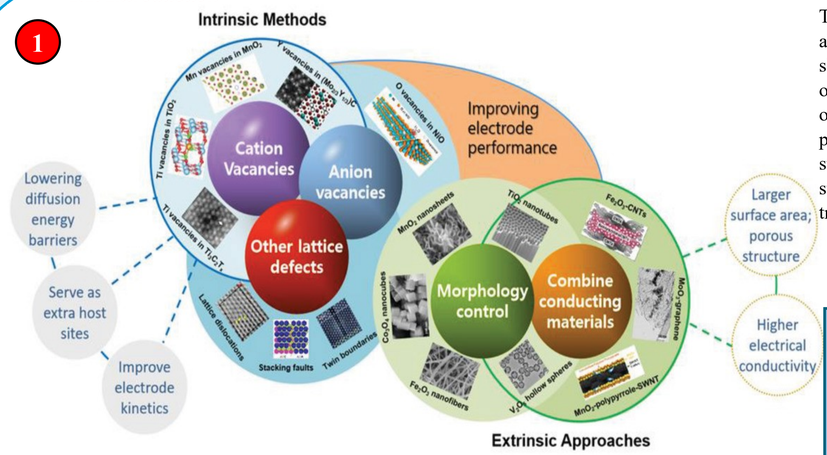

Figure 1. Schematic diagram showing the „extrinsic" and „intrinsic" approaches for improving the electrochemical energy storage performance [4]

Transition metal oxides based nanomaterials are frequently prepared by electrodeposition [1]. The tool to influence the activity of manganese(IV) oxide is the doping by other cations. The ED (electrodeposition) procedure modifies structure and defect states, the shape of nanocrystal-lites having strong influence on functionality of a transition metal oxide [2].

Strategies to mitigate problems

microstructure/ morphology controlling that provides large surface area and porous/hollow structures to facilitate the alkali cation adsorption/ intercalation and alleviate the structural strain to accommodate large volume variation	combining transitional metal oxides with conducting materials or other metal oxides to enhance the electrical conductivity and electrochemical reactivity

1.2. Methods

AAS, TGA, SEM, laser diffraction with light scattering, porosimetry, X-ray diffraction, Fourier IR spectroscopy, electrochemical measurements - RDE

2. Preparation of manganese dioxide materials and their characterization

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2.1. Electrodeposition oxide materials

Manganese dioxide samples were electrodeposited galvanostatically (i = 10 A/dm^2) on Pt anode. The anode area was 10 times smaller than the cathode area. Electrodeposition was carried out for 60, 120, 180 min.

The pristine fluoride-containing electrolyte consisted of 0.1 M HF + 0.7 M $MnSO_4$ and the dopant additives in the electrolyte were sulfates of the following cations in different concentrations: NH_4^+, Fe^{2+}, Co^{2+}. Electrolytic doping by Fe^{2+} and Co^{2+} of EMDs (electrodeposited manganese dioxides) included the binary or trinary cationic additives to affect the phase composition and functionality of the electrodeposition product (Tab. 1).

The resulting precipitate was filtered off, washed to a negative sample for sulfate ion. The precipitate was dried in an oven to constant weight (180 min at 110°C). The dried powder was ground in an agate mortar for 30 min and sieved through a sieve [1].

2.2. Characterization of the obtained materials

Table 1. Characterization of NH_4^+, Co^{2+}, Fe^{2+} doped Manganese(IV) oxides

Sample names	Electrolyte composition 0.1M HF, 0.7M $MnSO_4$	Calculated formula according to Ruetcshi's model of cationic vacancies
MNF-1	+ 1.5M $(NH_4)_2SO_4$*	$Mn_{0.84}^{4+}\ Mn_{0.04}^{3+}\ \square_{0.12}O_{1.48}OH_{0.52}$
MNF-2	+ 1.5M $(NH_4)_2SO_4$**	?
MNF-CoFe	+ 1.5M $(NH_4)_2SO_4$, 0.01M $FeSO_4$, 0.1M $CoSO_4$	$Mn_{0.63}^{4+}\ Mn_{0.34}^{3+}\ \square_{0.03}Co_{0.027}Fe_{0.008}O_{1.53}OH_{0.47}$
MNF-FeCo	+ 1.5M $(NH_4)_2SO_4$, 0.1M $FeSO_4$, 0.01M $CoSO_4$	$Mn_{0.13}^{4+}\ Mn_{0.57}^{3+}\ \square_{0.3}Co_{0.005}Fe_{0.1}O_{0.23}OH_{1.77}$

**electrodeposition time 60 min;*
***electrodeposition time 120 min.*

The chemical formula was calculated for each sample (Tab. 1) using AAS (Tab. 2) and TGA data. This formula was introduced in P. Ruetschi`s cationic vacancies model:

$$Mn_{1-x-y}^{4+}Mn_x^{3+}\square_y O_{2-x-4y}OH_{4y+x}$$

where x, y, and are molar fractions of Mn^{3+} and cationic vacancies ($\square$), respectively.

All obtained samples are nanoparticles (Fig. 2, Tab. 2).

Table 2. Average size of sample nanocrystals and the results of atomic absorption analysis

Sample names	Average length of nanoparticals, nm	Average nanoparticals diameter, nm	Content in samples, %		
			Mn	Fe	Co
MNF-1	372±10	23±2	51.89	-	-
MNF-CoFe	337±11	12±2	50.61	0.22	0.80
MNF-FeCo	-	19±2	35.21	2.91	0.15
MNF-2	62±5	-	?	?	?

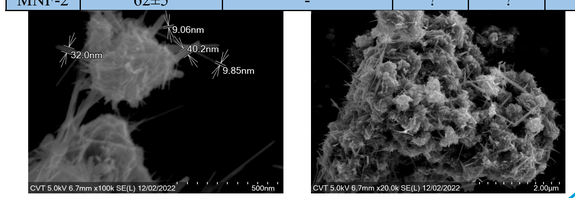

Figure 2. SEM image of an MNF-2 sample

3. Development of ink composition for electrochemical measurments on RDE

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3.1. Pretreatment of electrodes

Before the first use, electrodes are sandpapered with decreasing roughness (e.g. 400-1000-1500-2000-2500). Before each measurement, electrodes are polished with polishing paste (Al_2O_3 slurry; 1.0 µm and 0.05 µm) on a wet polishing cloth for 3-5 minutes, and rinsed thoroughly with water. No scratches must be visible on the glassy carbon surface. Before drop-coating of catalyst, electrodes are ultrasonicated in millipore water for 5 minutes, and let to dry in air [3].

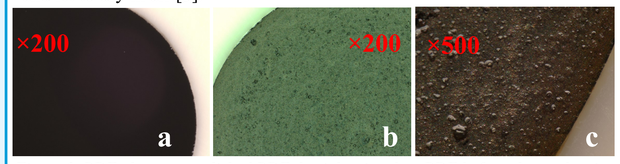

Figure 3. RDE photo. a—polished RDE, b—ink printed on RDE before electrochemical measurements, c—RDE after electrochemical measurements

3.2. Ink preparation protocol

1. Sonicate the oxide material in ethanol for 60 min.
2. Evaporate ethanol at 90°C for 60 min
3. Ultrasound disperse the precipitate in water for 45 min.
4. Addition of Nafion and sonication 15 min

Table 3. Ink Recipe

C_2H_5OH (ml)	0.833
H_2O (ml)	0.833
Nafion (5%) (ml)	0.167
MnO_2 (mg)	2.5
Ultrasonic (min)	60+45

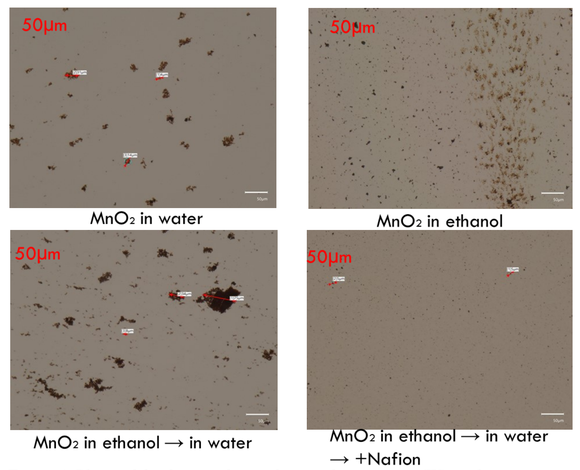

Figure 4. Photo of the degree of coagulation of manganese (IV) oxide in various solvents and their combinations

Reasons for using ethanol: H-bonding interactions, structure and dynamics of H-bonds, dipole-dipole interactions, induced-dipole interactions, gas-phase polarizability of the ethanol molecule is about five times greater than the corresponding value of the water molecule.

4. Protocol of optimitzation for electrochemical measurments on RDE

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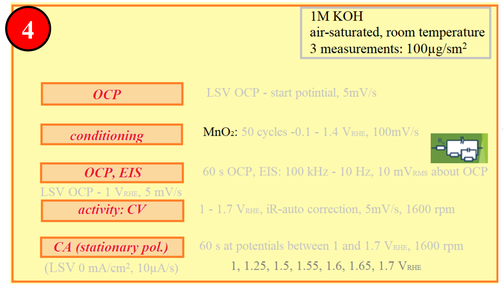

Figure 5. Protocol for electrochemical measurements

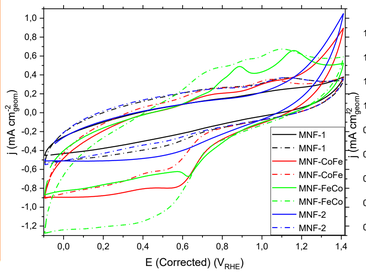

Figure 6. Comparison of current densities values of the second and last cycles (I 2-I 50)

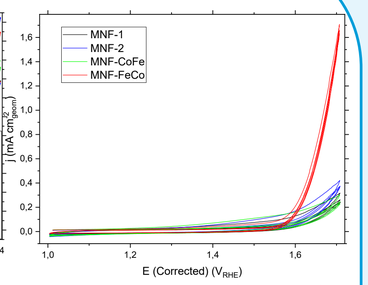

Figure 7. Comparison of activity of doped oxide materials

Conclusions

Investigated samples of doped manganese oxides/hydroxides are nanomaterials with improved performance provided by the electrolytic doping procedure.

The recipe of electrode ink for electrochemical measurements on RDE has been developed demonstrating the formation of stable films. These films remained stable after electrochemical measurements using the proposed in this work protocol for RDE in 1M KOH.

MNF-FeCo sample showed the best electrochemical characteristics (activity and process current densities) as an electrode nanomaterial for OER processes in alkaline electrolytes

References

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