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Polyanionic Molybdate Powders as Promising Electrode Materials Based on NASICON $\text{Fe}_2(\text{MoO}_4)_3$ Networks

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Abstract: In this paper, $\text{Fe}_2(\text{MoO}_4)_3$ (FMO) powders have been synthesized via an easy precipitation approach. The microstructural properties of the synthesized product were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Two FMO samples, 1 and 2, were synthesized using two reactants, sodium molybdate and ammonium heptamolybdate, respectively. In both cases, pure monoclinic structure with space group P2/a has been identified, via XRD measurements. The crystallite sizes, estimated from Scherer's formula, are of (38 ± 2) and (46 ± 4) nm according to the precursor used. Besides, the sample 1 showed a relatively larger specific surface area of $42.77 \text{ m}^2/\text{g}$, than the sample 2 with $35.28 \text{ m}^2/\text{g}$. The EDS microanalysis confirms the stoichiometric amount of the chemical elements. The SEM micrographs reveal a regular distribution of particles shape that presented grain size of order of (192 ± 52) nm for sample 1. While, the sample 2 presents a grains of (215 ± 59) nm size, with a less regular shape.

Keywords: Iron molydates; transition metal; SEM; microstructural analysis

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1. Introduction

Nowadays, the development of transition metal oxides (TMOs) with excellent electrochemical performance have been a subject of research effort in the worldwide [1]. Among these, Transition metal molybdates [2], have received intensive interest as the electrode for lithium-sodium storage (LIBs) and (SIBs), owing to their high capacity, abundant and environmentally friendly which can reduce the cost of batteries at large-scale [3]. The electrochemical activity of iron-based electrode materials, correlated with structure-

performance relations, it will be competitive electrodes for next-generation energy storage devices. The NASICON-type $\text{Fe}_2(\text{MoO}_4)_3$ with an ideal 3D open framework for Na^+ transportation has attracted some interest for sodium storage. [4]

This communication relates a comparative microstructural study of two FMO samples prepared in aqueous solutions, using two molybdate species, ammonium heptamolybdate and sodium molybdate.

2. Results and Discussion

The crystalline phases of the FMO samples were determined by XRD analysis, as displayed in Figure. 1. The diffraction peaks of both FMO samples fit monoclinic crystalline phase with the space group P2/a, that matches standard JCPDS No. 96-152-4204 ($a = 15.7070 \text{ \AA}$, $b = 9.2310 \text{ \AA}$, $\beta = 125.250^\circ$ and $c = 18.2040 \text{ \AA}$) [5]. The key structural parameters of FMO samples, determined from XRD measurements, are gathered on the table 1. The crystallite size (D) values were estimated from the Scherrer's formula, applied to the major diffraction peaks (40-2). The slight difference in the diffractograms of samples 1 and 2 leads to significant enhancement in physical properties. The sample 1 for example, presents a lower crystallite size associated to somewhat higher unit cell volume. Besides, the specific surface

area for sample 1 is higher (about 20%) than sample 2. This means that the former can constitute a better catalyst than the latter. [6]

The elemental composition of FMO, as well as their morphology were investigated by EDS and SEM analyses respectively. The obtained results are gathered in Figure.2. EDS measurements confirm the purity of the samples, as the elemental constituents, Fe, Mo and O are present in proportions closes to the expected formula (Table 2). Moreover no other element was observed, except carbon which is probably due to the substrates used in analysis (Fig. 2(c-d)). The micrographs show some agglomerated spherical particles (Fig.2(a-b)). A regular distribution of particles shape for sample 1 and non-uniform shape of the particles for sample 2. (Fig.2(e-f))

Table 1. Structural parameters of FMO powders.

	a (Å)	b (Å)	c (Å)	β (°)	V (Å ³)	D (nm)	S (m ² /g)
sample 1	15.648(4)	9.311(6)	17.889(4)	125.25(4)	2128.495(14)	38±2	42.768
sample 2	15.643(4)	9.309(6)	17.875(4)	125.25(4)	2125.693(14)	46±4	35.284

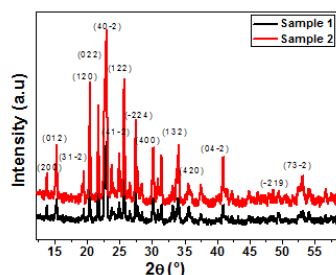


Figure 1. XRD patterns of the prepared iron molybdates FMO.

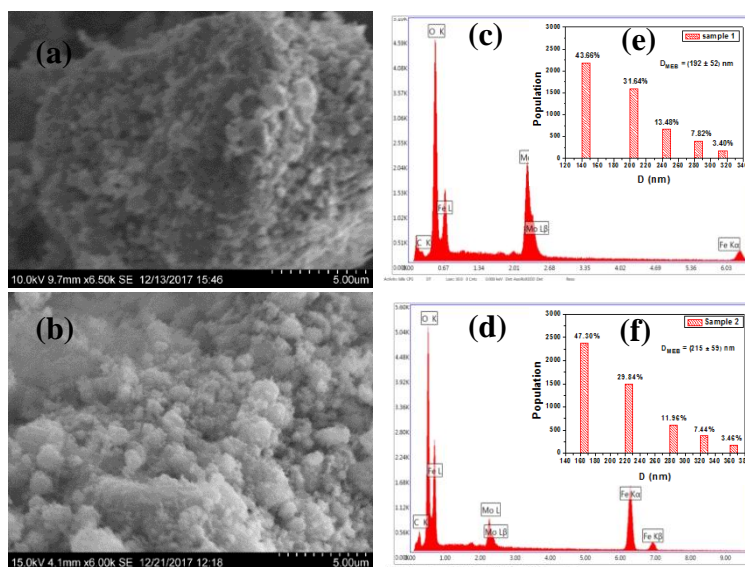


Figure 2. (a-b) SEM micrographs, (c-d) EDS spectrum and (insets e-f) histogram statistics of particles size distribution of FMO for the sample 1 and 2 respectively.

Table 2. Determination of the chemical composition by EDS of FMO.

Element	Experimental atomic %	Theoric atomic %	Difference %	Experimental molar ratio	Theoric molar ratio
O	71.32	70.59	1.02	12.12	12
Fe	11.60	11.76	0.16	1.97	2
Mo	17.08	17.65	3.23	2.90	3

3. Materials and Methods

The FMO powders was synthesized via a conventional precipitation method. An aqueous solution of Iron sulfur heptahydrate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was mixed with aqueous solution of either sodium molybdate dihydrate $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Sample 1) or ammonium heptamolybdate tetrahydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (Sample 2). The mixture solutions were stirred for 30 min, aqueous soda solution (NaOH) was added dropwise until pH=8 is reached. The reaction progressed under magnetic stirring at room temperature for 2 hours, leading to the formation of gel like precipitates. After the purification

process, the obtained powders were dried at 100 °C for 10 h and annealed in air at 500 °C for 5h. The crystal structure analyses were performed by powder X-ray diffraction with an analytical X'Pert spectrometer (Philips Xpert) using $\text{CuK}\alpha$ radiation source with wavelength of 0.15405 nm. The collection process was kept the same for different samples with a step size 0.016 degree in the 2θ range from 10–60 degrees. The particles morphology and composition were investigated by scanning electron microscope (S-3400N, HITACHI, Japan) coupled with Energy-dispersive spectroscopy.

4. Conclusions

In this study, we show that it is possible to use a simple rout of wet chemistry to obtain promising nanoscale iron-based materials, namely $\text{Fe}_2(\text{MoO}_4)_3$. XRD and EDS analyses show the presence of pure single-phase monoclinic $\text{Fe}_2(\text{MoO}_4)_3$ (FMO). The FMO synthesized from sodium molybdate (Sample 1) presents a specific surface area 20% larger than that obtained from ammonium heptamolybdate (Sample 2). This means that the former will be more efficient catalyst. Moreover, it permits an easier ion exchange, leading to a fast charge transport, and thus to enhancement of electrochemical responses. The obtained results are encouraging to continue in this path for electrode materials devices and environmental applications.

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Author Contributions

Conflicts of Interest

“The authors declare no conflict of interest”.

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