



Fluorine substituted molybdenum oxide as cathode material for Li-ion battery



D.P. Opra^{a,*}, S.V. Gnedenkov^a, A.A. Sokolov^{a,b}, A.B. Podgorbunsky^a, N.M. Laptash^a, S.L. Sinebryukhov^a

^a Institute of Chemistry, FEB RAS, Vladivostok 690022, Russia

^b Far Eastern Federal University, Vladivostok 690950, Russia

ARTICLE INFO

Article history:

Received 6 May 2015

Received in revised form

21 July 2015

Accepted 22 July 2015

Available online 23 July 2015

Keywords:

Molybdenum oxyfluoride

Li-ion battery

Cathode

Atomic substitution

Reversible capacity

ABSTRACT

Molybdenum oxyfluoride $\text{MoO}_{2.8}\text{F}_{0.2}$ has been synthesized by solid-phase method. Its morphological and structural features were studied by scanning electron microscopy and X-ray powder diffraction. It was established that the substitution of the O atoms for F atoms in MoO_3 structure leads to charge redistribution in the crystal lattice and conductivity increasing from $4.4 \cdot 10^{-9} \text{ S cm}^{-1}$ to $1.8 \cdot 10^{-6} \text{ S cm}^{-1}$. It was shown that molybdenum oxyfluoride characterized by higher discharge–charge stability in comparison with the oxide itself: 10-fold cycling in the range from 3.5 to 1.5 V yields 160 mA h g^{-1} and 120 mA h g^{-1} for $\text{MoO}_{2.8}\text{F}_{0.2}$ and MoO_3 , respectively.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Li-ion batteries (LIB) are the commonly used energy sources for state-of-art high-technology applications. At the same time the capacity of the most widespread LiCoO_2 cathode is much smaller ($120\text{--}150 \text{ mA h g}^{-1}$) than that of the graphite anode ($350\text{--}365 \text{ mA h g}^{-1}$). In addition the Co toxicity and high cost limits the usage of LIBs for high-energy applications, e.g., hybrid and electric vehicles, uninterruptible power supplies, unmanned underwater vehicles [1–3]. Note, that the other popular cathodes, e.g., LiMn_2O_4 , LiNiO_2 , and LiFePO_4 are more cost-effective and environmental friendly in comparison with LiCoO_2 . However, the low specific capacity is also typical of these cathode materials [4–6]. In this way, the synthesis of high energy, safety, and low cost cathode materials is a fundamental problem of LIB field.

MoO_3 with orthorhombic crystal lattice (space group $Pbnm$) is a promising cathode for LIB due to its thermodynamically stable two-dimensional layered structure. Each layer is formed by MoO_6 octahedra that share edges in the (001) direction and are connected by corners in the (100) direction. The interlayer interaction is mainly through the van der Waals forces between oxygen atoms. Two types of vacant sites (intralayers and interlayers) are available in MoO_3 crystal structure for hosting foreign ions like lithium [7,8].

The theoretical capacity of molybdenum oxide vs. Li^+/Li reaches $C=1117 \text{ mA h g}^{-1}$, the volume change during Li^+ intercalation–deintercalation is calculated to be as much as 104% [9,10]. However, slow solid-state diffusion of Li^+ as well as low conductivity decrease the reversible capacity of MoO_3 [11–13]. According to the reports [14–16] partial substitution of the O atoms for F atoms is a promising way for improvement of cycle performance of metal oxides. For example, it was established that fluorine substituted $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$, $\text{Li}_3\text{V}_2(\text{PO}_4)_3$, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ provide stable cycling even at high-rate up to 10C.

In this work molybdenum oxyfluoride $\text{MoO}_{2.8}\text{F}_{0.2}$ was prepared by solid state synthesis resulted in substitution of the O atoms for F atoms (the F/O substitution) in the MoO_3 structure. The effects of atomic substitution on structural, morphological and electrochemical parameters were investigated.

2. Experiment

Nonstoichiometric molybdenum oxyfluoride $\text{MoO}_{2.8}\text{F}_{0.2}$ was synthesized by interaction of two solids: H_2MoO_4 and NH_4HF_2 (the mole ratio of 1:0.3–0.5) at $420 \pm 10 \text{ }^\circ\text{C}$. For comparative analysis of physicochemical and electrochemical parameters of $\text{MoO}_{2.8}\text{F}_{0.2}$ the commercial MoO_3 (99.9% purity) was investigated also.

For the particle size averaging the $\text{MoO}_{2.8}\text{F}_{0.2}$ and MoO_3 was grinding in a planetary mill Fritch Pulverisette 7 (Germany) during

* Corresponding author.

E-mail address: ayacks@mail.ru (D.P. Opra).

20 cycles. Each cycle included an active (grinding during 10 min at 450 rpm) and passive stage (25 min pause). The milling process was conducted using a zirconia container and balls.

The morphology was investigated by scanning electron microscopy (SEM) using Hitachi S5500 (Japan) microscope. The crystal structure was characterized by X-ray diffraction (XRD) on Bruker D8-Advance (Germany) diffractometer. The conductivity was determined by electrochemical impedance spectroscopy (EIS) at room temperature using Solartron SI 1260 (Great Britain) analyzer.

The working electrode was consisted of 80 wt% $\text{MoO}_{2.8}\text{F}_{0.2}$ (or MoO_3), 10 wt% carbon black, and 10 wt% polyvinylidene fluoride. Its area was equal to 1.75 cm^{-2} (round disc). The mass of the active material was approximately 5 mg cm^{-2} . Lithium metal disc (thickness of 0.1 mm) was applied as both counter and reference electrodes. 1 M solution of LiBF_4 salt in the mixture of propylene carbonate and dimethoxyethane at a volume ratio of 3:1 was used as an electrolyte. The design of electrochemical half-cell is described in detail in [3–5].

The electrochemical performance was evaluated using a Solartron 1470E (UK) potentiostat/galvanostat. The parameters were measured by the galvanostatic discharge–charge at current density of 30 mA g^{-1} in the range from 3.5 to 1.5 V during 10 cycles. The measurements were carried out at least on six half-cells.

3. Results and discussions

The structure and chemical composition of $\text{MoO}_{2.8}\text{F}_{0.2}$ was investigated previously [17,18]. SEM method shows that the morphology of molybdenum oxyfluoride (Fig. 1) and commercial MoO_3 after grinding is similar. The high magnification SEM analysis of $\text{MoO}_{2.8}\text{F}_{0.2}$ reveals the heterogeneous surface of particles that seems to facilitate the electrochemical reaction with Li^+ ions.

XRD patterns (Fig. 2) of $\text{MoO}_{2.8}\text{F}_{0.2}$ and commercial MoO_3 are

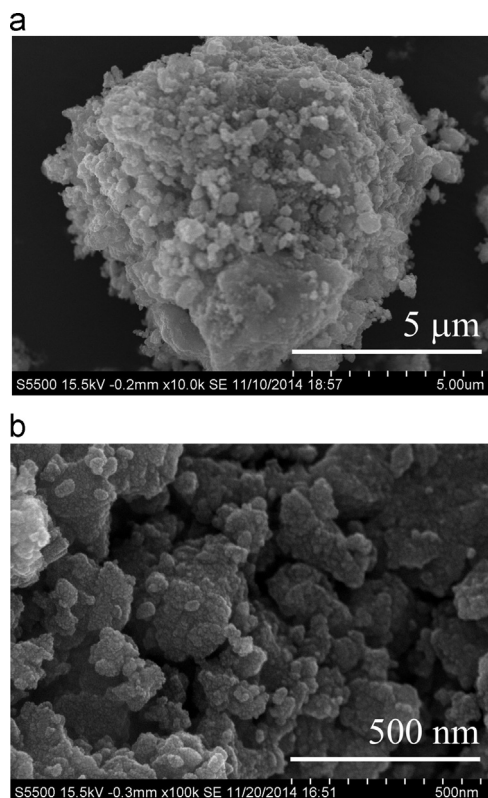


Fig. 1. SEM-images for $\text{MoO}_{2.8}\text{F}_{0.2}$.

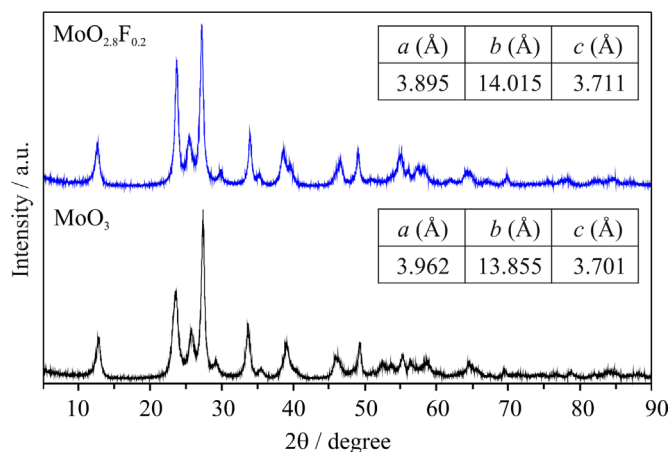


Fig. 2. XRD patterns of $\text{MoO}_{2.8}\text{F}_{0.2}$ and commercial MoO_3 .

similar and correspond to the orthorhombic phase (JSCD no. 01-089-5108, space group $Pbnm$), but their lattice parameters are somewhat different. Partial substitution of the O atoms for F atoms leads to the charge redistribution in the lattice due to the reduction of Mo^{6+} to Mo^{5+} . Accordingly the X-ray photoelectron spectroscopy data two doublets with the binding energies of 233.5 and 232.0 eV and their intensity ratio [17] confirm the oxyfluoride composition determined also chemically on fluorine content [18], that means the F/O atomic substitution.

Impedance spectra (Fig. 3) for both $\text{MoO}_{2.8}\text{F}_{0.2}$ and commercial MoO_3 consist of high frequency semicircle corresponds to the material conductivity and low frequency arc related to double layer at the sample/electrode interface. According to the EIS results the partial F/O substitution increases the conductivity of material, possibly, due to charge redistribution in the crystal lattice. In particular the conductivity of $\text{MoO}_{2.8}\text{F}_{0.2}$ was $1.8 \cdot 10^{-6} \text{ S cm}^{-1}$ while the MoO_3 yields only $4.4 \cdot 10^{-9} \text{ S cm}^{-1}$.

The discharge–charge cycling of $\text{MoO}_{2.8}\text{F}_{0.2}$ and commercial MoO_3 from 3.5 to 1.5 V vs. Li^+/Li at current density of 30 mA g^{-1} is

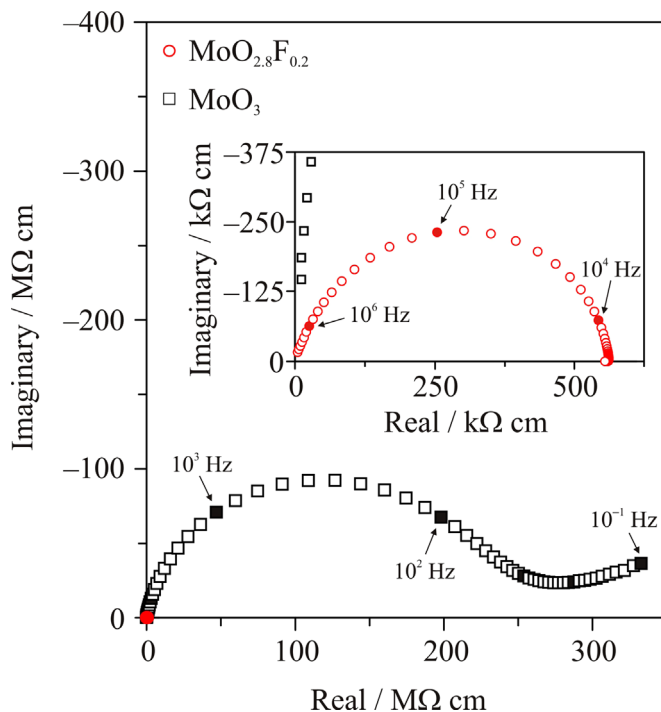


Fig. 3. Impedance diagrams for molybdenum oxyfluoride and oxide.

Download English Version:

<https://daneshyari.com/en/article/1642003>

Download Persian Version:

<https://daneshyari.com/article/1642003>

[Daneshyari.com](https://daneshyari.com)