



# Facile one step synthesis and enhanced electrochemical performance of Molybdenum dioxide and carbon co-modified lithium manganese silicate cathode materials for lithium-ion batteries



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## ABSTRACT

Through facile one step sol-gel method,  $\text{Li}_2\text{MnSiO}_4$ -based cathode materials have been successfully synthesized and co-modified with carbon and  $\text{MoO}_2$  coating. The phase compositions and morphology of the as-prepared products have been characterized by XRD, SEM and TEM. The physical characterization indicates the introduced  $\text{MoO}_2$  exists on the particle surface of orthorhombic  $\text{Li}_2\text{MnSiO}_4$ , forming a hybrid coating layer with amorphous carbon. Meanwhile, the addition of  $\text{MoO}_2$  improves the dispersion of particle size distribution. Therefore, the electrochemical performance of the pristine  $\text{Li}_2\text{MnSiO}_4/\text{C}$  has been significantly improved after coating  $\text{MoO}_2$ , especially in the case of 1 wt%  $\text{MoO}_2$  component. The optimal as-prepared sample exhibits a reversible capacity of 184.9 mA h/g at 0.1C and maintains 127.5 mA h/g even at a high rate of 1C. The excellent rate performance can be attributed to reduced interfacial resistance and enhanced lithium ion diffusion coefficient.

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## 1. Introduction

Rechargeable Li-ion batteries have been widely used in portable electronic devices due to its high energy density, long cycle life and low cost [1]. Recently, the usage of Li-ion batteries has increased in transport application and energy storage systems, which need high capacity and thermal stability cathode to meet the energy demands [2,3]. However, conventional cathode materials such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiFePO}_4$ , which can only allow one  $\text{Li}^+$  or even less than one  $\text{Li}^+$  ion in per unit formula to insert into cathodic host lattice, need to be improved with respect to energy density [4–6]. Fortunately, polyanion-type materials lithium orthosilicate,  $\text{Li}_2\text{MSiO}_4$  (M=Mn, Fe, and Co), have attracted a lot of interest recently as a new class of cathode materials due to the overwhelming advantages, such as cell safety, possibility of extraction of more than one  $\text{Li}^+$  ion in per unit formula, high theoretical capacity ( $>330\text{ mA h g}^{-1}$ ), and high thermal stability provided through strong Si–O bonding [7,8]. Among the lithium

orthosilicate,  $\text{Li}_2\text{MnSiO}_4$  is much more feasible to insert/extract two  $\text{Li}^+$  ions than  $\text{Li}_2\text{FeSiO}_4$  and  $\text{Li}_2\text{CoSiO}_4$  [8], due to possible oxidation of  $\text{Mn}^{4+}/\text{Mn}^{3+}$  couple within the potential range of present electrolyte systems.

Nevertheless,  $\text{Li}_2\text{MnSiO}_4$  suffers from the drawbacks of the poor electronic conductivity ( $\sim 10^{-16}\text{ S cm}^{-1}$ ) and the inherent instability of its delithiated structure, which limits its high-rate performance [7]. Nowadays, a lot of strategies such as carbon coating, particle size reduction and cation doping have been employed to address the shortcomings of  $\text{Li}_2\text{MnSiO}_4$ , but the electrochemical performance is still far from satisfactory [9–13].

Surface coating or modifying with metal oxide is also an effective way in enhancing the electrochemical performance. Coating of ZnO [14],  $\text{Al}_2\text{O}_3$  [15], and  $\text{SiO}_2$  [16] on the surface of  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  particles could suppress the formation of HF and the dissolution of transition metal ions.  $\text{TiO}_2$  [17],  $\text{ZrO}_2$  [17,18],  $\text{CeO}_2$  [19], ZnO [20] and  $\text{Cr}_2\text{O}_3$  [21] have been used to construct the surface-coated  $\text{LiMn}_2\text{O}_4$  phase. Besides, coating or modifying  $\text{LiFePO}_4/\text{C}$  composites with oxides ( $\text{SiO}_2$  [22], CuO [23], and  $\text{V}_2\text{O}_3$  [24]) can also improve the electrochemical performance. In a word, the surface modification can effectively suppress the side reaction on the electrode surface and decrease the charge transfer resistance, which could significantly improve the electrochemical

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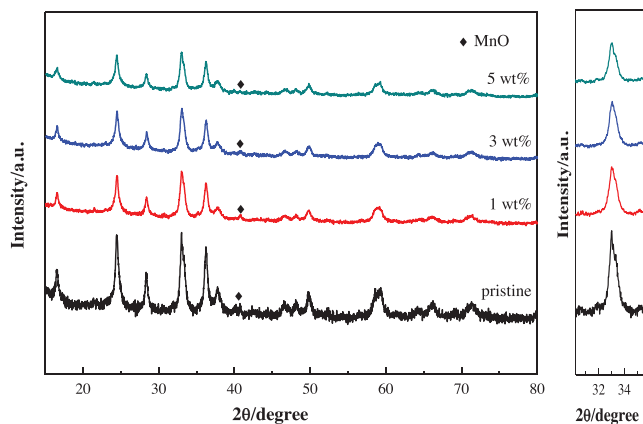


Fig. 1. XRD patterns of pristine  $\text{Li}_2\text{MnSiO}_4/\text{C}$  and  $\text{MoO}_2$  coated  $\text{LiMnSiO}_4/\text{C}$ .

performance of the materials. However, the mixing coating of carbon and metal oxide on the surface of  $\text{Li}_2\text{MnSiO}_4$  has not been reported up to now.

In this paper, molybdenum dioxide ( $\text{MoO}_2$ ) and carbon co-modified  $\text{Li}_2\text{MnSiO}_4$  composites are prepared as the cathode material by facile one step sol-gel method. Herein,  $\text{MoO}_2$  is chosen

as the coating layer owing to its high electrical conductivity [25] and stability in the air. The phase compositions and morphology of the products have been characterized by XRD, SEM and TEM. The electrochemical performance is investigated by galvanostatic charge-discharge measurement and electrochemical impedance spectroscopy.

## 2. Experimental

The  $\text{MoO}_2$  and carbon co-modified  $\text{Li}_2\text{MnSiO}_4$  cathode materials were prepared by facile one step sol-gel method. Firstly, a stoichiometric amount (the molar ratio of  $\text{Li}:\text{Mn}:\text{Si}$  is 2:1:1) of  $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ ,  $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$  and  $\text{Si}(\text{OC}_2\text{H}_5)_4$  (TEOS) were dissolved in ethanol and distilled water mixed solution ( $V_e/V_w=2:1$ ), and acetic acid was added as catalyst under magnetic stirring at room temperature. Then glucose and ammonium molybdate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ) were added to the above solution under stirring respectively. After adequately magnetic stirring, the transparent solution was evaporated at  $80^\circ\text{C}$  in oil bath to form wet gel, and dried at  $120^\circ\text{C}$  for 24 h under a vacuum atmosphere. The resulting precursor after grinding finely was pre-sintered at  $400^\circ\text{C}$  for 4 h, then pressed into pellets and calcined at  $650^\circ\text{C}$  for 6 h at a flow of  $\text{N}_2/\text{H}_2(V:V=95:5)$ . Then cooled to room temperature, the  $\text{MoO}_2$  and carbon co-modified  $\text{Li}_2\text{MnSiO}_4$  cathode materials with  $\text{MoO}_2$  content of 1 wt%, 3 wt%, and 5 wt% were obtained respectively. Also,  $\text{Li}_2\text{MnSiO}_4/\text{C}$  without coating

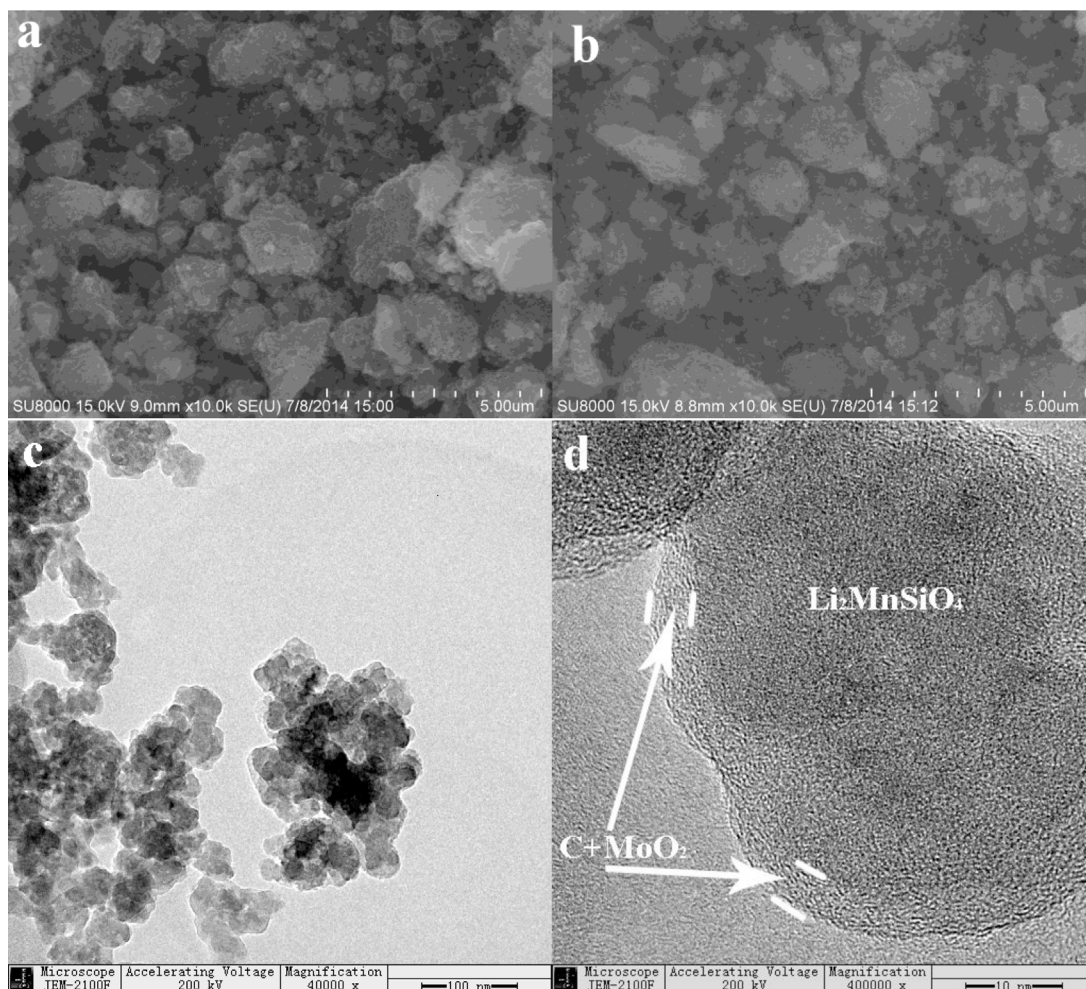


Fig. 2. SEM images of (a)  $\text{Li}_2\text{MnSiO}_4/\text{C}$  and (b) 1 wt%  $\text{MoO}_2$ -coated  $\text{LiMnSiO}_4/\text{C}$ , (c) TEM and (d) HRTEM of 1 wt%  $\text{MoO}_2$ -coated  $\text{LiMnSiO}_4/\text{C}$ .

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