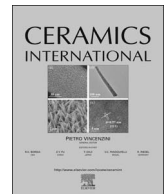




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## SmPO<sub>4</sub>-coated Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> as a cathode material with enhanced cycling stability for lithium ion batteries

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### ABSTRACT

SmPO<sub>4</sub> coated Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> cathode materials were prepared by the precipitation method and calcined at 450 °C. The crystal structures and electrochemical properties of the pristine and coated samples are studied by X-ray diffraction, scanning electron microscopy, high resolution transmission electron microscopy, electron diffraction spectroscopy, galvanostatic cycling, cyclic voltammetry, and electrochemical impedance spectroscopy (EIS). It has been found that the electrochemical performances of the Li-rich cathode material have been substantially improved by SmPO<sub>4</sub> surface coating. Especially, the 2 wt% SmPO<sub>4</sub>-coated sample demonstrates the best cycling performance, with capacity retention of 88.4% at 1 C rate after 100 cycles, which is much better than that of 72.3% in the pristine sample. The improved electrochemical properties have been ascribed to the SmPO<sub>4</sub> coating layer, which not only stabilizes the cathode structure by decreasing the loss of oxygen, but also protects the Li-rich cathode material from side reaction with the electrolyte and increases the Li<sup>+</sup> migration rate at the cathode interface.

### 1. Introduction

Due to the increasingly serious energy crisis, people are actively find and research the new green and clean energy including super capacitor, lithium-ion and sodium-ion batteries etc [1–4]. Lithium-ion batteries are one of the most promising energy storage devices for electric vehicles (EVs) and hybrid electric vehicles (HEVs), because of their high energy density, high power density, stable charge/discharge cycling and no memory effect [5,6]. The cathode material provides the Lithium source for Li extraction and insertion processes, and is the key limiting component to further development of Lithium-ion batteries. In this regard, many cathodes, such as LiCoO<sub>2</sub>, Li<sub>2</sub>MnO<sub>4</sub>, and LiFePO<sub>4</sub> have been developed. Recently, Li-rich layered oxides have attracted particular attention, due to their high specific capacity (> 250 mA h g<sup>-1</sup>) compared with other cathode materials [7,8].

Li-rich layered oxides, denoted as Li(Li<sub>1/3-2x/3</sub>Ni<sub>x</sub>Mn<sub>2/3-x/3</sub>)O<sub>2</sub> or xLi<sub>2</sub>MnO<sub>3</sub>(1-x)LiMO<sub>2</sub> (M=Mn, Ni, Co, etc.), are solid solutions consisting of two different structures: the LiMO<sub>2</sub> phase (R3m) and the monoclinic Li<sub>2</sub>MnO<sub>3</sub> phase (C2/m) [9]. The initial electrochemical reaction mechanism of Li-rich layered oxides is unique: the oxides

undergo an active process during the first charge in order to obtain an excessive reversible capacity [10]. This activation reaction of Li<sub>2</sub>MnO<sub>3</sub> gives a high voltage plateau in the first charging curve, which may lead to the irreversible deintercalation of Li<sub>2</sub>O from the layered lattice at high voltage. The irreversible active reaction, together with the decomposition of the electrolyte in high potential, usually results in the low initial coulombic efficiency of this kind of Li-rich layered oxides. Moreover, the phase change from a layered to a spinel structure during subsequent cycling may lead to poor cycling stability [11].

In order to improve the electrochemical properties of Li-rich layered oxides, several strategies have been employed, such as ion-doping [12–15], nanoarchitecture [16–18], and surface coating. Among the above-mentioned approaches, surface coating is one of the most effective strategies, because coatings can generally i) improve the surface stability of the coated materials, ii) provide a physical barrier that suppresses any detrimental chemical side reactions between electrode surface and electrolyte, and iii) enhance the electronic conductivity within the electrode laminate. As demonstrated in previous reports, surface coating of metal oxides (Al<sub>2</sub>O<sub>3</sub>, MoO<sub>3</sub>, RuO<sub>2</sub>, and Cr<sub>2</sub>O<sub>3</sub>) [19–22], fluoride (FeF<sub>3</sub>) [23], phosphate (LaPO<sub>4</sub>) [24] and

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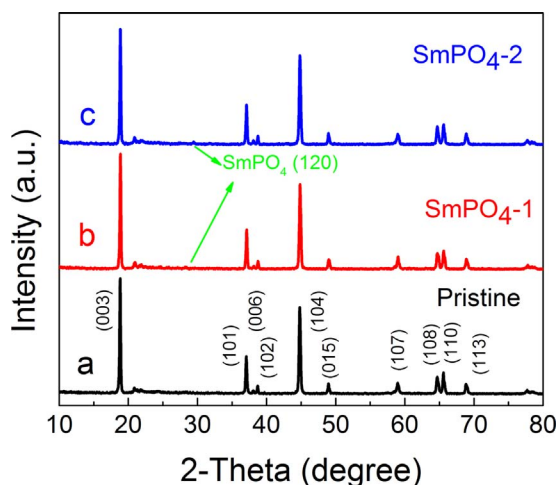


Fig. 1. XRD patterns of the (a) Pristine, (b) SmPO<sub>4</sub>-1 and (c) SmPO<sub>4</sub>-2 samples.

borate (AlBO<sub>3</sub>) [25] can substantially improve the initial discharge capacity and greatly improve the cyclability, due to the formation of a stable SEI film to alleviate the electrolyte decomposition and retain the oxide ion vacancies in the lattice at subsequent charge–discharge cycles.

Recently, the surface coating with metal phosphate have attracted much attention as these metal phosphates are believed to be potential active coating materials for cathodes compounds in Lithium-ion batteries. The Li-metal–P–O coating layer for MPO<sub>4</sub> coated cathodes, compared with other Li<sup>+</sup> ion conductor (for instance Al<sub>2</sub>O<sub>3</sub>), is conductive to enhance the stable capability of electrodes during the charge–discharge process [26]. In addition, rare earth element has a special structure due to the different arrangements of 4f electron bring forth abundant energy levels [27]. Herein, SmPO<sub>4</sub> is employed as a

coating material to enhance the initial coulombic efficiency and cycling stability of Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> (LMNCO) cathodes. In this work, SmPO<sub>4</sub> coated LMNCO is successfully prepared via a facile chemical precipitation route. Experimental results show that electrode of LMNCO coated by 2 wt% SmPO<sub>4</sub> exhibits high initial coulombic efficiency and excellent cycling stability compared with the pristine material. In particular, the effects of coating on the structure and electrochemical properties are investigated in detail.

## 2. Experimental section

Li<sub>1.2</sub>Mn<sub>0.54</sub>Ni<sub>0.13</sub>Co<sub>0.13</sub>O<sub>2</sub> (LMNCO) was synthesized by a sol–gel method using citric acid as the chelating agent. Stoichiometric amounts of LiCOOCH<sub>3</sub>·2H<sub>2</sub>O, Ni(COOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Co(COOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, and Mn(COOCH<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were dissolved in de-ionized water. Then the solution was added dropwisely into citric acid solution under continuous stirring. After being stirred thoroughly, the solution was heated at 80 °C and a continuous stirring was applied until a clear viscous gel was formed. The gel was dried in an oven at 80 °C to obtain the precursor powder. After heating at 450 °C in air for 5 h, the powder was ground and then calcined at 900 °C for 12 h in air. A 10% excess of lithium was used to compensate for lithium loss during the calcinations.

For preparation of SmPO<sub>4</sub> coated LMNCO composite, the required amount of SmCl<sub>3</sub>·6H<sub>2</sub>O was dissolved in de-ionized water, followed by adding NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> solution under constantly stirring. Then the as-prepared LMNCO was dispersed in the above solution, and the mixture was heated at 80 °C and stirred vigorously until the solvent was evaporated. After that, the wet powder was dried at 80 °C overnight. After mild grinding, the as-obtained powder was further heated at 450 °C for 4 h in the flowing argon to obtain the final coated sample. Herein, the coated SmPO<sub>4</sub> contents were controlled at 1 and 2 wt%, which were labeled by SmPO<sub>4</sub>-1 and SmPO<sub>4</sub>-2, respectively.

Powder X-ray diffraction (XRD) measurement was performed on

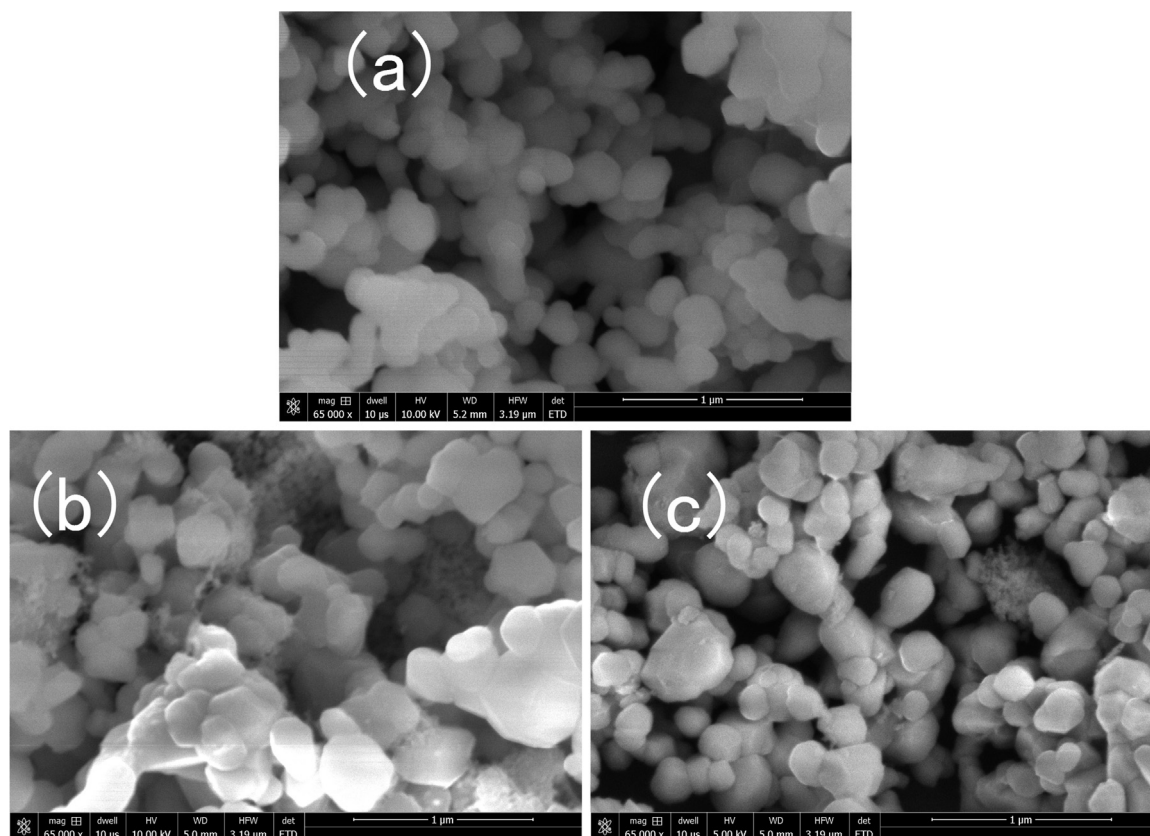


Fig. 2. SEM images of (a) the Pristine, (b) SmPO<sub>4</sub>-1 and (c) SmPO<sub>4</sub>-2 samples.

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