

Full paper

New insight into atomic-scale engineering of electrode surface for long-life and safe high voltage lithium ion cathodes



Sixu Deng^{a,b,1}, Biwei Xiao^{a,1}, Biqiong Wang^a, Xia Li^a, Karthikeyan Kaliyappan^a, Yang Zhao^a, Andrew Lushington^a, Ruying Li^a, Tsun-Kong Sham^c, Hao Wang^{b,*}, Xueliang Sun^{a,*}

^a Department of Mechanical and Materials Engineering, University of Western Ontario, London, Ontario, Canada N6A 5B9

^b The College of Materials Science and Engineering, Beijing University of Technology, Beijing 100124, PR China

^c Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

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ABSTRACT

Spinel LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is a promising high voltage cathode material for lithium ion batteries (LIBs). However, dissolution of Mn and unwanted side reactions between LNMO and the electrolyte raises several safety issues while also resulting in deteriorated electrochemical performance of LIBs at high working voltages. Here, we report the use of ultrathin atomic layer deposited (ALD) AlPO₄ thin film as a coating material for LNMO electrodes to circumvent the stated issues. The as-prepared AlPO₄ coated LNMO demonstrates excellent capacity retention with prolonged cycle life compared to the bare one. Synchrotron based X-ray spectroscopy was employed to understand how ultrathin coating layer improve the cycle life, and then develop a detailed mechanism for the effect of coating layer. Our studies revealed that using atomic scale coating layer with improved thermal stability effectively impede the side-reactions occurrence at high voltage, resulting in significantly improved safety and electrochemical performances.

1. Introduction

Spinel LiNi_{0.5}Mn_{1.5}O₄ (LNMO) is considered as a promising high voltage cathode material for use in next generation lithium ion batteries (LIBs) due to its high operating voltage plateau (about 4.7 V vs. Li⁺/Li) and theoretical specific capacity of 147 mA h g⁻¹, effectively improving the energy density of batteries for use in electric vehicles (EVs) [1–3]. However, using such high voltage (beyond 4.5 V) exceeds the voltage window of conventional carbonate based LiPF₆ electrolytes, leading to rapid electrolyte decomposition and unwanted side reactions occurring between the active electrode and the electrolyte species [4–6]. Furthermore, high voltage charging process results in exothermic reactions occurring between the flammable electrolyte and metastable Li_xNiMnO, raising overheating symptom of batteries and triggering a number of safety hazard [7–9]. Meanwhile, decomposition of electrolyte causes the formation of an insulating solid electrolyte interphase (SEI) layer, thereby impeding Li⁺ diffusion during the charge/discharge process, leading to serious capacity fading [2,3,10,11]. Furthermore, dissolution of Mn is another serious issue of LNMO, which causes destroyed material structure and reduced cycle life of LNMO [12–14].

To address these challenges, many strategies have been employed to improve the electrochemical performances of LNMO-based batteries, including morphology control, element doping and surface modification [15–18]. Among the available strategies, application of a surface coating is considered as an effective method for providing a stable interface between the active material and electrolyte. A number of coating materials have been employed for use on LNMO, including metal oxides (Al₂O₃ [19], ZnO [20], SiO₂ [21], ZrO₂ [22], Y₂O₃ [23]), fluorides (BiOF [24]) and metal phosphates (Li₃PO₄ [25], FePO₄ [26]). These coating materials aim to prevent side reactions and dissolution of metal ions to improve performances. Among them, AlPO₄ has been considered as a safe coating materials providing improved thermal stability [7,8], and has been widely applied as a coating for other cathode materials (e.g., Li[Li_{0.2}Fe_{0.1}Ni_{0.15}Mn_{0.55}]O₂ [27], LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ [28] and LiNi_{0.8}Co_{0.2}O₂ [29]). Cho et al. reported that LiCoO₂ particles coated with AlPO₄ dramatically reduced the heat evolution in the charged state [30–32]. The high electronegativity of PO₄³⁻ with Al³⁺ ions enables to effectively resist the reaction between electrode materials and electrolyte, which both enhances the safety and improves the electrochemical performances of cells [32–34].

Various methods had been adopted to coat cathode with AlPO₄,

* Corresponding authors.

E-mail addresses: haowang@bjut.edu.cn (H. Wang), xsun@eng.uwo.ca (X. Sun).

¹ Sixu Deng and Biwei Xiao contribute equally to this work.

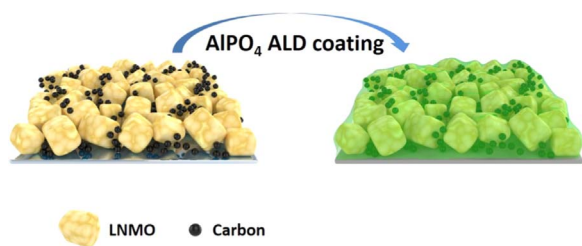


Fig. 1. Schematic diagram of AlPO_4 coating on LNMO electrode via atomic layer deposition.

including sol-gel [35] or wet-chemical [36] techniques. However, these coating approaches have limited control over surface coverage, thickness and uniformity. Unlike other surface modification methods, atomic layer deposition (ALD) is a novel coating technique used for the deposition of highly conformal and uniform layers with well controlled thickness [37–40]. In our group, ALD coatings such as LiTaO_3 and FePO_4 have been used on various cathode materials including $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC) [41] and LNMO [42]. Al_2O_3 ALD coating on the surface of LNMO is the most studied coating material, and has been shown to suppress side reactions from occurring between the electrode and the electrolyte as well as mitigating decomposition of the SEI. Kim et al. demonstrated that LNMO electrode coated with Al_2O_3 can dramatically suppress self-discharge effects as well as dissolution of transition metals [19,43]. Comparing with Al_2O_3 , AlPO_4 coating is expected to improve both reliability and electrochemical performance of LNMO cathodes at high voltages.

For the first time, we reported the use of ultrathin AlPO_4 coating on high voltage LNMO electrodes via ALD (shown in Fig. 1). Cycling stability and rate capability of as-prepared LNMOs, with detailed electrochemical mechanisms, will be discussed through the use of a series of electrochemical characterization techniques. More importantly, synchrotron based X-ray studies are determined to understand the coating effect of ALD AlPO_4 on LNMO. It has been demonstrated that the coating layer with improved thermal stability provides a stable interface for LNMO and can effectively prevent the occurrence of side-reactions and dissolution of Mn, resulting in an improved electrochemical performance of Li-ion batteries. Our study also focuses on a correlation between coatings thickness and electrochemical performances.

2. Experimental

2.1. Preparation of LNMO electrodes

Commercial LNMO powder was purchased from Daejung Energy Materials Co., Ltd., South Korea. Electrodes were prepared by casting a slurry of commercial LNMO, acetylene black (AB) and polyvinylidene fluoride (PVDF) in N-methyl-pyrrolidone (NMP) on aluminum foil and dried at 80 °C under vacuum overnight. The weight ratio of active material: AB: PVDF was 8: 1: 1.

2.2. Preparation of ALD AlPO_4 coated LNMO electrodes

Amorphous aluminum phosphate (AlPO_4) was deposited on LNMO electrodes at 250 °C using trimethyl phosphate [TMPO, $(\text{MeO})_3\text{PO}$], trimethylaluminum (TMA) and water (H_2O) as precursors in a Savannah 100 ALD system (Cambridge Nanotech, USA). Source temperature for TMPO was 75 °C while TMA and H_2O were held at room temperature (RT). The deposition was achieved by following a sequence of TMPO (2 s pulse)- purge (10 s)- H_2O (0.5 s pulse)- purge (15 s)- TMA (0.5 s) pulse- purge (10 s)- H_2O (0.5 s pulse)- purge (15 s). Nitrogen gas (99.999%) was used as a carrying and purging gas at a flow rate of 20 sccm. The thickness of the AlPO_4 thin film was controlled by varying the cycle numbers (n) by repeating the above

procedure. Commercial LNMO cathode electrodes were coated using 2, 5, 10, 20 and 50-ALD cycles of AlPO_4 (denoted as ALP-n).

2.3. Characterization

X-ray power diffraction (XRD) measurements were carried out on a Bruker D8 Advance Diffractometer (Cu-K α source, 40 kV, 40 mA). Raman spectroscopy was performed using a HORIBA Scientific LabRAM HR Raman microscope with an excitation wavelength of 532.4 nm generated by an argon laser. The morphologies and structures of bare and AlPO_4 coated LNMO was observed using a field emission scanning electron microscope (FESEM, Hitachi S4800), transmission electron microscopy with elemental mapping images (TEM, Hitachi H-7000), and high-resolution transmission electron microscopy (HRTEM, JEOL 2010F). All synchrotron X-ray studies were carried out at the Canadian Light Source (CLS). X-ray absorption near edge structure (XANES) measurements using total electron yield (TEY) was carried out on the high resolution Spherical Grating Monochromator (SGM) beamline equipped with a 45 mm planar undulator and three gratings with a photon energy range of 250–2000 eV. X-ray photoemission spectroscopy (XPS) was performed at the variable line spacing plane grating monochromator (VLS PGM) beamline at 200 eV photon energy with a total resolution of 100 meV. For differential scanning calorimetry (DSC) measurements, cells were charged to 5.0 V and held at that voltage for 2 h. After disassembling the cells, the positive electrodes were scraped from the aluminum current collector. Approximately 5 mg of the positive electrode was hermetically sealed in a stainless steel pan. The data were acquired using a TA instrument (SDT Q600) in a nitrogen atmosphere at a heating rate of 5 °C min^{-1} .

2.4. Electrochemical measurements

CR2032 coin cells were assembled in an argon-filled glove-box using lithium metal as the counter electrode and Celgard K2045 as the separator. The electrolyte was composed of 1 M LiPF_6 dissolved in ethylene carbonate (EC)-dimethyl carbonate (DMC) with a volume ratio of 1: 1. Cyclic voltammetry (CV) experiments were studied using a Bio-logic multichannel potentiostat 3/Z (VMP3) with a scanning rate of 0.1 mV s^{-1} and at a potential range of 3.5–5.0 V (vs Li^+/Li). Electrochemical impedance spectroscopy (EIS) tests were measured between the frequency range of 0.01 Hz to 100 kHz by versatile multichannel potentiostat 3/Z (VMP3). Charge/discharge tests were carried out on Arbin BT2000 with a voltage range of 3.5–5.0 V.

3. Results and discussion

X-ray-diffraction patterns of bare LNMO and ALP-50 are shown in Fig. 2a. All the reflections are well indexed based on the cubic spinel structure of LNMO and lack any indication of rock-salt impurity phases. No peaks of AlPO_4 can be observed in the XRD pattern of ALP-50 because of the ultrathin and amorphous nature of ALD AlPO_4 coating. As can be seen from Raman spectra in Fig. S1, all LNMO samples (bare and AlPO_4 coated LNMO) show a strong peak at 164 cm^{-1} indicating all samples follow an ordered phase $\text{P4}_3\text{32}$ space group [44–46]. The peak at 638 cm^{-1} is assigned to symmetric Mn-O stretching of the MnO_6 octahedra, and two peaks around 496 cm^{-1} and 407 cm^{-1} are associated with the Ni^{2+} -O stretching mode in the structure [47]. Compared with bare LNMO, the Ni-O and Mn-O vibrations of AlPO_4 coated LNMO show gradual blue shifts with the increase of ALD cycles. This may be due to the AlPO_4 layer on the surface of LNMO restricting vibration of Ni-O and Mn-O bonds, leading to higher vibrational wavenumbers [48]. The surface morphology of the as-prepared LNMOs was characterized via FESEM (Fig. S2). Interestingly, surface of LNMO becomes gradually rougher with increased number of ALD cycles. A high-resolution TEM image of

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