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# Layered/Layered Homostyructure Ion Conductor Coating Strategy for High Performance Lithium Ion Batteries

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ABSTRACT

The $Li_2MnO_3$ coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ electrode has been sucessfully synthesized through a PVP-chelation and syn-lithiation strategy. X-ray diffraction (XRD) and X-ray photoelectron Spectrometer (XPS) characterizations are applied to verify the existence of the $Li_2MnO_3$ surface layer. The complete and nanoscale $Li_2MnO_3$ coating layer strongly adheres to the host material because of the layered/layered homostyructure, improves the content of Mn element on the surface of the electrode and has three-dimensional path for $Li^+$-ion diffusion. Due to the numerous unique and dramatic advantages of the $Li_2MnO_3$ surface layer, the layered/layered homostyructure electrode exhibits superior cycle stability, rate capability and other electrochemical properties. The newly developmental coating material and versatile nanocoating strategy can also be popularized and applied in other electrode materials.

## 1. Introduction

Layered lithium-mixed transition metal oxides, $LiMO_2$ (M = Ni, Co, Mn) have appeared to be candidates as cathode materials for lithium-ion batteries, due to their unique advantages such as high energy density, good thermal stability, low cost, and low toxicity [1–6]. However, there are still some drawbacks for layered $LiMO_2$ materials to prevent their sustainable and high-power applications. For example, the intrinsic lower $Li^+$-ion conductivity of layered $LiMO_2$ materials result in inferior rate performance for lithium-ion batteries [7–10]. The highly reactive $Ni^{4+}$ or $Co^{4+}$ are unstable in organic electrolyte, which could lead to capacity fading and produce a series of safety issues [7,11].

Based on these existing challenges for $LiMO_2$ materials, surface modification has been used as an effective strategy to improve their electrochemical properties [12–18]. At present, the mainly coating materials are electrochemically inert oxides and phosphates such as $ZrO_2$, $Al_2O_3$ et al. [14,18]. Unfortunately, these coating materials are ion insulator, which are not favorable for both $Li^+$-ion conduction of cathode materials and interfacial charge transfer of the electrode [19]. A class of coating materials of ion conductor, such as $Li_2TiO_3$, $Li_2ZrO_3$ and $Li_2SiO_3$, can avoid the aforesaid drawbacks because of their unique structure. These coating materials can not only act as a protective layer to stabilize the surface structure of cathode materials, suppress metal-ion dissolution and unfavorable interfacial side reactions, but also have three-dimensional path for $Li^+$-ion diffusion which can effectively increase $Li^+$-ion conduction [20–26]. For example, we have demonstrated the availability of the $Li_2SiO_3$ coating material in ameliorating the electrochemical performance of layered cathode materials [25,26].

Monoclinic $Li_2MnO_3$, similar to aforementioned ion conductor coating materials, also has three-dimensional path for $Li^+$-ion diffusion [27]. (Fig. 1b). More importantly, $Li_2MnO_3$ possesses some unique advantages in comparison to other coating materials. Firstly, the layered $Li_2MnO_3$ has the interlamellar (002) d-spacing value of 0.480 nm which can match well with (003) d-spacing of $LiMO_2$ (0.468 nm). The simultaneous existence of the two phases of $Li_2MnO_3$ and $LiMO_2$ in lithium-rich materials further proved the $Li_2MnO_3$ material, as a surface layer, could bond well with $LiMO_2$ materials [28,29]. Furthermore, the homostyructure and similar interlamellar d-spacing is favorable for the formation of the $Li_2MnO_3$ surface layer with ideal crystal structure, which can better preserve the three-dimensional ionic channels. Secondly, the $Li_2MnO_3$ coating layer can increase the content of Mn element on the surface of the layered $LiMO_2$ materials, forming a concentration-gradient structure which is advantageous for the improvement of the cycle stability and safety performance [5,30–32]. In this study, we selected $Li_2MnO_3$, which possesses numerous dramatic advantages compared with other coating materials, as the coating layer to improve the electrochemical performances of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$.

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As to the coating strategy, It is difficult to establish a uniform, complete and controllable coating layer on the host materials through conventional approaches such as mechanical mixing and so on [33–35]. It has been reported that metal ions tend to entangle onto the backbone of the poly(vinyl pyrrolidone) (PVP) and its long polymeric chain structure will surround the samples [36–38]. Therefore, in our coating strategy, the $Ni_{0.8}Mn_{0.1}Co_{0.1}O_2(OH)_2$ precursor was first coated with the PVP, then the dissolved $Mn^{2+}$ ions were complexed with the entire PVP backbone previously coated on the hydroxide precursors. In this way, the $Mn^{2+}$ ions can uniformly distribute on the surface of the hydroxide precusor. Finally, a syn-lithiation method was adopted to get the $Li_2MnO_3$ coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (Fig. 1a). Our studies show that the electrochemical properties of layered $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ materials have been significantly enhanced by coating a layer of $Li_2MnO_3$.

## 2. Experimental section

### 2.1. Materials preparation

Firstly, the hydroxide precusor ($Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$) was prepared by a co-precipitation (CP) method. Stoichiometric amounts of nickel sulfate, manganese sulfate and cobalt sulfate were dissolved in deionized water. The NaOH solution was added into the above solution under violently stirring. The obtained hydroxide precusor was then filtered, washed, and dried at 80 °C overnight. Secondly, 10 mmol of the $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ precursor was mixed with 1 mmol of $Mn(CH_3COO)_2{\cdot}4H_2O$ in deionized water, in which 0.3 g of poly(vinyl pyrrolidone) (PVP) had been previously dissolved at 50 °C for 12 h. The mixed solution was then dried at 80 °C overnight. Finally, the PVP-Mn-coated hydroxide precusor was mixed with stoichiometric amounts of LiOH. One part amounts of LiOH was used to lithiate the hydroxide precursor to form $LiMO_2$, the other part was used to lithiate the manganese acetate to form $Li_2MnO_3$. The mixtures were then calcinated in the air atmosphere at 800 °C for 12 hours with a heat rate of 5 °C $min^{-1}$ to get the $Li_2MnO_3$ coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$. During this syn-lithiation process, the hydroxide precusor $Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)_2$ was lithiated to $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, simultaneously the outer manganese acetate was lithiated to $Li_2MnO_3$. The pristine $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ was prepared using the same synthesis process without addition of $Mn(CH_3COO)_2{\cdot}4H_2O$.

### 2.2. Materials characterization

Powder X-ray diffraction (XRD) was performed on Rigaku Ultima IV-185 with Cu Kα radiation between 10 and 80° 2θ at a scan rate of 1° 2θ $min^{-1}$. Elemental analysis measurements were carried out on a SPECTRO ARCOS FHS12 ICP-OES Spectrometer. Particle morphologies of the prepared powders were observed by scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). XPS spectra was obtained using a Kratos Axis ULTRA X-ray photoelectron Spectrometer under UHV conditions.

### 2.3. Electrochemical Measurement

For prepartion of the positive electrode, 80 wt% active material, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) were grinded to slurry with N-methylpyrrolidinon, and then spread on aluminum foil with doctor blade. The electrodes were dried overnight at 120 °C in a vacuum oven. The loading density of the active material is about 3–4 $mg/cm^2$. The 2016-type coin cells were assembled in an Ar-filled glove box using Li foil as the counter electrode. The electrolyte was 1 mol/L $LiPF_6$ in a 1:1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and the separator was Celgard 2500. Galvanostatic charge-discharge cycling was tested between 3.0-4.3 V (vs. $Li/Li^+$) using automatic galvanostat (NEWARE). PITT tests were carried out on the Metrohm-Autolab (PGSTAT 302N). All electrochemical measurements were performed at 25 °C.

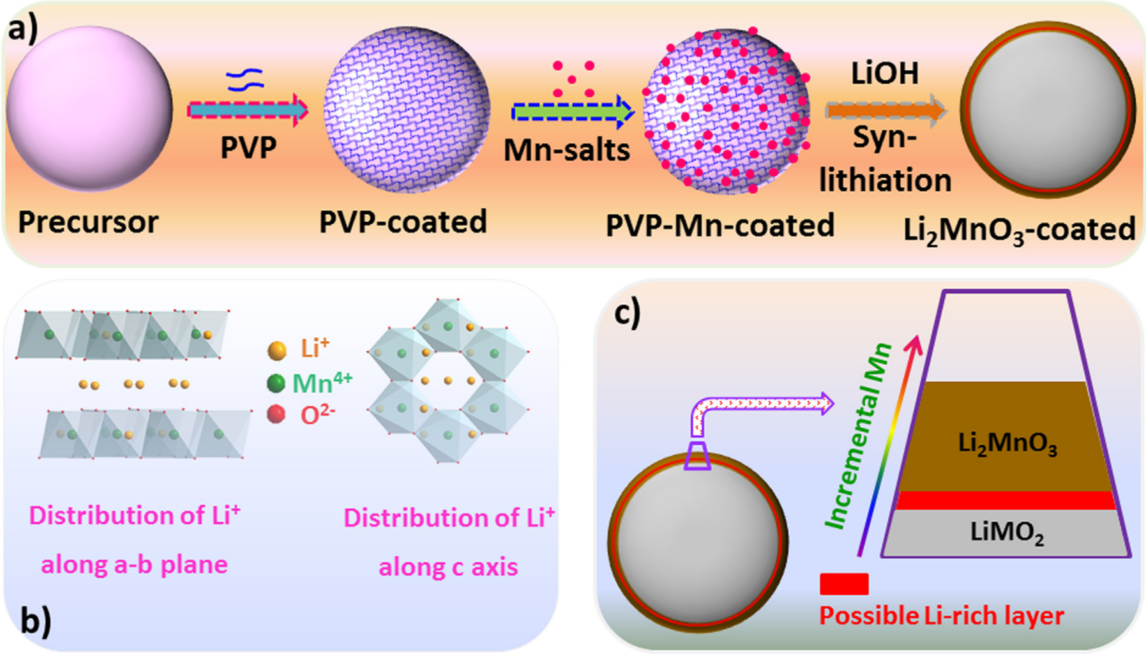

**Fig. 1.** (a) Schematic illustration of the preparation process for the $Li_2MnO_3$ coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$; (b) The structure of $Li_2MnO_3$, distribution of $Li^+$ along a-b plane and c axis; (c) Details of the interface between the $Li_2MnO_3$ surface layer and the $LiMO_2$ host material.