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# Improved electrochemical performances of yttrium oxyfluoride-coated $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ for lithium ion batteries<sup>☆</sup>

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## ABSTRACT

The Li-rich layered oxides show a higher discharge capacity over 250 mAh/g and have been developed into a promising positive material for lithium ion batteries. A rare earth metal oxyfluoride YOF-coated  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  composites have been synthesized by a simple wet chemical method. Crystal structure, micro-morphology and element valence of the pristine and YOF-coated  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  materials are characterized by XRD, SEM, TEM, and XPS. The results indicate that all materials exhibit a typical layered structure, and are made up of small and homogenous particles ranging from 100 nm to 200 nm. Besides YOF layer with a thickness of approximately 3–8 nm is precisely coated on the surface of the  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ . Constant current charge/discharge tests at various current densities show that the electrochemical performance of 2 wt% YOF-coated  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  has been improved significantly. 2 wt% YOF-coated  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  delivers the highest discharge capacity of 250.4 mAh/g at 20 mA/g among all the samples, and capacity retention of 87% after 100 charge/discharge cycles at 200 mA/g while that of the pristine one is only 81.6%. The superior electrochemical performance of 2wt% YOF-coated sample is ascribed to YOF coating layer, which could not only reduce side reactions between the electrode and liquid electrolyte, but also promote lithium ion migration.

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## 1. Introduction

The Li-rich layered oxides (LLOs),  $x\text{LiMO}_2 \cdot (1-x)\text{Li}_2\text{MnO}_3$  (M refers to common transition metals), have been widely investigated as cathode materials for the next generation of high energy density lithium-ion batteries (LIBs), especially in the field of all-electric vehicles (EVs) and energy storage systems [1, 2]. Their most attractive features are higher specific capacity, lower cost and less toxicity than commercialized layered transition metal oxide,  $\text{LiCoO}_2$  [3]. Unfortunately, the drawbacks including poor rate performance, discharge voltage decay and irreversible capacity loss during the first cycle, have obstructed their commercial application. One reason for these disadvantages is that the electrolyte tends to decompose at high voltage (over 4.5 V). However, the high voltage is needed to activate the  $\text{Li}_2\text{MO}_3$  type C2/m component to achieve larger capacity [4]. The byproducts of the electrolyte decomposition always contain HF, causing transition metal dissolution [5].

The surface modification is one of the most practical and efficient approaches to improve the electrochemical performance as well as structural stability of cathodes [6,7]. The most common materials used for surface modification can be divided into the following categories: metal oxides such as ZnO [8],  $\text{Al}_2\text{O}_3$  [9], MgO [10], metal fluorides such as  $\text{AlF}_3$  [11],  $\text{FeF}_3$  [12],  $\text{MgF}_2$  [13], phosphates such as  $\text{FePO}_4$  [14] and sulfides such as  $\text{MoS}_2$  [15]. Among various candidate materials,  $\text{Y}_2\text{O}_3$ , a trivalent oxide of d-block transition metal Y, was predicted as a promising coating material by a first-principles thermodynamic framework [16]. Moreover, many research groups found that  $\text{Y}_2\text{O}_3$  could improve electrical contacts with the support of layer metal oxides and then promote electron transfer. Wu et al. [17] and Liu et al. [18] reported that  $\text{Y}_2\text{O}_3$  coating could availably enhance the electrochemical properties of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ . In addition, metal fluorides such as  $\text{AlF}_3$  [11],  $\text{CaF}_2$  [13],  $\text{MgF}_2$  [19] and  $\text{LaF}_3$  [20] are more stable as coating materials for cathodes compared with most metal oxides under the corrosion of HF in the electrolyte. Combining the advantages of yttrium oxide and metal fluorides,  $\text{YF}_3$  has been applied to stabilize the surface structure of cathode materials in the electrolyte. Liu et al. [21] prepared yttrium fluoride-coated  $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$  materials, which showed effective increase of discharge capacity,

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39 lower charge transfer resistance and diffusion impedance. How-  
 40 ever, metal fluorides can cause lithium ion loss during cycling.  
 41 Some amount of lattice oxygen dissolves out the lattice to form  
 42 O vacancy, which results in poor rate performance and potential  
 43 fade during cycling. Based on previous reports, some oxyfluorides,  
 44 not only have the advantages of fluorides, but also show more ex-  
 45 cellent chemical and thermal stability than fluorides. Weng et al.  
 46 [22] reported that rare earth metal oxyfluoride-LaOF with defec-  
 47 tive anion vacancies structure was beneficial to absorb and acti-  
 48 vate oxygen. Lee et al. [23] found that BiOF coating layer could  
 49 significantly improve the electrochemical performance of spinel  
 50  $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.05}\text{Mn}_{1.85}]\text{O}_4$  by reducing HF attack. Yttrium oxyfluoride  
 51 (YOF), as a typical oxyfluoride, has superior performance in ionic  
 52 conductivity in comparison to  $\text{YF}_3$ . Research has shown that the  
 53 relatively large radius of the oxygen ion substitution of fluorine  
 54 ion can significantly increase the cell size, expand the ion trans-  
 55 port bottleneck size, thus improve ionic conductivity and lithium  
 56 ion transference numbers. Therefore we expect that YOF-coated  
 57  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  materials could be effective to improve  
 58 the rate performance and cycle life as cathode materials for com-  
 59 mercial applications. And, there are still no reports on the effect  
 60 of YOF coated Li-rich cathode materials on the voltage fade during  
 61 repeated cycling.

62 Herein, we report different amounts of YOF coated Li-rich lay-  
 63 ered oxides,  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  (LLO). The pristine sample  
 64 was synthesized through supersonic co-precipitation method as-  
 65 sisting with high temperature solid state method [24]. The YOF-  
 66 coated LLO composites were prepared via chemical deposition. The  
 67 LLO and different amounts of YOF-coated LLO materials have been  
 68 investigated thoroughly among microstructure and electrochemical  
 69 properties.

## 70 2. Experimental

### 71 2.1. Preparation of the pristine LLO and YOF-coated samples

72 The pristine material LLO was synthesized via supersonic co-  
 73 precipitation. A stoichiometric ratio (0.54:0.13:0.13) of manganese  
 74 acetate tetrahydrate, nickel acetate tetrahydrate and cobalt acetate  
 75 tetrahydrate was dissolved in deionized water and then stirred  
 76 at 50 °C continuously. Then, the desired amount of LiOH aque-  
 77 ous solution was added dropwise to the above mixed solution to  
 78 form precipitation. During all above procedures, a supersonic-wave  
 79 treatment was applied. Then, the precipitates were filtered and  
 80 washed several times with deionized water. After that, the precu-  
 81 sor powders were dried at 80 °C overnight. The dried precipitates  
 82 and 5% excess lithium carbonate were ground in the agate mortar.  
 83 The compounds were calcined at 500 °C for 8 h and then 850 °C  
 84 for 5 h in a muffle furnace to gain the LLO sample.

85 A wet chemical method was applied to obtain YOF-coated LLO.  
 86 Yttrium nitrate  $[\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}]$  and ammonium fluoride  $(\text{NH}_4\text{F})$   
 87 were separately dissolved in deionized water. Then the as-prepared  
 88 LLO powder was immersed into  $\text{Y}(\text{NO}_3)_3$  aqueous solution under  
 89 magnetic stirring. During intensive stirring, a certain concentra-  
 90 tion of ammonium fluoride aqueous solution was slowly dropped  
 91 into the above solution simultaneously with the desired amount  
 92 of  $\text{NH}_4\text{OH}$  solution. Then the mixing solution was heated at 80 °C  
 93 for 5 h in order to evaporate the water and then dried at 80 °C  
 94 in a vacuum oven. The obtained materials were calcined at 500 °C  
 95 for 5 h in the air atmosphere. The composites coated with 0 wt%,  
 96 2 wt%, and 5 wt% YOF were marked as LLO, YC-2 and YC-5, respec-  
 97 tively.

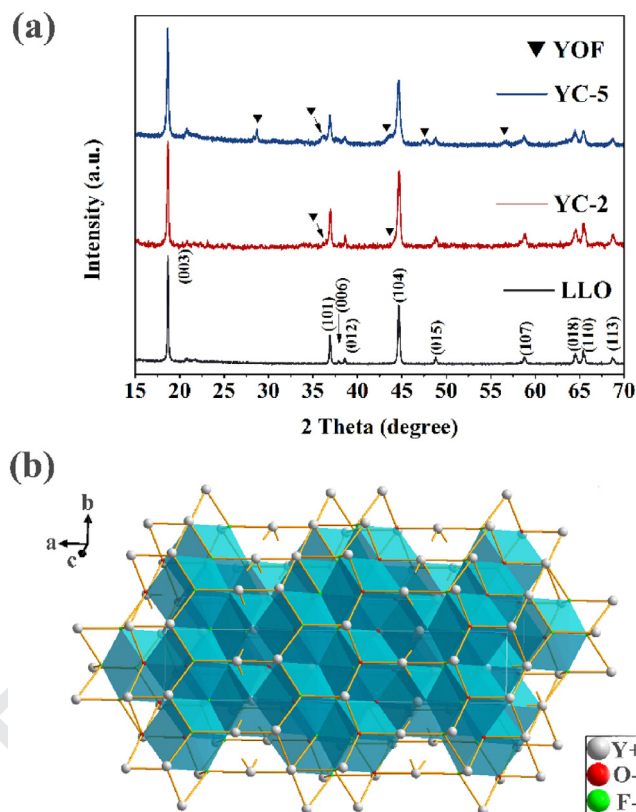


Fig. 1. (a) The XRD patterns of LLO before and after coating with various amounts of YOF; (b) the crystal structure of the rhombohedral phase YOF.

### 98 2.2. Structure and morphology characterization

99 The crystal structures of the pristine and YOF-coated materi-  
 100 als were identified by X-ray diffraction (XRD, Bruker D8-Focus)  
 101 equipped with  $\text{Cu K}\alpha$  radiation at a scanning rate of 5 °/min within  
 102  $2\theta$  degree ranging from 15°–70°. The morphology and elements  
 103 distribution of samples were investigated by field emission scan-  
 104 ning electron microscopy (FESEM, Hitachi S-4800) equipped with  
 105 energy dispersive X-ray spectroscopy (EDS). The YOF coating layer  
 106 was confirmed by transmission electron microscopy (TEM, JEM-  
 107 2100F). The surface chemical state and composition were analyzed  
 108 by X-ray photoelectron spectroscopy (XPS, PerkinElmer, PHI 1600)  
 109 using an  $\text{Al-K}\alpha$  light source.

### 110 2.3. Electrochemical measurements

111 The charge and discharge experiments were performed with a  
 112 half-cell (CR2032), which comprised a cathode, a lithium metal an-  
 113 ode and a separator made by a porous polypropylene film (Celgard  
 114 2000). The cathode electrodes were prepared with active materi-  
 115 als, carbon black and polyvinylidene fluoride at a mass ratio of  
 116 8:1:1. The electrochemical performance tests were performed gal-  
 117 vanostatically at various current densities ( $1\text{C} = 200 \text{ mA/h/g}$ ) with a  
 118 cut-off potential range between 2.0 and 4.8 V (vs.  $\text{Li}^+/\text{Li}$ ) on LAND  
 119 CT-2001A instrument. Electrochemical impedance spectra (EIS) was  
 120 conducted on a Zahner IM6e electrochemical workstation with the  
 121 frequency range of  $10^6$  Hz to 0.01 Hz. Cyclic voltammetry (CV) was  
 122 carried out with a CHI600E electrochemical workstation scanning  
 123 at 0.2 mV/s in the voltage range of 2.0–4.8 V.

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