



Mixed lithium ion and electron conducting $\text{LiAlPO}_{3.93}\text{F}_{1.07}$ -coated LiCoO_2 cathode with improved electrochemical performance



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ABSTRACT

LiCoO_2 (LCO) has been functionally modified by mixed lithium ion and electron conducting $\text{LiAlPO}_{3.93}\text{F}_{1.07}$ (LAPF) for the first time. Due to the unique coating layer with accepted Li-ion diffusion rate and electronic conductivity, the LAPF-coated LCO exhibits outstanding rate capability and cycle stability in the voltage range of 2.75–4.55 V. This material delivered a specific capacity of $206 \text{ mAh}\cdot\text{g}^{-1}$ up to 0.5C rate and the capacity retention was 91.7% after 50 cycles, which is a remarkable improvement comparing with uncoated LCO (34.8%). It also exhibited superior rate capability with a discharge capacity of $161.4 \text{ mAh}\cdot\text{g}^{-1}$ at 4C. The functionalized LAPF coating technique is an efficient approach to improve the electrochemical performance of LCO and can also be referred for other layered oxide cathode materials.

1. Introduction

Lithium ion batteries (LIBs) are receiving significant attention as the most efficient energy storage devices by virtue of high energy density [1,2]. They have been widely applied to portable electronics, power tools and show great promise as power sources for hybrid electric vehicles, pure electric vehicles and energy storage systems [3,4].

As commercial cathode material for LIBs, LiCoO_2 dominates lithium battery market for portable applications due to its high energy density, reasonable rate capability and good cyclability [5,6]. Although the theoretical capacity of LCO is about $274 \text{ mAh}\cdot\text{g}^{-1}$, it only delivers a reversible capacity of about $145 \text{ mAh}\cdot\text{g}^{-1}$ because of the irreversible structural transformation and interfacial instability in the lithium-poor state [7–9]. Cho [10] reported the AlPO_4 -coated LiCoO_2 material with an impressive overcharge stability attribute to the strong P=O bond in coating layer and the formation of $\text{LiAl}_x\text{Co}_{1-x}\text{O}_2$ solid solution. The AlPO_4 -coated LiCoO_2 showed good cycling stability at the cut-off voltages of 4.6 V and 4.8 V [11,12]. However, AlPO_4 coating layer acts as an insulator for both electron and lithium ion, which will affect the kinetic properties of LiCoO_2 during intercalation/de-intercalation of lithium ions. In this regard, conductive oxides or lithium ion conductors, such as Al-ZnO, Li_2ZrO_3 and so on [13–17], have been introduced as alternative coating materials to improve the electronic or ionic conductivity of the coating layer. Here, we designed a mixed electronic and ionic conductor as a coating material for the LiCoO_2

cathode.

As a Li-ion conductor, the Li-ion diffusion coefficient of tavorite-type LiAlPO_4F is calculated to be $10^{-12} \text{ cm}^2\cdot\text{s}^{-1}$ [18], which is comparable with LiCoO_2 [19]. However, LiAlPO_4F shows poor electronic conductivity. As is well known, ions doping is an effective way to improve the electronic conductivity [20,21]. So overstoichiometric fluorine was introduced to synthesize $\text{LiAlPO}_{4-x}\text{F}_x$ for the improved electronic conductivity. In this communication, $\text{LiAlPO}_{3.93}\text{F}_{1.07}$ (LAPF)-coated LCO was synthesized by a freeze drying method. The modified LCO shows excellent cycling behavior and rate performance in the voltage range of 2.75–4.55 V.

2. Experimental

The LCO coated by 2 wt% LAPF (LCO@LAPF) was synthesized by a freeze drying method, as described in ref. [22]. 25 mL of aqueous solution containing 137.6 mg $\text{CH}_3\text{COOLi}\cdot 2\text{H}_2\text{O}$, 506.3 mg Al $(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, 155.3 mg $\text{NH}_4\text{H}_2\text{PO}_4$ and 52.5 mg NH_4F (5 at.% excess) together with 768.6 mg citric acid as dispersant was stirred to the clear and transparent LAPF solution ($\sim 0.06 \text{ mol}\cdot\text{L}^{-1}$). Then 10 g commercial LiCoO_2 powders (obtained from Pulead Technology Industry Co., Ltd.) were added and vigorously stirred for 2 h at room temperature. The well-dispersed suspension transferred into plastic bag, and dip into the liquid nitrogen to freeze rapidly. Then the ice in the obtained solid mass was sublimed at -45°C and sub-atmospheric pressure with vacuum

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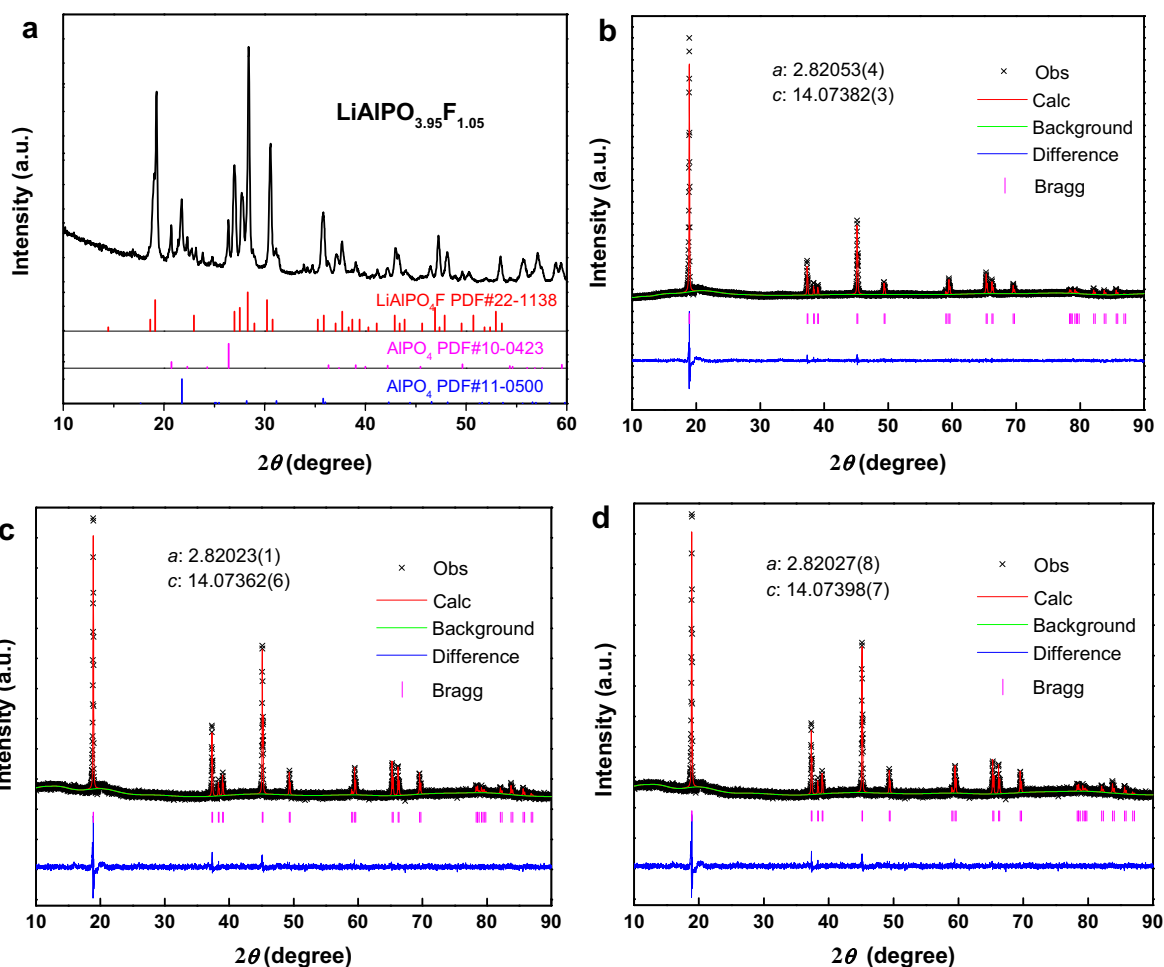


Fig. 1. (a) XRD pattern of $\text{LiAlPO}_{3.93}\text{F}_{1.07}$ powder, XRD patterns of pristine LCO (b), LCO@LAPF (c) and LCO@AP (d) samples.

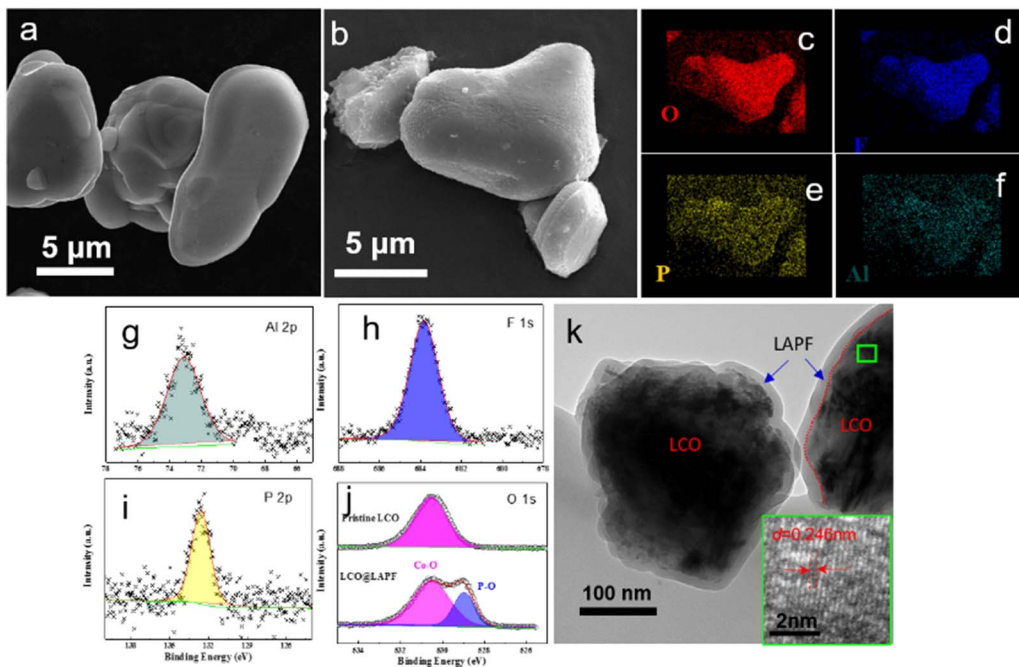


Fig. 2. SEM morphologies of pristine LCO (a) and LCO@LAPF (b) samples, the elemental mapping of O (c), F (d), P (e) and Al (f), core-level XPS spectra of (g) Al 2p, (h) F 1s, (i) P 2p, and (j) O 1s, (k) TEM image of the LCO@LAPF sample.

freeze dryer. The dry powder was calcined at 600 °C for 4 h in air to obtain LCO@LAPF material. The referential 2 wt% AlPO_4 -coated LCO (LCO@AP) sample was synthesized with the same method using

0.07 mol L^{-1} AlPO_4 aqueous solution with 615.0 mg $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 188.6 mg $\text{NH}_4\text{H}_2\text{PO}_4$ as raw material. 10 g LAPF powder was synthesized by mixing the 6.855 g $\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$, 25.312 g Al

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