



Carbon Modified Li-rich Cathode Materials $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$ Synthesized via Molten Salt Method with Excellent Rate Ability for Li-ion Batteries



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ABSTRACT

Li-rich layered oxide cathode $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$ is synthesized via a low temperature molten salt method, and the carbon modified samples are fabricated through coating sucrose on the precursors with different sucrose ratios. The crystal structure and morphology of the pristine and the carbon modified samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The crystal structure appears as a hexagonal $\alpha\text{-NaFeO}_2$ layered structure (space group: $R\bar{3}m$) and is kept after carbon modified. The carbon element distributes uniformly on the surface of the modified samples verified by Energy Dispersive Spectrometer (EDS). The electrochemical performance of the $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$ Li-rich cathode materials is greatly improved after carbon modification. The cycling stability of the carbon modified samples is also highly improved compared with the pristine. Particularly the rate performance is enhanced by the appropriate coating content of sucrose (1:6), the discharge capacities are 160mAh/g, 133mAh/g and 78mAh/g at 2 C, 3 C and 5 C rate respectively. They also have 83.4%, 82.5% and 83.4% capacity retention after 50cycles at 2 C, 3 C and 5 C respectively. Electrochemical Impedance Spectroscopy (EIS) results demonstrate that the charge transfer resistance of the carbon modified sample decreases obviously. It is suggested that the carbon modification could minimize the cell polarization and increase the electronic conductivity of the Li-rich cathode materials. Additionally, the annealing process of sucrose coating may offer much higher local temperature to improve the crystallization and volatile the excess Li source to suppress Li_2CO_3 impurity formation verified by the result of XPS.

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1. Introduction

The growing energy demand of the modern information technology and mobile industry depends on lithium-ion batteries for power storage [1]. The Li-rich layered materials $\text{Li}_{1+x}(\text{M}_y\text{Mn}_{1-y})_{1-x}\text{O}_2$ (also write as $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Ni}, \text{Co}, \text{Fe} \dots$ Transition Metal) are attracting particular interest, because of high discharge capacity, energy density and low cost. The Li_2MO_3 component can stabilize the material structure and enhance the discharge capacity of the cathode by extracting the lithium ions concomitant with release of oxygen. The typical Li-rich cathode materials, such as $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.2}\text{M}_{0.6}]\text{O}_2$ and $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$, can achieve high discharge capacity over 250mAh/g when charged above 4.6 V vs Li [2] compared to traditional cathode materials such as LiCoO_2 and

LiMn_2O_4 . Among them, the Fe-Mn based Li-rich cathode materials $\text{Li}_{1+x}(\text{Fe}_y\text{Mn}_{1-y})_{1-x}\text{O}_2$ not only have excellent theoretical capacity and energy density [3] but also low cost and environment friendly, because Fe element is much more inexpensive and abundant compared to Ni and Co. Based on the above advantages, the Fe-Mn based cathode materials could be widely studied and applied in the future. However, there are several drawbacks in the Fe-Mn based materials, such as the disorder of Li and Fe atoms impedes the migration of Li^+ and worsen the electrochemical performance [4], and the Li_2MnO_3 component with worse conductivity leads to poor rate property.

To overcome these shortcomings, various synthesis approaches have been investigated to synthesize nano-size cathode materials with high activity. The synthesis method of $\text{Li}_{1+x}(\text{Fe}_y\text{Mn}_{1-y})_{1-x}\text{O}_2$ mainly contains three steps referred to Tabuchi's group: coprecipitation- hydrothermal - calcinations [5–8]. The synthesis process is complex, which needs to control reaction conditions precisely, such as pH, temperature and dripping speed. A relatively simple synthesis route in our previous report [9], the

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modified Pechini method, was employed to synthesize the nano-sized $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$ which exhibit high discharge capacity of about 200mAh/g(0.2 C), 140mAh/g(1 C), 110mAh/g(2 C) respectively. Considering the synthesis temperature is important to control the grain growth [10], we explored a novel simple method, low temperature molten salt method, to synthesis $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$. During the synthesis process, all raw materials existed as molten state at eutectic temperature to obtain the molecule-level mixing of raw materials. Therefore, a uniform mixture and nanosized precursor could be prepared and heat treated at low temperature.

Besides that, the high specific surface area of nano-size particles could induce poor stability of surface to form thick solid/electrolyte interfacial (SEI) layer by a reaction of the cathode surface with the organic electrolytes [11]. To improve the surface stability and conductivity of $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$, carbon modification on the surface of the nano-size particles is suggested in this report.

Carbon coating is a possible way to enhance the rate and cycle performance. The carbon surface modified layers are improving the surface electronic conductivity and lithium-ion diffusion. Most carbon coating route is coating carbon source on the pristine materials and then the decomposition of carbon source in inert atmosphere. But it is detrimental to the Li-rich materials that calcined in inert or reducing atmosphere, because the transition metal ions could be reduced and then damage the structure of the material. In order to improve lithium ion diffusion and the conductivity of $\text{Li}_{1+x}(\text{Fe}_y\text{Mn}_{1-y})_{1-x}\text{O}_2$, low temperature molten salt method was used to synthesize the precursor in nanosize (~20 nm), then coated sucrose and calcined in air for a short time to carbonize. The existence of residual carbon was characterized by high frequency infrared carbon sulfur analyzer and EDS mapping technology. And the electrochemical performance of carbon modified nano Fe-Mn based Li-rich cathode materials was also investigated.

2. Experiment

$\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$ powders were synthesized using low temperature molten salt method. Lithium acetate ($\text{LiCH}_3\text{COO}\cdot\text{H}_2\text{O}$, m.p.:56~58 °C), manganese acetate ($\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$, m.p.:80 °C) and ferric nitrate ($\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$, m.p.:47.2 °C) salts were used as starting materials. At first, stoichiometric amounts of the materials of Li, Fe and Mn salts were mixed in a breaker with 5 mol. % excess of $\text{LiCH}_3\text{COO}\cdot\text{H}_2\text{O}$ using to compensate any lithium evaporative losses. And then these materials were heated up to their melting temperature (80 °C) for 30 min in a water bath with mechanical stirring. The obtained black sand-like mixture was preheated at 200 °C in an oven for 5 h to obtain the precursor.

In order to prepare carbon modified $\text{Li}_{1.26}\text{Fe}_{0.22}\text{Mn}_{0.52}\text{O}_2$, the precursor was dispersed into ethanol and deionized water (3:1 v/v) to obtain a suspension, then the sucrose solution (0.5 g sucrose/10 mL distilled water) was added to the suspension with stirring. The mixture solution was transferred to ultrasound for 30 min then concentrated at 80 °C in water bath with magnetic stirring to obtain gel precursors. The gel precursors were dried in a vacuum oven at 80–120 °C for 12 hours. The dried gel precursors were ground, and sintered at 600 °C for 10 min in a tube furnace with 5 °C/min heating rate. Take out the samples after the temperature cooling down to 500 °C in air and put into the liquid nitrogen for 30 min to obtain the target products. Different ratios of precursor and sucrose were prepared such as 1:1, 1:4, 1:6, 1:8(sucrose/precursor, wt%) which sampled as CM1, CM4, CM6, CM8. The CM1 was prepared just for comparing and observing the carbon layer. The precursor without sucrose also sintered at 600 °C for 10 min.

Thermogravimetric (TG) analyses were measured on a Seiko Instruments 6300 TG-DTA device with the precursor being heated from 25 to 1000 °C at rate of 5 °C/min. Powder X-ray diffraction (XRD) patterns of the synthesized materials were carried out using D8 Advance with Cu K α radiation at room temperature. Particle morphology and element mapping (use copper conductive adhesive) of the powders were observed using SEM (JEOL, JSM6400). For HRTEM analysis, the cathode was dispersed in EtOH, and then transferred onto Cu grids for further analysis. HRTEM images of the samples were recorded using a field-emission transmission electron microscope (Philips Tecnai G2 F20). The surface area of the materials was determined using the Brunauer-Emmett-Teller (BET; QuantaChrome Autosorb-iQ) method with nitrogen as a desorption gas. The carbon content of the modified simple was quantitatively determined by high frequency infrared carbon sulfur analyzer (HCS-800B, DeKai Instrument Co. Limited, ShangHai). An Axis Ultra (Kratos Analytical Ltd.) instrument with monochromatized Al-K α radiation and an energy resolution of 0.48 eV was used for X-ray photoelectron spectroscopy (XPS), the binding energy (BE) of XPS was referenced to C1s spectrum of carbon support at 284.80eV.

Electrochemical characterizations were performed using a CR2032 coin cell for electrochemical analysis with a lithium metal as the anode electrode separated by glass microfiber filters. The electrolyte solution was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a 1:1 volume ratio. The cathode electrode was composed of 80 wt% active material, 10 wt% carbon black and 10 wt% polytetrafluoroethylene. All processes were performed in an Ar-filled glove box. The galvanostatic charge/discharge profile was measured at a voltage range of 2.0–4.8 V at 0.2 C, 1 C, 2 C, 3 C, 5 C (1C=200 mA/g), at room temperature for 50 cycles. Electrochemical impedance spectroscopy (EIS) was performed on an electrochemical workstation (VMP3).

3. Results and Discussion

3.1. TG and Crystal structure analysis

TG analysis was measured to define the calcinations temperature (Fig. 1). The minor weight loss before 200 °C may be attributed to the adsorbed water, crystal water and small portion decomposition of acetate. The major weight loss between 200 and 500 °C may be assigned to decomposition of the acetate and organic polymers. The main weight loss ends at about 500 °C, hence the calcinations temperature was defined at 600 °C.

The diffraction peaks of the precursor powders that heat treated at 200 °C for 5 h are messy, shown in Fig. 2a, indicating the decomposition of organics is not completely. And the peaks of Li_2CO_3 are relatively strong among them. Fig. 2b shows diffraction patterns of the pristine and carbon modified samples. All peaks can be indexed based on a hexagonal $\alpha\text{-NaFeO}_2$ structure (space group: $R\bar{3}m$). There are some weak peaks of Li_2CO_3 in the pattern of the pristine; however no impurities were detected such as Li_2CO_3 in carbon modified samples. The formation of Li_2CO_3 in the pristine may be caused by the less loss of the excess Lithium source heat-treated at 600 °C for a short time. For the carbon modified samples, the instantaneous combustion of sucrose coating during the heat-treatment will greatly elevates the actual calcined temperature and increases the loss of the lithium; therefore Li_2CO_3 impurities were not detected. Additionally, some weak diffraction peaks between 20° and 25° of 2 θ can be observed in the XRD patterns of the samples. It is considered as the superlattice ordering of Li and Mn in the transition metal layer [3,12], indicating the existence of a layered structure with Li_2MnO_3 character which can be indexed to the monoclinic unit cell C2/m [13,14]. There are no diffraction peaks for carbon perhaps due to its amorphous state of the

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