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Lithium-rich cathode material doped with rare earth elements for application in lithium-ion battery

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Abstract

The influence of doping was investigated on the properties of layered $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ with a α-$NaFeO_2$ prepared using $LiCH_3COO.2H_2O$, $Mn(CH_3COO)_2.4H_2O$, $Ni(CH_3COO)_2.4H_2O$ and $Co(CH_3COO)_2.4H_2O$ via hydrothermal reaction. X-ray diffraction (XRD), Transmission electron microscopy (TEM), charge-discharge and electrochemical impedance spectroscopy (EIS) tests were applied to investigate structure, morphology and electrochemical performance of the lithium-rich doped sample. XRD analysis confirms that the uniform solid solution has been formed in the as-prepared compound without any impurities. It is shown that the crystal lattice parameters (a, c) of the doped compound is bigger than pristine compound. TEM image of the compound shows that cubic-like microparticles with a mean grain size of 600 nm have been formed. Galvanostatic charge-discharge test exhibits that doped sample has a discharge capacity of 257 $mAh.g^{-1}$ in the voltage range of 2-4.8V. EIS results demonstrate that doping decreases charge transfer resistance and enhances conductivity and reaction kinetics due to high current ions and electrons of the doped element.

Keywords: Lithium-ion battery; Layered lithium-rich cathode material; Doping; Rare earth element; Hydrothermal method.

Introduction

With the rapid development of the hybrid electric vehicles (HEVs) and electric vehicles (EVs), the demands for lithium-ion batteries (LIBs) with higher energy density become very important. LIBs are the state of the art power sources of modern consumer's electronics. It has highest energy density and operating potential among all the rechargeable battery technologies. Its overall electrochemical performance truly depends on the cathode materials since it exhibits lower capacity compared to anode materials. So one way to hit LIBs with higher energy density is to find better positive electrodes [1, 2]. Since Sony released firs LIBs with lithium cobalt oxide ($LiCoO_2$) cathode material, LiCoO2 has dominated the share of cathode materials market for LIBs for a quite long period due to its promising electrochemical properties such as high electric conductivity and good reversible during lithium insertion and de-insertion process. However, the relatively low specific capacity and high cost of $LiCoO_2$ hinders its further application. Manganese based oxides with layer structure have been studied intensively as attractive candidate cathode material for LIBs. Unfortunately, the $LiMnO_2$ has been found to suffer from phase transformation on cycling, which causes capacity fading during cycling. Some strategies such as partially substitution of Mn with foreign metal ions have been involved to suppress the phase transformation. The discovery of polyanion based cathode materials, such as LiFePO4 and LiMnPO4, with olivine structure has drawn great attention owing to the advantages of being abundant, high thermal stability, environmentally benign, and inexpensive. However, poly-anion materials show critical disadvantages of poor electronic and ionic conductivities, which is believed to be the main reason for the high polarization at high charge-discharge rate. Therefore, carbon coating and nanostructure approaches are required to overcome the above demerits [3]. In recent years, a Lithium-rich layered solid solution system Li_2MnO_3–$LiMO_2$ (M = Ni, Co, Mn, etc.) has attracted attention for its higher specific capacity (250 mAh.g^{-1}), lower cost, higher safety and environmental friendliness comparing to the commercial cathode materials [4, 5]. Unsatisfactorily, its poor diffusion coefficient and electronic conductivity result in the poor rate capacity and cycle property [6]. One possible way to enhance rate capability of such Li-excess cathode materials is to coat particle surface with conductive agents which also function in suppressing the growth of SEI layer. From this view point, a variety of materials such as Al, Al_2O_3 and RuO_2, AlF_3, $LiCoPO_4$ and Li–Ni–PO4 have been used for surface modification and proved to be effective in improving their electrochemical performance. However, how to combine excellent electronic conductivity with inert physical protection both derived from the same coating layers still needs more investigation. In addition, a careful control of coating layer thickness must be achieved to avoid hindering of active Li diffusion resulted from too thick coating layers [7]. Another way to improve rate capacity of Lithium-rich cathode materials is to control construction of the material morphology and shorten lithium ion diffusion with nano- sized particles. Recently, various structured electrode materials, such as nanorods or tubes, nanosheets or plates, hollow or core-shell spheres ordered/disordered mesoporous/macroporous materials and three dimensional (3D) network architectures have been fabricated via various methods but it is difficult to construct controllable morphology of the Lithium-rich layered oxide (LLOs) materials due to complex components including lithium, manganese, nickel and cobalt [8,9]. Finally substituting or doping additional ions into to the structure of lithium-rich layered oxide materials (especially Mn and Ni substitution) can reduce the cation mixing, stabilize the layer structure and improve the initial columbic

efficiency of Li-rich and Li[$Ni_{1/3}Mn_{1/3}Co_{1/3}$]O_2 cathode materials. In general, rare earth elements (REEs) are particularly suitable for doping into LLOs owing to their outstanding thermo-mechanical stability, high resistance to both oxidizing and reducing conditions at high temperature, and strength to resist attacks by moisture or chemical reactions [10].

In this study, to improve the cycle performance and initial coulombic efficiency of lithium-ion batteries, we partially substituted Mn^{2+} in LLOs with by REE ion. This strategy is highly attractive for synthesis of high-performance LLO electrodes in a simple, economic and efficient way. It is considered that REE ion-O with stronger bond energy than Mn-O will benefit the stability of the bulk layered structure, and most importantly, doping REE ions with a "super-large" radius (rREE^{3+} = 99 pm) vs. Mn^{4+} (r Mn^{4+} = 54 pm) is expected to expand Li$^+$ pathways in this layered structure. The structural, morphological and electrochemical properties of REE ion doped LLO materials were then carefully investigated.

Experimental

Synthesis

The Li$_{1.2}$Mn$_{0.49}$Ni$_{0.13}$Co$_{0.13}$RE$_{0.05}$O$_2$ was prepared by mixing stoichiometric amounts of LiCH$_3$COO.2H$_2$O, Co(CH$_3$COO)$_2$.4H$_2$O, Mn(CH$_3$COO)$_2$·4H$_2$O, Ni(CH$_3$COO)$_2$·6H$_2$O and RE(NO$_3$)$_3$.6H$_2$O in a water–ethanol system. In order to compensate for the loss of Li at high reaction temperature, approximate additional 20% of Li$_2$SO$_4$·H$_2$O was made up. The mixture was stirred at 160 °C for 16 h in a sealed autoclave and then dried at 80 °C. At last the mixture was calcined at 650 °C for 14 h in air in a muffle furnace.

Characterization

The phase identifications of synthesized powders were conducted with X-ray diffraction (XRD, EQuniox 3000, Intel FRANCE) using Cu Kα radiation between 5° and 118° (2θ degree) at a step size of 0.1° in 10 minutes for analyzing (λ= 0.15418 nm). The morphology of the powders was observed with transmission electron microscopy (SIGMA 900).

Electrochemical performance

For the electrochemical test, the Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ electrode were fabricated contains on a dry basis 85%wt the Li$_{1.2}$Mn$_{0.54}$Ni$_{0.13}$Co$_{0.13}$O$_2$ powder either with or without REE doped, 10% acetylene black and 5wt% PVDF in NMP. The slurry was coated onto Al foil with a coating thickness of 200μm, and then dried in vacuum overnight. Metallic lithium foil was used as the anode electrode; 1M LiPF$_6$ in ethylene carbonate (EC) as the electrolyte. The cells were assembled in an Argon-filled gloved box. Cyclic voltammetry (CV) was measured by an electrochemical working station at a scan rate of 0.15 mVs^{-1} between 2–4.8 V. Electrochemical impedance spectroscopy (EIS) was conducted also on the same electrochemical working station with an AC oscillation of 5mV amplitude over the frequencies between 1 MHz to 10 mHz. All the EIS were collected at first discharged cycle (2 V) at room temperature (25 °C). The spectra are fitted with an equivalent circuit as shown in the inset image. Galvanostatic charge/discharge measurements were carried out in the voltage range of 2–4.8 V using a battery tester (Kimiastat-5 V/10 mA, Kimia pardaz rayane, Iran) with different current densities.

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Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the cathode. The XRD peaks of the composite demonstrates the formation of highly crystalline phase with an ordered layered structure devoid of any detectable impurity phases.
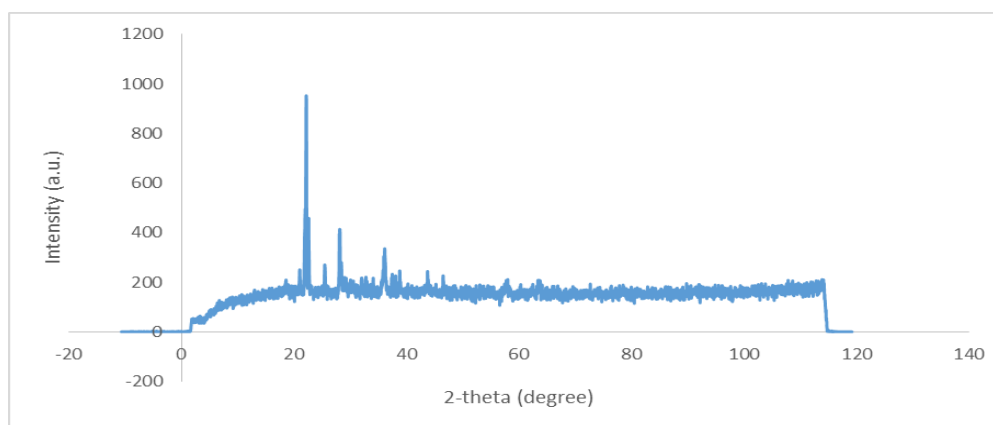

Fig. 1. X-ray powder diffraction patterns of the $Li_{1.2}Mn_{0.59}Ni_{0.13}Co_{0.13}REE_{0.03}O_2$ sample.

Fig. 2. Particles of composite appear to have micrometer with irregular shapes. The particle-sizes are observed to range between 600 nm-1μm.
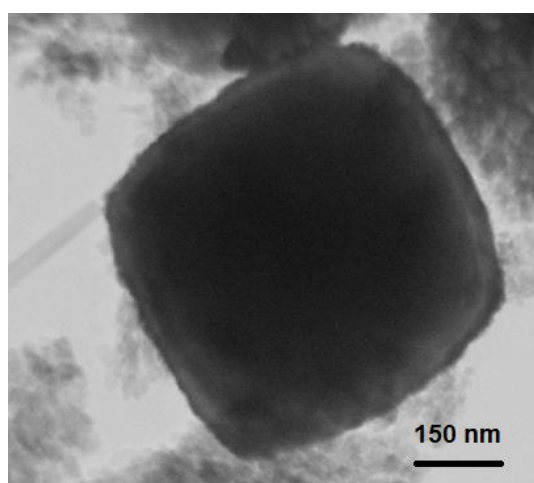

Fig. 2. TEM micrographs of $Li_{1.2}Mn_{0.59}Ni_{0.13}Co_{0.13}REE_{0.03}O_2$ sample, prepared by hydrothermal method

EIS measurement was carried out under fully discharged state at 25 °C. The impedance spectra curve was composed of a depressed semicircle in high frequency region and a straight line in low frequency region.
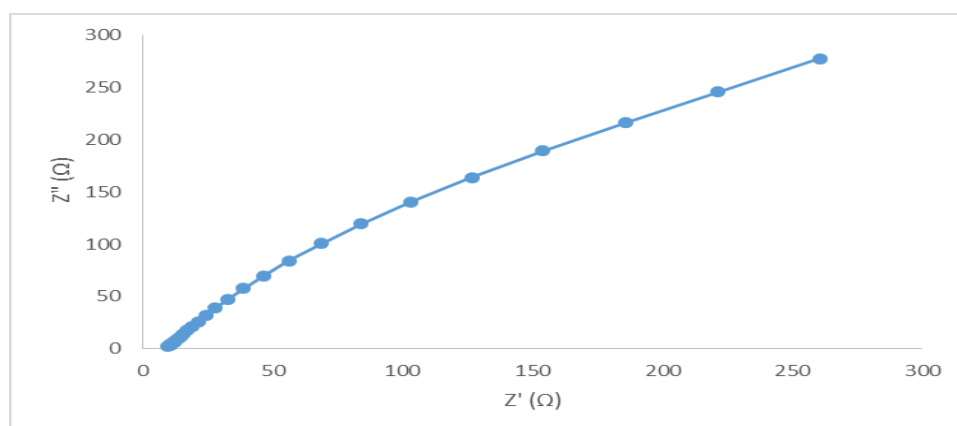

Fig. 3. Electrochemical impedance spectroscopy (EIS) results of the cathode in the frequency range between 1 MHz and 10 mHz
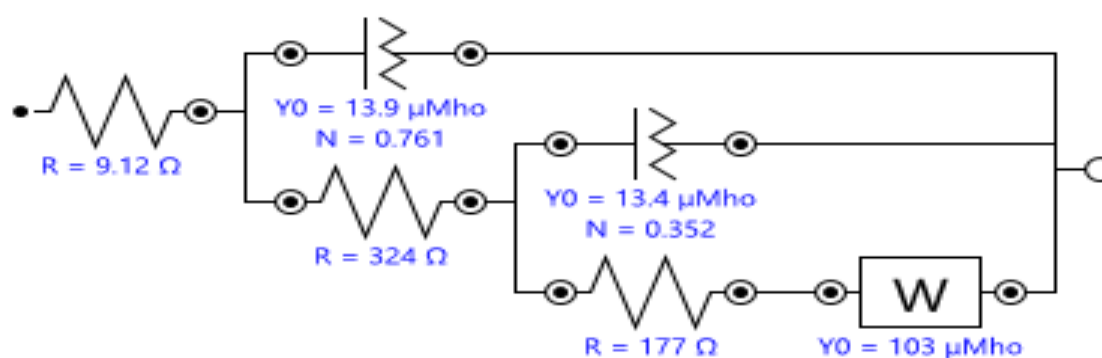

Fig. 4. Equivalent circuit of the cathode in the frequency range between 1 MHz and 10 mHz

Fig. 4 shows the initial discharge curves of sample. The charge–discharge process were operated over the potential range of 2–4.8 Vat 0.1C (12.5 mA.g^{-1}). The initial discharge capacities of sample is about 257 mAh.g^{-1}.
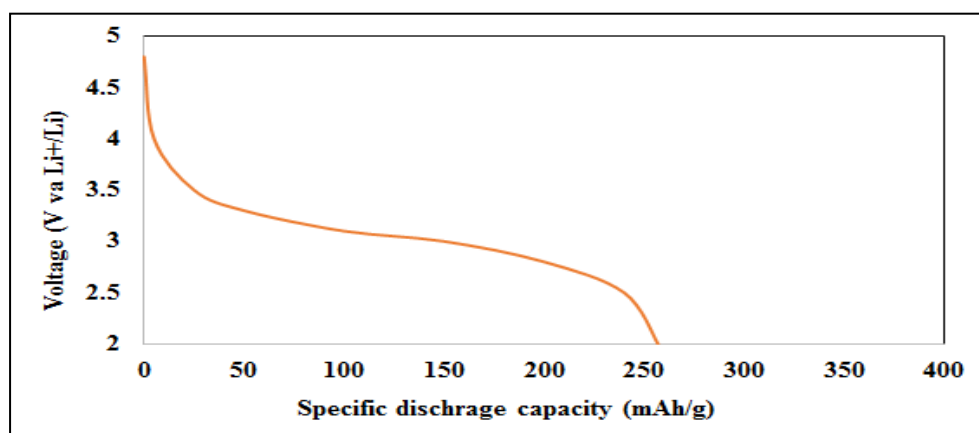
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Fig. 5. Initial discharge curve of sample

Conclusion

Layered $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ cathode material was successfully synthesized by hydrothermal method, a suitable amount of REE^{3+} substitution for Mn^{4+} in $Li[Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13}]O_2$ material results in significant improvement in capacity, cycling stability and rate performance. The doped cathode material presented remarkable capacity of 257 mAh^{-1} at the first cycle. EIS measurements clearly show that the REE^{3+} with larger radius such as Y^{3+} can promote the migration of Li^+ by expanding the layered structure, and thus improve the reversibility of the electrode reactions and restrain the increase of charge transfer resistance of the cathode during cycling. All of these contribute to the improvement of battery performance for the doped sample.

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