

Investigation on high performance electrodes active materials for advanced lithium-ion rechargeable batteries

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High capacity layered $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ ($x = 0.11$) cathode and high voltage $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel anode for the full cell systems have been studied. With combined this cathode and anode materials in an advanced lithium ion battery, a new electrochemical reaction has been demonstrated. It exhibited the initial discharge capacity of 173 mAhg^{-1} and also was maintained at the average specific capacity of 170 mAh/g and more than 90% capacity retention. In addition, the battery can cycle at C/10 up to 30 cycles with a very stable capacity delivery. Taking an average voltage of 2.5 V, a specific energy density value of 400 Wh/kg was obtained. These environmentally benign Mn-rich layered cathode and spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode materials are going to be future electrodes for Li-ion rechargeable batteries in hybrid electric vehicle applications.

Keywords: Layered cathode, Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, Li-ion batteries, Full cell system, Charge-discharge

Introduction

Development of low emission cars such as hybrid electric vehicles (HEVs), plug-in hybrid electric vehicles (PHEVs), and also zero emission fully electric vehicles (EVs) is the main theme of future generation of automobile market. Sustainability of PHEV and EV usage depends on the accessibility of suitable energy storage systems like superlative high energy lithium batteries, which have a foremost position in the portable consumer electronics market. The rising requirements of low emission cars confront to spot the low cost materials with high power performance for lithium ion batteries. The prime factor in EVs is the energy storage system which must possess high power capability as well as safety. The commercial lithium secondary battery's carbon anode has significant problems with long cycling, such as structural instability due to weak carbon-carbon bond, formation of lithium dendrites, and passivation layer of carbonaceous materials by electrolyte reaction [1-2]. Enhancements in energy storage systems require shifting from current lithium ion battery technology to new superior chemistry based on high performance electrode materials. Good examples are lithium metal alloy anodes [3, 4] and spinel and layered cathodes [5, 6]. In this work, the electrochemical cycling studies of the $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ based electrode materials for Li-ion rechargeable batteries will be demonstrated.

Experimental

Synthesis of electrode materials

Cathode active $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ material was prepared on the basis of our previous work [7]. Lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode materials were synthesized via molten salt method using the precursor materials such as $\text{LiOH}\cdot\text{H}_2\text{O}$, TiO_2 , LiCl-KCl that act as a flux. The stoichiometric quantities of these precursors are ground, mixed well and heated at 800°C for 10 hrs. The resulted samples were washed repeatedly with distilled water and then with ethanol to remove the residual molten salt. The synthesized electrode materials were analyzed using an X-ray diffractometer (D8 Discover with GADDS, Bruker AXS) in the 2θ range from 10 to 80° with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406\text{\AA}$). Surface morphology and particle size were observed using a field emission-scanning electron microscope (FE-SEM, Leo Supra 55, Genesis 2000, Carl Zeiss) and a field emission-transmission electron microscope (FE-TEM, JEM 2100F, Jeol), respectively.

Cell fabrication

To prepare the electrode materials, 90 wt% of the electrode active materials, 5 wt% of Super P black as a conductive agent, 5 wt% polyvinylidene fluoride (PVDF) as a binder and N-methyl-2-pyrrolidone (NMP) were mixed to form slurry. After 15 minutes of grinding with mortar, the viscous slurry was coated on aluminium and copper foil respectively for cathode and anode and then dried in oven at 100°C for 5hrs. The dried coating electrode was pressed under a 7 ton/cm^2 load and then was punched out with size of 14 mm in diameter, which used

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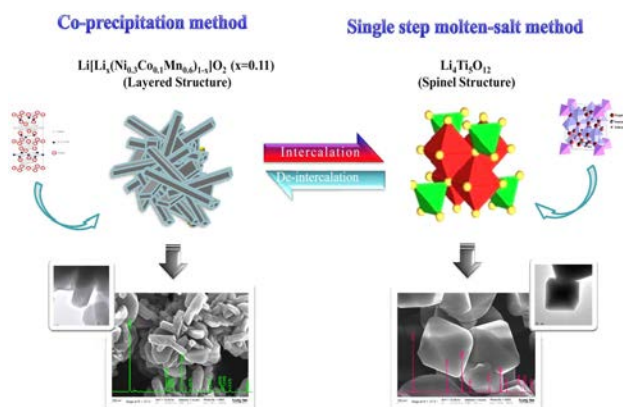


Fig. 1. Schematic diagram of full cell system of Mn-rich $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ ($x = 0.11$) cathode materials with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel anode.

as the cathode. The punched cathode was additionally dried at 120 °C for 5hrs in vacuum oven. The thickness of the cathode film was about 44 μm . The 2032 coin-type cells (20 mm in diameter and 32 mm in thickness) were assembled in a glove box under high purity argon atmosphere (less than 1 mg/L of O_2 and H_2O concentrations). The cell consisted of a prepared cathode, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode, micro porous membrane (Celgard 3501) as a separator, and a non-aqueous 1 M LiPF_6 in ethylene carbonate (EC): diethyl carbonate (DEC) (1 : 1 vol%) (StarLyte, Ukseung Chemical Co., Ltd.) as an electrolyte. The fabricated coin cells were charged to 4.6 V vs. Li/Li^+ and then discharged to 1.0 V vs. Li/Li^+ with constant current density using an Arbin electrochemical cycler. The schematic representation of full cell system is given in Fig. 1.

Results and discussion

The XRD patterns of both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ electrodes are shown in Fig. 1. The patterns confirm well-crystallized cubic spinel framework structure for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and layered framework structure for $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ [7, 8]. The charge-discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ battery at C/10 rate shown in Fig. 2. At C/10 rate the crystallized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ exhibited a high reversible capacity and an excellent rate capability of 171 mAh/g [9], representing the high discharge capacity retention of anode due to the zero strain insertion property of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This indicates the potential application for lithium ion batteries with high performance and high capacity. The electrochemical mechanism responsible for insertion and extraction is given below;

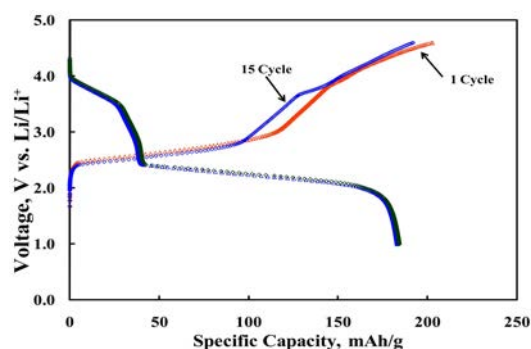
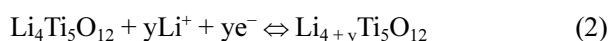
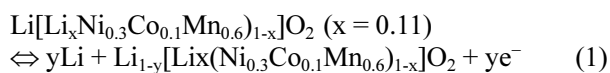


Fig. 2. Charge-discharge capacity of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ ($x = 0.11$) full cell at C/10 rate.

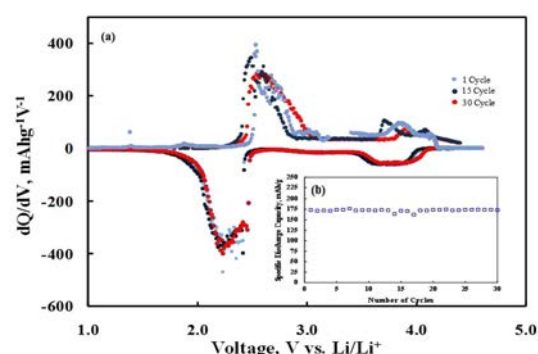


Fig. 3. (a) Differential capacity and (b) cycle life of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ ($x = 0.11$) full cell at C/10 rate.

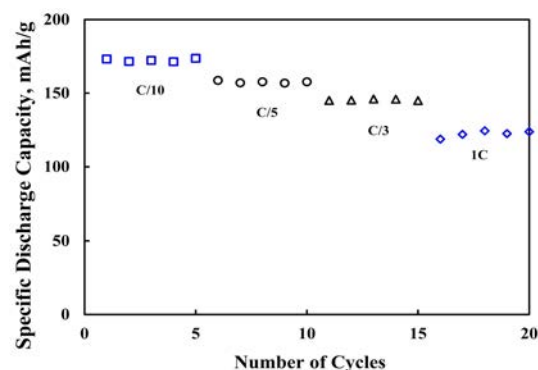


Fig. 4. Cycle life of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ ($x = 0.11$) full cell at various current rates.

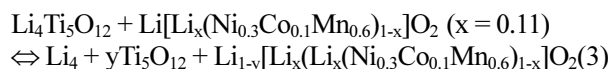


Fig. 3(a) shows differential charging and discharging voltage profiles of $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$. The peak currents of anode and cathode are comparable. More over the cycles of 1, 15 and 30 are almost overlapping, which represents excellent cycle reversibility [10]. Fig. 3(b) shows the cycling response of the battery. The tests show that the practical working voltage of the battery ranges between 1.0 V to 4.6 V while the specific capacity related to the cathode mass is the order of 171 mAh/g.

In addition, the battery was cycled at various current rates which shows the battery can do very stable capacity delivery at various current rates shown in Fig. 4. The cell was first cycled at C/10 for 5 cycles, and then the discharge-charge rate was increased stepwise to 1C. It can be seen in Fig. 4 that the cell voltage and discharge capacities both exhibit a tendency to decrease with increasing discharge current density. In terms of charge and discharge rates, the battery has high rate capability and can be cycled at 1C rate, still delivering 125 mAh/g with the capacity decay of 2%. Stable cycle life and high rate capability of the battery were fully rely on both anode and cathode structure and morphology which was obtained by utilizing advanced lithium ion battery technology

Conclusions

The experimental result is quite credible in demonstrating that the battery discussed here fulfills the requirements expected by advanced lithium ion battery technology. By utilizing new chemistry based on a combination of a stable, high performance $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode with a stabilized $\text{Li}[\text{Li}_x(\text{Ni}_{0.3}\text{Co}_{0.1}\text{Mn}_{0.6})_{1-x}]\text{O}_2$ cathode, a new type of lithium ion battery, having high energy content and good rate capability is acquired. To our knowledge, a lithium ion battery having this type of unique electrode combination is firstly reported. On the foundation of the performance demonstrated here, this battery is a new good contender for powering low emission hybrid electric vehicles.

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