

ELECTROCHEMICAL PERFORMANCE OF $\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Al}_{2x}\text{O}_2$ BY HYDROTHERMAL METHOD

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Abstract

In lithium ion batteries, lithium cobalt oxide is extensively used as a cathode material. However, cobalt has high cost and toxicity, researchers have been investigating for the development of a cobalt free cathode material. $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ is one of the most alternative materials due to its high capacity and energy density. Besides, Al is used to improve the stability. Al-substituted $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ exhibits high rate capability and cycle performance. The hydrothermal method of $\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Al}_{2x}\text{O}_2$ ($x = 0.01, 0.02, 0.05, 0.1$) results in enhancement of electrochemical performance and stability. The precursors were prepared by stirring in a mixture of de-ionized water and NH_4OH for 2h. Afterwards, the mixtures were heated in a Teflon lined autoclave for 4h followed by calcination at 900 °C for 12h. The cyclic performance of $\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Al}_{2x}\text{O}_2$ was measured in the range of 2.0 to 4.5 V. It was observed that $\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Al}_{2x}\text{O}_2$ exhibited the highest capacity at $x = 0.05$.

Introduction

Lithium-ion secondary batteries have been used in a variety of applications ranging from portable electronics such as mobile phone and laptop computer to power source of hybrid electric vehicles. Recently, capacity of the battery is received attention by increasing in battery usage, the cathode materials are spotlighted because of total battery capacity is determined by the cathode materials. The present lithium ion secondary batteries use lithium cobalt oxide, LiCoO_2 , cathode material for commercially available lithium ion batteries. However, Co has many disadvantages such as expensive price, toxicity and safety problem at high temperature. To reduced Co content or less available, many researchers are studied alternative materials such as LiMn_2O_4 , LiNiO_2 , $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, $\text{Li}(\text{Mn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3})\text{O}_2$, etc. Among all possible materials, spinel lithium manganese oxide and its derivatives are considered as the most potential materials because of its low material cost, high natural abundance, environmental harmlessness and good safety. However, spinel lithium manganese oxide has problems which is its severe capacity fading during charge-discharge cycling such as Jahn-Teller distortion due to Mn^{3+} ion, the dissolution of manganese into electrolyte, loss of crystallinity during cycling and electrolyte decomposition at high potential regions. Layered transition metal oxides are the most important cathode material, especially for large sized batteries. Various attempts have been made to enhance the cycling

stability due to lithium manganese oxide exhibits severe capacity fading on cycling mainly due to dissolution of Mn in to the electrolyte via the disproportionation reaction ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$) and Jahn-Teller distortion of trivalent Mn ions. In this respect lithium manganese oxide added or doped with other transition metals constitutes attractive choice as cathodic material on account of their ability to supply potentials close to 5 V on extensive cycling. Among this class of materials, lithium manganese nickel oxide exhibited the best electrochemical performance such as high discharge capacity, flat plateau at 4.8 V, good cycling stability on lithium on extraction and insertion, good rate capability and high energy density. The theoretical capacity of lithium manganese nickel oxide which has a spinel structure is as high as 146.7 mAh g^{-1} , and due to its high working potential, the energy density of lithium manganese nickel oxide is higher than the lithium cobalt oxide. Thus, $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_2$ is a potential candidate of high energy cathode materials, which might be used in hybrid electric vehicles in the future. In recent years, several investigations have been made to enhance the electrochemical and structural stability of cathode materials and safety of battery by substitution with Al, Fe, Cr, Sn, Ru, Co and Zn. Among these materials, aluminum is a very commonly used substitution in cathode materials. In some cases small amounts of aluminum doping improve the capacity of electrode materials. Al-substituted lithium manganese nickel oxide material is showed relatively good rate capability and cycle performance.

A variety of synthesis methods for preparation of lithium manganese nickel oxide have been reported; solid state reaction, sol-gel, co-precipitation, spray pyrolysis, microwave synthesis and assistant ultrasonic process. As a synthesized method of cathode material, co-precipitation method has been widely used to synthesize binary or ternary electrode materials. However, co-precipitation method can decrease the degree of Li/Ni or Li/Mn/Ni oxide cation mixing, it should be very difficultly to control the synthesis conditions with co-precipitation method in order to avoid the oxidation of Mn^{2+} . Ultrasonic process has reported that good stoichiometric control with uniform particle size distribution can be obtained by an ultrasonic bath. However, lithium manganese nickel oxide losses oxygen and disproportionates to a spinel structure when it is heated above $650 \text{ }^\circ\text{C}$. Solid state reaction also produces larger particles of irregular shape and poor control of stoichiometry. All these methods could be difficult to obtain stoichiometric lithium manganese nickel oxide, chemical in-homogeneity, broad particle size distribution and long reaction time or unwanted phases.

In this paper, Al-substituted $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder is prepared by hydrothermal method. Hydrothermal synthesis as one of the liquid phase synthesis is a method using aqueous solution under high temperature and pressure. Hydrothermal method has many advantages such as fast response time, low energy consumption, excellent uniform size particles distribution and controlled size and purity with temperature and time. The hydrothermal $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder has been focused on the improvement of electrochemical properties and stability.

Experimental

$\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder was synthesized by two different methods; the co-precipitation method and hydrothermal method. Stoichiometric amounts of LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with a molar ratio of 1.00:0.475:0.475:0.05 were completely dissolved in de-ionized water. Amount of sufficient NH_4OH (28~30%) solution was added into stirring solution for 12 h. The mixed precipitation was then filtered, washed and dried overnight at $80 \text{ }^\circ\text{C}$ in vacuum oven. And then, $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder was heated at $900 \text{ }^\circ\text{C}$ in 12 h. On the other hand, $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder was also prepared by hydrothermal method. LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were

dissolved in de-ionized water with NH_4OH solution under continuous magnetic stirring for 12 h in air. The mixed solution transferred into a Teflon-lined autoclave, and then the autoclave was heated at $150\text{ }^\circ\text{C}$ for 24 h and cooled naturally to room temperature. The product was washed and dried at $80\text{ }^\circ\text{C}$ for overnight. The mixture was calcinated for 12 h. The cathodes were prepared for measured electrochemical performance by mixing $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder, carbon black and PVDF in a weight ratio of 80:10:10 using NMP as the solvent. Lithium metal was used as the anode, and the electrolyte solution was composed of 1M of LiPF_6 dissolved in EC/DEC by 1:1 in volume ratio onto an aluminum foil.

Results and discussion

The results of X-ray diffraction patterns of the $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powders are presented in Fig. 1. The diffraction patterns of all samples are sharp and well-defined. All the Al-substituted $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ power peaks by hydrothermal method are similar with space group $\text{Fd}\bar{3}m$. The diffraction patterns have sharp peaks and crystalline structure as the more well-distributed in the form. The separation of 311/222 peak is represented the layered character of structure and is evidenced as the good indicators of electrochemical properties. The structure difference corresponds to the disordering degree of the cations (Li, Mn, Ni and Al) on the 3b site. According to the disordering of the 3b site cations in $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ can increase the volume of the unit cell.

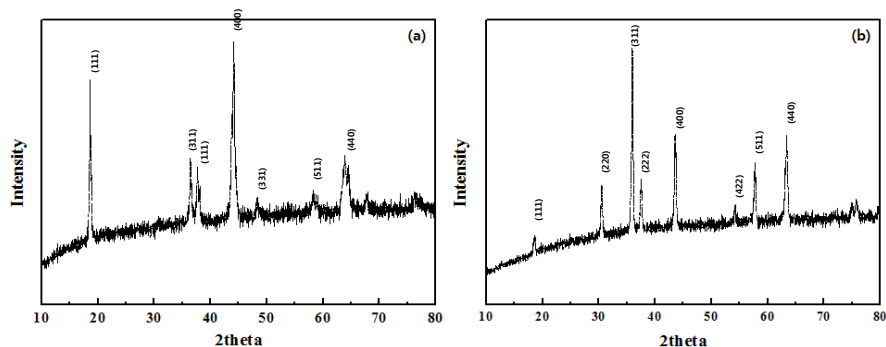


Fig 1 XRD patterns of $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powder by (a) co-precipitation method And (b) hydrothermal method

Fig. 2 shows FE-SEM images of $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ powders synthesized by different method (a) co-precipitation method, (b) hydrothermal method. The particle size in hydrothermal method is 100~350 nm, which significantly smaller than that synthesized by co-precipitation method. Moreover, the size distribution is much narrower in hydrothermal method, indicating a greater uniformity of as fabricated powders. Therefore, the precursor by hydrothermal method has an irregular uniform structure morphology and the size distribution is broader than that of the other precursor.

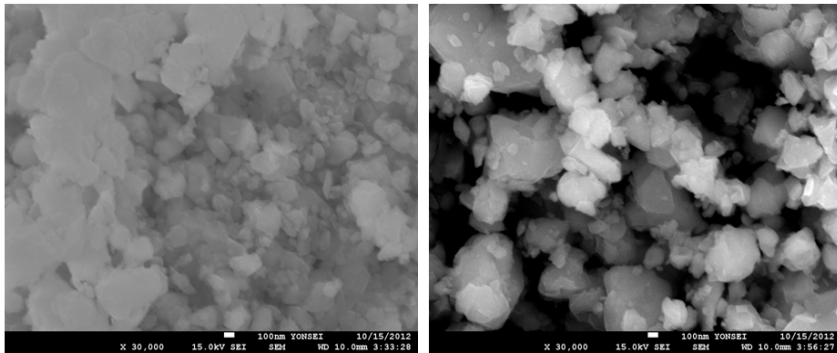


Fig. 2 FE-SEM images of $\text{LiMn}_{0.475}\text{Ni}_{0.475}\text{Al}_{0.05}\text{O}_2$ by (a) co-precipitation method and (b) hydrothermal method

The specific capacity and capacity retention of the as-prepared Al-substituted lithium manganese nickel oxide were measured by a 2032 type coin cell using Al-substituted lithium manganese nickel oxide as active material. Initial charge and discharge profiles of lithium metal/Al-substituted lithium manganese nickel oxide cell under charge-discharge conditions are shown the cell voltage plotted versus specific gravimetric capacity for the initial charge-discharge cycle operated in the voltage range of 2.5–4.7 V at room temperature. The initial charge and discharge curves of Al-substituted lithium manganese nickel oxide cathode material by co-precipitation method measured with a constant current density of 20 mA g^{-1} between 2.0 and 4.5 V versus Li metal. All cells show the same of the shape charge/discharge curves. Al-substituted lithium manganese nickel oxide by co-precipitation method exhibits the initial discharge capacity of about 100 mAh g^{-1} and capacity retention is 90% after 20 charge/discharge cycling. However, the prepared Al-substituted lithium manganese nickel oxide by hydrothermal method exhibits the initial discharge capacity of about 125 mAh g^{-1} and capacity retention is as high as 94% after 20 charging/discharging cycling. Compared with the Al-substituted lithium manganese nickel oxide by co-precipitation method and hydrothermal method has a larger initial discharging capacity and higher capacity retention rate. The reason may be related with its better crystallinity, regular morphology and uniform size powder distribution and also this comment is well consistent with the SEM results mentioned above. Combining this with the electrochemical behavior, the structure of Al-substituted lithium manganese nickel oxide synthesized by the hydrothermal method is very stable for lithium ions insertion and extraction. These may be explained that small size particles Al-substituted lithium manganese nickel oxide can provide lithium ion diffusion pathways and enhance cycle stability, smaller particles can provide more interfacial area for contact within the liquid electrolyte and hence can increase the opportunity for lithium ions to intercalate back into the host structure. Therefore, we believe that hydrothermal method is an important factor to achieve higher capacity with good cycle character. A small amounts of aluminum is used doping material in cathode materials for improve the capacity of cathode materials. The observed increases have been attributed to improved stability, structural modifications and microstructural effects. Aluminum doping has also shepherd to improvements in retention of capacity during cycling and performance at discharge currents. The improvements are attributed to improved charge transfer kinetics and improved stability with the electrolyte.

Conclusion

Al-substituted lithium manganese nickel oxide by hydrothermal method shows a homogeneous spherical morphology with layered structure, small uniform size powder distribution and has high initial discharge capacity of 125 mAh g⁻¹ and good cycling performance. Compared with the hydrothermal method and co-precipitation method, specific capacity and capacity retention by hydrothermal method is better than the co-precipitation method due to small size particles distribution and regular morphology. Al-substituted lithium manganese nickel oxide by hydrothermal is stable for lithium insertion and extraction. Therefore, it is concluded that the Al-substituted manganese nickel oxide using hydrothermal method is a promising cathode material for advanced lithium secondary ion batteries.

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