Understanding the underlying mechanism of the enhanced performance of Si doped $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ cathode material

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ABSTRACT

Si with $x = 0.000, 0.015, 0.030$, and 0.050 is successfully doped into layered $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ using a sol − gel method. Si doping results in a decrease in lattice constant, Li/Ni mixing, stress, and size of primary particles. Si is distributed at the Mn site probably nonuniformly to cause two different states of Si^{4+}. Si doping exerts no influence on the 2p bands of Ni^{2+}, and however gives rise to a slight splitting of $2p_{3/2}$ band of Mn^{4+}, and tends to increase the diffusion activation energy of Li^+. The optimum performance is achieved for $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ with $x = 0.015$ which has the highest BET surface area. Detailed analysis of structural modifications allows one to conclude that the remarkable alleviation of agglomeration of primary particles other than the optimization of structure related parameters such as the lattice constant, metal − oxygen bond length, ordering, cation mixing, size, and stress is responsible predominantly for the performance improvement. This study suggests that silicon is not an effective dopant for performance improvement of layered $LiMO_2$ simply from the perspective of structural modifications and optimization.

1. Introduction

Over the past decade, much attention has been paid to the development of lithium-ion batteries owing to the increasing demand for power sources with higher energy and power density. $LiCoO_2$ has been one of the most widely used cathode materials for its easy synthesis and excellent reversibility since the commercialization of lithium ion batteries. However, $LiCoO_2$ also suffers from many drawbacks such as high cost, toxicity and relatively low practical capacity (about $140\,mAh\,g^{-1}$, around half of its theoretical capacity), which limits its extensive application [1,2]. Recently, layered lithium nickel manganese oxides, $LiNi_xMn_{1-x}O_2$ crystallizing in the O3 structure same as $LiCoO_2$ (space group $R\bar{3}m$) have been extensively investigated and considered as the promising alternative material for the commercialized LiCoO [3–6]. Among them, $LiNi_{0.5}Mn_{0.5}O_2$ is one of the most attractive cathodes because

of its relatively higher specific capacity (about $200\,mAh\,g^{-1}$), lower cost, better thermal stability and nontoxicity [5–8]. Unfortunately, $LiNi_{0.5}Mn_{0.5}O_2$ normally has a low electrical conductivity [9] and a mixing of Li/Ni cations (about 10 at%) [10–12] owing to the close ionic radii of Li^+ (0.76 Å) and Ni^{2+} (0.69 Å), [13] which results in its poor rate capability and cycling performance.

To date, many approaches of improving the electrochemical performance of $LiNi_{0.5}Mn_{0.5}O_2$ such as partial substitution of transition metal [14–19] surface coating [9,20,21] and size reduction of particles [22–24] have been proposed. Elemental doping is known as a viable way capable of modifying crystal structures and thus improving electrochemical properties of cathode materials. Some alien metal ions, such as Co, [14,15] Li, [16] Al, [17] Mg, [18] Cr, [19] Ti, [25] Zr, [26] and Mo, [27] have been chosen as the dopants to improve either rate capability or cycle stability of $LiNi_{0.5}Mn_{0.5}O_2$. However, little has been known about the doping of non-metal ions into the transition metal site for $LiNi_{0.5}Mn_{0.5}O_2$ yet. Indeed, Si as a non-metal dopant was believed to be effective in facilitating Li^+ diffusion and ameliorating electrochemical properties of $LiCoO_2$, [28] $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ [30–32]. Normally, from the perspectives of both bond energy (Si − O: ∼$799.6\,kJ\,mol^{-1}$; Ni −

O: $\sim 382.0\,\mathrm{kJ\,mol^{-1}}$; Mn – O: $\sim 402.9\,\mathrm{kJ\,mol^{-1}}$) and possible valence match (Si^{4+} and Mn^{4+}), the improvement of electrochemical performance of $LiNi_{0.5}Mn_{0.5}O_2$ can be anticipated by Si doping. Also, Si is environmentally friendly and abundant on earth, which makes it attractive for the practical applications. In addition, exploration of the underlying mechanism of Si doping influencing the performance of $LiNi_{0.5}Mn_{0.5}O_2$ is favorable for the optimization of performance.

In this paper, $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ ($x = 0.00, 0.015, 0.030$ and 0.050) was synthesized by using a sol-gel method, and the effects of Si doping on the morphology, structure, diffusion barrier of Li^+, chemical valences of Ni and Mn, rate capability, and cycle performance of $LiNi_{0.5}Mn_{0.5}O_2$ were investigated in detail. A small amount of Si doping was found to improve the electrochemical performances of $LiNi_{0.5}Mn_{0.5}O_2$ significantly. The underlying mechanism of performance improvement was also discussed.

2. Experimental

2.1. Materials preparation

$LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ ($x = 0.000, 0.015, 0.030$ and 0.050) was synthesized by using a simple sol-gel method. Stoichiometric amounts of $LiNO_3$, $Ni(NO_3)_2\cdot6H_2O$ and $Mn(NO_3)_2\cdot6H_2O$, and citric acid with a molar ratio of 1:1 (citric acid to the total metal ions) were dissolved in deionized water. After the complete dissolution, nano-sized SiO_2 ($\sim 20\,\mathrm{nm}$ diameter) according to $x = 0.000, 0.015, 0.030$ and 0.050 was added and dispersed by sonication for 2 h. Then, the temperature of the solution was raised to 80 °C with stirring till clear viscous gels were formed. The gels were dried at 200 °C for 4 h to obtain the precursor powders. Finally, the precursor powders were heated at 500 °C for 3 h, followed by annealing at 850 °C for 10 h in air.

2.2. Structural characterization

The structures of the samples prepared above were characterized by X-ray diffraction (XRD). The XRD data were collected on a D8 Focus (Bruker) diffractometer with a Cu Kα radiation in an angle range of 10–80°. Their morphologies were observed by Scanning Electron Microscopy (SEM) (NOVA NanoSEM 430, FEI Company, USA). Nitrogen adsorption/desorption isotherms were acquired at 77 K using a Micromeritics TriStar II 3020 instrument (USA). Specific surface areas were calculated by the Brunauer–Emmet–Teller (BET) method. X-ray photoelectron spectra (XPS) were recorded using an ESCALab 250 electron spectrometer from Thermo Scientific Corporation (USA).

2.3. Electrochemical measurements

Electrochemical tests of the samples were performed using CR 2025 coin cell. The active materials with different Si contents, acetylene black and PVDF (poly (vinylidene fluoride)) were mixed with a weight ratio of 80:10:10, and then grinded using NMP (N-methyl-2-pyrrolidone) as the solvent. The slurries thus obtained were pasted onto an aluminum foil and dried under vacuum at 110 °C for 12 h. The foils were punched into discs and pressed under 20 MPa to form cathodes. The cells were assembled in a glove box filled with highly pure argon using a lithium metal as the counter electrode and Celgard 2316 as the separator. 1 M $LiPF_6$ dissolved in a mixture of EC (ethylene carbonate), EMC (ethyl methyl carbonate) and DMC (dimethyl carbonate) with a volume ratio of 1:1:1 was used as the electrolyte. Electrochemical measurements were carried out on a battery test system (BTS–5 V, Neware Company, China) at room temperature (RT). Cyclic voltammetry (CV) at RT, and electrochemical impedance spectra (EIS) at

different temperatures were acquired on an electrochemical workstation (CHI660D, Shanghai Chenghua Company, China).

3. Results and discussion

The effects of Si doping on the structures of $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ ($x = 0.000, 0.015, 0.030$, and 0.050) were studied by XRD, and their XRD profiles are shown in Fig. 1. The reflections of the XRD profiles were indexed to the $\alpha - NaFeO_2$ structure with space group of $R\overline{3}m$, as reported. [5,6] All samples are of single phase except for a trace impurity of Li_2SiO_3 for $x = 0.050$, as revealed by the inset in Fig. 1. The clear splittings of (006/012) and (018/110) reflections were observed to reveal the formation of a well ordered hexagonal layered structure which are indicated by the magnified profiles in the insets in Fig. 1 [33]. Thus, the amount of Si substitution for Mn, $x = 0.050$ is regarded as the doping limit of a single phase under the present experimental conditions, which may be determined by their fairly large difference in ionic radius (Si^{4+}: 0.40 Å, and Mn^{4+}: 0.54 Å).

Crystal structure has been known to normally have a significant effect on the performance of an electrode material. To study the possible structural changes induced by the Si doping, Rietveld refinements were performed on their XRD data by adopting a model based on the $\alpha - NaFeO_2$ structure. A little amount of Ni and Li is reasonably supposed to occupy the 3a and 3b sites, respectively, due to the mixing effect caused by their close ionic radii (Li^+: 0.69 Å, Ni^{2+}: 0.76 Å) while Si is considered to replace Mn at the 3b site partly. The large difference in scattering contrast between Ni and Li enables one to refine the occupancies of Ni at the 3a site and of Li at the 3b site. The simulated and experimental XRD patterns agree very well, as shown in Fig. 1. The refined parameters are outlined in Table 1. The lattice constants a and c both increase with the increased Si amount, which is basically in accord with the change for the Si doped $LiNi_xMn_yCo_{1-x-y}O_2$, but at variance with the decrease followed by the increase for the Si doped $LiCoO_2$ [28,34]. The c/a values for all the samples are well above 4.90, and tend to decrease slightly with the Si amount, which suggests an ordered hexagonal structure [35]. The integrated intensity ratio of the (003) to (104) peaks falls well below 1.0, implying a significant cation mixing. The Li/Ni mixing was refined to be around 10%, and tends to decrease a little bit with the Si content, as shown in Table 1 [10–12]. Such a small drop of less than 1% in mixing percentage is actually negligible. The integrated intensity ratio, $(I_{006} + I_{012})/I_{101}$ also represents the ordering degree of the hexagonal structure in which the lower the ratio, the higher the hexagonal ordering is
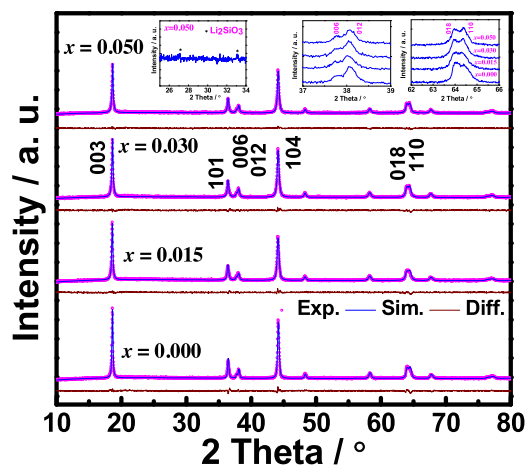

Fig. 1. Experimental, simulated and different XRD profiles of $LiNi_{0.5}Mn_{0.5-x}Si_xO_2$ ($x = 0.000, 0.015, 0.030$, and 0.050).