Improved Cycling Stability of Cobalt-free Li-rich Oxides with a Stable Interface by Dual Doping

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ABSTRACT

Li-rich cobalt-free oxides, popularly used as a cathode with high capacity in lithium ion battery, always suffer from poor cycling stability between 2.0 and 4.8 V *vs* Li$^+$/Li, especially when cycled at high temperatures (>50 °C). To overcome this issue, Na$^+$ and Al^{3+} dual-doped Na$_x$Li$_{1.2-x}$Mn$_{0.6-x}$Al$_x$Ni$_{0.2}$O$_2$ Li-rich cathode is prepared in this study. It is shown that the side reactions between cathode and electrolyte during cycling are suppressed. The improved cycling performance is observed for all of the doped samples, among which the sample with $x = 0.03$ exhibits the highest capacity retention of 86.1% after 200 cycles between 2.0 and 4.8 V at 2C (1C = 200 mA g^{-1}) and shows a remarkable cycling stability, even at a high temperature of 55 °C (a capacity retention of 92.2% after 100 cycles). Moreover, the average voltage of the sample with x = 0.03 after 100 cycles at 0.5C remains at 3.11 V with a retention ratio of 86.6%. This work provides a new strategy to develop Li-rich cobalt-free cathodes with excellent cycling stability for lithium ion batteries at high temperatures.

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1. Introduction

Unprecedented efforts have been focused on finding the perfect cathodes with high capacity, high energy density, and long lifetime for lithium ion batteries to satisfy the needs of energy storage. Among the types of alternative cathodes, Li-rich Mn-based oxides (xLi$_2$MnO$_3$-(1-x) LiMO$_2$, M = Mn, Co, Ni) are well considered as one of the most promising cathodes for lithium ion batteries because of the high capacity (over 250 mAh/g) and low cost [1–3]. However, these Li-rich cathodes suffer from a rapid capacity loss and voltage decay during cycling, especially at high temperatures. How to overcome these problems remains a substantial challenge for the practical applications of these cathodes [4,5].

Atomic doping or elemental substitution is thought to be a simple and effective method to improve the electrochemical performance of Li-rich Mn-based oxides. Commonly, there are three sites for doping or substitution: lithium site in lithium ion layers, transition metal site and oxygen site in the transition metal layers. In lithium ion layers, the widely used alien ions for lithium ions are Na$^+$ [6,7], K$^+$ [8] and Mg^{2+} [9], which have a larger radius than Li$^+$ ion. The larger doping or substitution ions in lithium layers can serve as pillars after de-lithiation, in case of the collapse of bulk

materials. Doping with the larger alien ions can improve the ionic diffusion kinetics due to the expansion of the lithium slab distance. In the transition metal layers, cations such as Al^{3+} [10–12], Fe^{3+} [13], Sn^{4+} [14], Ti^{4+} [15,16], and Zr^{4+} [17], have been chosen. Researchers have concluded that introducing those ions could partly improve the cycling stability of Li-rich oxides by enhancing thermal stability, preventing the structure degradation, and suppressing the side reactions. In addition, some anionic doping, such as BO$_3$$^{3-}$ [18], PO$_4$$^{3-}$ [19], and F$^-$ [20], also can fix the transition metal ions in Li-rich oxides, attributing to a better cycling stability.

A majority of studies about substitution or doping have focused on the mono doping in lithium ion layers (LILs) or transition metal ion layers (TMILs), while efforts about dual doping in the both layers are rarely reported in Li-rich oxides. It is well known that the capacity loss of Li-rich oxides is related to the evolution of LILs, but also dependent on the features of TMILs due to the existence of Li$_2$MnO$_3$. When charged to 4.8 V, migration of transition metal ions to lithium layer would initiate the formation of spinel phase and voltage decay [21]. Furthermore, the collapse of the layered structure leads to an electrochemical inactive rock-salt phase, due to the absence of lithium ions in lithium slabs [22]. In addition, the strong side reactions between Li-rich oxides and electrolyte under a high de-lithiation state can dissolve the transition metal ions, leading to a thick solid electrolyte interphase (SEI) layer, which can increase the impendence and hinder the movement of lithium ions

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back to the Li-rich oxides [23]. Therefore, simultaneously controlling the capacity loss and voltage decay provoked by the variations in LILs and TMILs is highly needed for Li-rich cobalt-free oxides, especially when applied at high temperatures.

In this work, dual doping with Na^+ and Al^{3+} is introduced into LILs and TMILs of cobalt-free Li-rich oxides $Na_xLi_{1.2-x}Mn_{0.6-x}Al_xNi_{0.2}O_2$ with an aim to improve the cycling stability by combining the advantages of sodium and aluminum ions. The investigation of the structure, valence state, electrochemical performance and surface chemical changes of the pristine and doped samples after cycling demonstrates that Na and Al dual doping plays an important role in stabilizing Li-rich cathodes during prolonged cycles. Moreover, the increase of the covalence for Mn-O bonds can suppress the side reactions between cathode and electrolyte, which contributes to an excellent cycling stability.

2. Experimental

2.1. Sample Preparation

Dual doped $Li_{1.2-x}Na_xMn_{0.6-x}Al_xNi_{0.2}O_2$ (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05) oxides were successfully synthesized via a sol-gel method using a citric acid as the chelating agent. Using an un-doped sample as an example, the detailed preparation procedure could be described as follows. First of all, given amounts of lithium acetate (10% excess), transition metal acetates and citric acid (with a molar ratio of 2 for transition metal ion to citric acid) were dissolved in 200 ml distilled water, and pH value of the mixed solution was adjusted to 1–2 using nitric acid. Secondly, the solution was dried in a water bath at 80 °C for 8 h to obtain a gel. Then, the gel was dried in an oven at 160 °C for 12 h to evaporate the residual water. The obtained powder was calcinated in air at 500 °C for 5 h and then at 900 °C for another 12 h. Finally, the samples were cooled down to room temperature in furnace. For the dual-doped samples, the synthetic procedures were the same, except that sodium chloride and aluminum sulfate were used as the sodium and aluminum sources, respectively, to replace the same amount of lithium acetate and manganese acetate. The corresponding samples with different x values were named as D0, D1, D2, D3, D4, and D5, respectively.

2.2. Sample Characterization

Crystallographic structures of all samples were identified by powder X-ray diffraction (XRD) on a Rigaku miniflex apparatus with a Cu Kα (λ = 1.5418 Å) radiation source, and the XRD patterns were collected in the two-theta range from 10° to 80° with a step of 0.02°. Structural refinement was performed using General Structure Analysis System (GSAS). KCl powders were chosen as the internal standard for peak positions calibration. The chemical compositions of the pristine and doped samples were analyzed by inductive coupled plasma atomic emission spectrometry (ICP-AES). Field-emission scanning electron microscopy (SEM) (JEOL, model JSM-6700) was used to conduct morphology studies. X-ray photoelectron spectroscopy (XPS) was performed using an ESCA-LAB MKII apparatus with a monochromatic Al Kα X-ray source. The charging shift was calibrated using C1s photoemission line at a binding energy of 284.8 eV.

2.3. Electrochemical Test

Electrochemical performance of the samples was measured using CR-2025-type coin cells. The cathode laminate was fabricated by coating a slurry of the active materials (80 wt %), super P conductive carbon (10 wt %), polyvinylidene fluoride (PVDF) binder (10 wt %) and N-methyl-2-pyrrolidone (NMP) solvent onto an aluminum foil by the doctor blade technique. The obtained film was dried in a vacuum oven at 100 °C for 12 h. The cells were assembled in an argon-filled glove box with the water and oxygen concentrations under 1 ppm, using the metallic lithium foil as the counter electrode and Cellgard 2400 as the membrane. The electrolyte was 1 M $LiPF_6$ dissolved in ethyl carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume). The charge and discharge tests were performed on a Neware Test System by galvanostatically cycling the cells at room temperature with a voltage window between 2.0 and 4.8 V. Electrochemical impedance spectroscopy (EIS) was performed using an electro-chemical workstation (CHI660), and the applied frequency range was 100 kHz to 10 mHz. In this study, 1C rate corresponded to a current density of 200 mA g^{-1}.

3. Results and Discussion

3.1. Structure and morphology

Chemical compositions determined by ICP for $Na_xLi_{1.2-x}Mn_{0.6-x}Al_xNi_{0.2}O_2$ are listed in Table 1. The actual compositions of samples are in well agreement with their nominal compositions. The crystal structure and phase purity of un-doped and dually-doped samples were examined by XRD. As shown in Fig. 1, all diffraction peaks of the obtained samples can be indexed in terms of a typical hexagonal layered structure (space group R$\bar{3}$m), except for the broad weak peaks at two theta of 20–25° that are attributed to the Li_2MnO_3-like component (monoclinic structure with C2/m symmetry). These weak diffractions are characteristic of the LiM_6 cation ordering that occurs in the transition metal layers of Li_2MnO_3 [24]. The clear splitting of paired peaks (006)/(012) and (108)/(110) demonstrates a layered structural feature. To inspect the variation of lattice parameters, magnification of the peaks in two-theta range 18–20° is shown in the right panel of Fig. 1. It is seen that (003) reflection shifts towards lower diffraction angle after the doping, which indicates that an expansion of c-axis could be induced by Na^+ and Al^{3+} dual doping. No impurity peaks are found in all of the dual-doped samples, even at a high content of sodium and aluminum (x > 0.03) under the precision of XRD. Therefore, sodium and aluminum ions are successfully doped in the crystal lattice without changing the layered structure.

To further confirm the effects of Na and Al dual doping on the lattice parameters of the Li-rich oxides, we refined XRD patterns of the samples by Rietveld method using GSAS software [25]. The fitted results are based on both trigonal $LiNi_{0.5}Mn_{0.5}O_2$ (R$\bar{3}$m) and monoclinic Li_2MnO_3 (C2/m) phases for the pristine and doped samples. For the doped samples, all of the Na and Al atoms are firstly considered to be doped in the trigonal phase. The obtained lattice parameters are listed in Table 2 and the corresponding refined XRD patterns are shown in Fig. S1. Dual doping of Na and Al slightly increases the value of a and c. XRD of D5 was also refined by introducing some amounts of Na into Li_2MnO_3 lattice. The obtained

Table 1
Experimentally measured metal-ion contents in bulk materials by ICP for samples D0 to D5.

Doping level	Li	Na	Mn	Al	Ni[*]
D0	1.196	0.004	0.598	0.005	0.200
D1	1.185	0.010	0.594	0.011	0.200
D2	1.183	0.017	0.578	0.021	0.200
D3	1.168	0.027	0.575	0.029	0.200
D4	1.157	0.044	0.561	0.038	0.200
D5	1.152	0.051	0.549	0.048	0.200

[*] The contents are calculated based on ICP results and normalized to Ni content to 0.2 (theoretical value in $Li_{1.20}Mn_{0.6}Ni_{0.2}O_2$).