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Graphic for

Electrochemical Activation, Voltage Decay and Hysteresis of Li-rich Layered Cathode Probed by Various Cobalt Content

Electrochemical activation, voltage decay and hysteresis of Li-rich layered cathode probed by various cobalt content

Yingqiang Wu,^{a,b} Leqiong Xie,^b Xiangming He,^{*c} Linhai Zhuo,^d Limin Wang,^{*a} Jun Ming^{*a,e}

^a *State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, P. R. China;*

^b *Huadong Institute of Lithium-ion Battery, Zhangjiagang 215600, China*

^c *Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China*

^d *College of Chemistry and Chemical Engineering, Taishan University, Taian, 271021, P. R. China.*

^e *Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal, 23955-6900, Kingdom of Saudi Arabia*

^{*}Corresponding Author. E-mail: hexm@tsinghua.edu.cn; lmwang@ciac.ac.cn; jun.ming@ciac.ac.cn.

Abstract

The high capacity of Li-rich layered cathode materials have attracted great attention for the greater energy density lithium ion (Li-ion) batteries, but the understanding of knowledge associated with electrochemical behaviours are still needed to improve their performances further. In this study, different amount of Co content is designed in Li-rich layered compounds ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$, $0 \leq x \leq 0.2$), and the stepwise electrochemical activation process is applied to explore the features. We discover that the substitution of Co^{3+} ions can accelerate the electrochemical activation of Li_2MnO_3 component, and the Co-doped compound delivers much higher capacities even they suffer an apparent voltage decay comparing to the Co-free one. Besides, a fast metal ions migration exists (*e.g.*, from the metastable tetrahedral site to the lower energy cubic site) in initial dozens of cycles (*e.g.*, 30 cycles at 0.1C); thereafter, they likely return to the original octahedral site, as demonstrated in the voltage decay and hysteresis analysis.

1. Introduction

Li-rich layered compound with the chemical formula of $x\text{Li}_2\text{MnO}_3 \cdot (1-x) \text{LiMO}_2$ ($M = \text{Ni, Co and Mn}$) is one of the most promising cathode for the greater energy density lithium ion (Li-ion) batteries due to the extremely high capacity up to 250 mAh g^{-1} .^[1-7] However, in-depth analysis of this complex compounds, including the associated electrochemical behaviors as varying the compositions, is still urgently needed to understand and overcome their drawbacks. For example, it generally requests an electrochemical activation process, where the electrode need to be charged over 4.6 V (vs. Li/Li^+) to extract the Li^+ as “ Li_2O ” from the Li_2MnO_3 (where it forms MnO_2) for desired high capacity.^[1,8] As a result, a high first-cycle capacity loss occurred, because only one Li^+ can be reinserted into the MnO_2 in the following discharge and the oxygen loss becomes irreversible.^[9] Besides, the voltage decay, originated from the migration of transition metal ions into lower energy cubic sites in the lithium layers,^[10,11] can lower the energy output,^[12,13] where the accompanied hysteresis can also lead to a low energy efficiency.^[10,14,15] Thus, to date, an understanding of these challenges studied from different viewpoints is required to develop more efficient strategies for improving their performance.

It was reported that the Co doping has a great effect on electrochemical performance of the layered cathode. For example, an increased rate capability is confirmed as increasing the Co content in the layered $\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$ due to the increased cation ordering, where the inferior chemical stability of $\text{Co}^{4+/3+}$ redox couple in deep charge also gives rise to lower reversible capacity.^[16,17] While for the

Li-rich layered cathode, the cation ordering become more complex when trivalent Co ions were doped into the transition-metal layers. Although Co-doped Li-rich layered compound are being widely studied,^[18,19] many significant points still need to be studied, such as the electrochemical differences of electrode as varying the Co content. Particularly, the effect of Co doping on the electrochemical activation process, voltage decay and hysteresis are rarely reported. And also, whether it can reverse or accelerate the cation migration (voltage decay and hysteresis) in cycling remains an unknown issue. Thus, herein the electrochemical behaviours, cycle performance and rate capacity of Li-rich layered compound ($0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$, $0 \leq x \leq 0.2$) are monitored as varying the Co content, where a stepwise electrochemical activation process is studied. The voltage decay and hysteresis were further analysed to understand the structural variation of layered compounds as cycling.

2. Experimental

2.1 Materials synthesis

The Li-rich layered compound were synthesized by a carbonate co-precipitation method. Typically, the mixed aqueous solution of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ were pumped into a continuous stirred tank reactor (CSTR), where the Na_2CO_3 and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution were also fed into the reactor simultaneously for the precipitation. The molar ratio of Ni/Co/Mn is finely controlled in precursor solution as requested. The precipitated carbonate powders were filtered, washed and dried at 120 °C completely, and then the metal oxide was collected after a thermal treatment at 500 °C for 12 h. Subsequently, the oxide was mixed with Li_2CO_3 and then the mixture

was calcined at 850 °C for 12 h in air under a heating rate of 2 °C min⁻¹, giving rise to the Li-rich layered compounds.

2.2 Electrode preparation

The cathodic electrode was prepared as below. As-prepared Li-rich layered compound, acetylene black and the binder of poly(vinylidene fluoride) (PVDF) with the weight ratio of 8:1:1 were mixed in N-methylpyrrolidinone (NMP) to form a uniform slurry first, and then it was casted on aluminum foil. The electrode was dried at 120 °C in vacuum oven overnight, and the loading density of the active materials (*i.e.*, cathode powders) is controlled around at 7.5 mg cm⁻².

2.3 Characterizations and Electrochemical Measurement

The morphology and size distribution of powders were characterized by the field emission scanning electron microscopy (SEM, JSM6301F). The crystalline information of layered compound was acquired by a Bruker AXS D8 ADVANCE powder diffractometer equipped with a Co K α radiation source operating at 35 kV and 40 mA. The electrochemical measurement of electrode were performed using 2032 coin cell, which has a configuration of electrode | separator (Celgard 2320 micro-porous separator membrane) | metallic lithium foil in the electrolyte of 1.0 M LiPF₆ in EC/ EMC (3:7 by weight). The cell was assembled in an Argon-filled glove box, where the content of O₂ and H₂O was strictly maintained below 1.0 ppm. The cut-off voltage were controlled at 2.0-4.8 V (*vs.* Li/Li⁺), and the galvanostatic charge/discharge curves were recorded by the Land instrument. In the stepwise electrochemical activation process,^[20-22] the electrode was firstly charged to 4.5 V and

discharged to 2.0 V for 2 cycles, and then the charged voltage was changed to 4.6 V, 4.7 V and 4.8 V in sequence, under which the battery performed two cycles with the discharge voltage of 2.0 V.

3. Results and Discussion

As-prepared Li-rich layered compound $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$ ($0 \leq x \leq 0.2$) with varied Co content has a high uniformity and dispersion with spherical size of 14 μm (Figure 1a-b, Figure S1). The tap-density of product can achieve the value as high as 2.3 g cm^{-3} . The XRD patterns confirm that the $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$ powders are the standard layered $\alpha\text{-NaFeO}_2$ structure (R-3m) (Figure 1c). The weak and broad superlattice reflection peak around 21° , corresponding to the characteristic of Li/Mn ordering in the transition-metal layer ($\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$), indicate that the compounds are Li-rich layered materials.^[23] Note that the intensity of the superlattice reflection peaks around 21° decreases as increasing the Co content (Figure 1d). It results from the doping of Co, which can disturb the ordering of Li/Mn in the transition-metal layer and then affect the electronic interactions between the manganese and nickel ions.^[23]

To analyse the difference of Li-rich layered compounds as varying the Co content, the stepwise electrochemical activation process is applied,^[20-22] because the traditional “one step” charged procedure directly to the high voltage (*e.g.*, 4.8 V) conceals many imperceptible phenomena. Figure 2a-e shows the (dis-)charge curves and the irreversible capacity (C_{ir}) of the electrodes charged step by step to 4.5 V, 4.6 V, 4.7 V and 4.8 V, respectively. Several distinct features can be summarized: (i) the

voltage plateau for the electrochemical activation of Co-free electrode ($\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$, $x=0$) is as high as 4.56 V, while for the Co-doped electrodes, it become obvious when it was charged to 4.5 V and prolong gradually as increasing the Co content to $x = 0.2$; (ii) the electrochemical activation of Co-doped cathode was completed at the voltage of 4.6 V, while the Co-free electrode need to be charged up to 4.7 V; (iii) the irreversible capacity (C_{ir}) increased as increasing the content of Co particularly from 0.15 to 0.2. For example, it can achieve 70 mAh g^{-1} for the electrode of $x = 0.2$ charged to 4.5 V, whilst it was only 24 mAh g^{-1} for the Co-free electrode (Figure 2e); (iv) the delivered capacity of the electrodes increased fast when the Co was doped, and the optimized content was $x = 0.15$.

The results indicate that the substitution of Co^{3+} ions can accelerate the electrochemical activation of the Li_2MnO_3 component, but the Co content should be controlled for balancing the performances. As further confirmed by the dq/dv plots in Figure 2f-j, the electrochemical activation of Co-free electrode starts around at 4.53 V and completed until 4.7 V. By contrast, the activation of Co-doped electrodes can begin at 4.4 V and almost done at 4.6 V (Figure 2h-j). The reasons should be related to the chemical instability of the $\text{Co}^{4+/3+}$ redox couple. In detail, the Li^+ ions were extracted from the electrode materials accompanied by the oxidization of Co^{3+} ions, where electrons were removed from the t_{2g} band of the $\text{Co}^{3+}:3d^6$ configurations. But, the fact was that the electrons can be removed from the $\text{O}^{2-}:2p$ band (oxidation of O^{2-} ions), because the top of the $\text{O}^{2-}:2p$ band overlap significantly with t_{2g} band of the $\text{Co}^{3+}:3d^6$ configurations.^[24,25] In this way, a low activation voltage around 4.5 V was

observed for the Co-doped sample. For the $\text{Ni}^{3+}:\text{3d}^7$ and $\text{Mn}^{3+}:\text{3d}^4$ configurations, however, they either barely overlap with or lie well above the $\text{O}^{2-}:\text{2p}$ band.^[24,25] Thus, the Co-free electrode needs a higher voltage to extract the Li^+ as “ Li_2O ” from the Li_2MnO_3 ($\text{Li}_2\text{O}\cdot\text{MnO}_2$) compound.

The electrochemical differences were further studied based on representational electrodes of $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ ($x=0$) and $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.14}\text{Co}_{0.12}\text{O}_2$ ($x = 0.15$). The first, the Co-doped electrode demonstrates much higher rate capacities in the rate test. As shown in Figure 3a-b, the Co-doped electrode can deliver capacities of 283.7, 254.3, 232.9, 189.9, 167.6 and 149.2 mAh g^{-1} at the rates of 0.1C, 0.5C, 1C, 3C, 5C and 7C (where define 1C = 200 mA g^{-1}) respectively, which are much higher than 231.6, 203.1, 184.8, 154.3, 133.4 and 115.4 mAh g^{-1} of Co-free electrode under the same variation of rates. Besides, the Co-doped electrode exhibits a very stable cycle performance with an initial capacity of 277.6 to 279.8 mAh g^{-1} after 80 cycles at the 0.1C, where the specific energy density maintains around 982.4 and 925.7 Wh kg^{-1} (vs. Li-rich cathode. Figure 3c-d). While the Co-free electrode shows the lower capacities and specific energy densities around 235.5 to 267.2 mAh g^{-1} and 844.2 to 905.9 Wh kg^{-1} . The comparative results reveal that the substitution of Co^{3+} ions can give rise to much higher rate capacities and energy densities, but suffer from the voltage decay result in the decrease of the specific energy density (Figure 3d).

Note that both two kind of electrodes suffer from the voltage decay, as demonstrated in the (dis-)charge curves (Figure 4a-b). The dq/dv plots in Figure 4c-d show that three peaks change dramatically: (i) the peak around at 3.25 V (*i.e.*, the

Mn^{4+} reduction in the layered MnO_2) shifts to the lower potentials and increases in magnitude toward 3.0 V; meanwhile, a new peak appears at 2.1 V and increases gradually as cycling. It demonstrates the transformation of the layered structure to a spinel-like configuration, where the transition metal ions migrate into the lithium layers, giving rise to the voltage decay.^[10,26] (ii) The third peak located at 3.8 V (corresponding reduction peak at $\sim 3.75\text{V}$), attributed to the oxidation-reduction of $\text{Co}^{4+/3+}$, $\text{Ni}^{4+/3+}$ and $\text{Ni}^{3+/2+}$ in the layered component, decreases and shifts to the lower potentials. These observations show that the Co-doped electrode suffers more rapid voltage decay (Figure 4d), where the average voltage decay is 2.92 mV per cycle while the value is 2.47 mV per cycle for the Co-free electrode (Figure 4e, Figure S2). Thus, the substitution of Co ions can accelerate the migration of the transition metal ions, especially the Ni ion, resulting in the rapid voltage around at 3.8 V as cycling.

However, both two electrodes show similar voltage decay trend in initial 30 cycles, demonstrating a fast migration of transition metal ions into the lithium layers in initial cycles (Figure 5a). The comparative voltage hysteresis, another indicator of structural variation, was further analyzed. The first, the resultant energy efficiency is around 90% (Figure S3), demonstrating the limited effect of Co^{3+} for the energy efficiency. The difference of average charge/discharge voltage (*i.e.*, $\Delta V = V_{\text{charge}} - V_{\text{discharge}}$) is 445.4 mV and 406.4 mV for the Co-doped and free electrode respectively, as confirmed by the (dis-)charge curves (Figure 5b). The value of ΔV indicates that the hysteresis decreases gradually in initial 30 cycles and thereafter it increases as cycling (Figure 5c). Based on the voltage decay trend in Figure 5a, three features can

be summarized: (i) the transition metal ions those migrated to metastable tetrahedral sites in charge have a main trend of movement to the lower energy cubic sites in lithium layer in discharge for initial dozens of cycles (*e.g.*, 30 cycles at 0.1C) (Figure 5d, yellow area), as confirmed by the rapid voltage decay; (ii) Later, the transition metal ions likely return to the original octahedral site from the metastable tetrahedral sites rather than move to the cubic sites in the discharge, because the diffusion resistance might increase as the spinel-like configuration formed in the structure after initial 30 cycles (Figure S4), as demonstrated in the hysteresis (Figure 5d, light blue area). The transition metal ions occupied in the cubic sites can induce the formation of spinel-like configuration (Figure S5) and then the diffusion resistance (*i.e.*, energetic barrier) of the transition metal ions diffuse into the cubic sites increases.^[27-29] The schematic migration trend of transitional metal ions is illustrated in Figure 5d; (iii) the substitution of Co ions demonstrates limited effect to the hysteresis and the energy efficiency.

Conclusions

In summary, the electrochemical behaviors of Li-rich layered compounds with different content of Co were studied, in which the stepwise electrochemical activation is applied to discover the details. The substitution of Co^{3+} ions can accelerate the electrochemical activation of Li_2MnO_3 and deliver much higher and stable rate capacities comparing to that of Co-free electrode. Preliminary results demonstrate that the migration of metal ions to the lower energy cubic sites from the metastable tetrahedral site is obvious in initial dozens of cycles; thereafter they trend to return to

the original octahedral site. This research is significant to knowledge and design Li-rich cathode with an improved and balanced performances for feasible commercialization.

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Figure caption

Figure 1 SEM images of the Li-rich layered compounds powders of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiMn}_{0.5-x}\text{Ni}_{0.5-x}\text{Co}_{2x}\text{O}_2$, (a) $x = 0$, (b) $x = 0.15$. (c) Comparative XRD patterns of chemical compounds with different content of Co and (d) a detail intensity of the superlattice reflection peaks around 21° .

Figure 2 Electrochemical activation of the Li-rich layered electrodes by a stepwise process, where the electrode was charged to (a) 4.5 V, (b) 4.6 V, (c) 4.7 V and (d) 4.8 V, and (e) the corresponding irreversible capacity (C_{ir}) of the electrode with various Co content. The current is 20 mA g^{-1} . (f-j) $\text{d}q/\text{d}v$ plots of the charge curves from 4.3 V to 4.8 V in the stepwise electrochemical activation process, where the activation voltage shifts to the lower values as increasing the Co content from $x = 0$ to $x = 0.2$.

Figure 3 Voltage *vs.* capacity profiles of Li-rich layered electrode in the rate test, (a) $x = 0$, (b) $x = 0.15$, (c) Comparative cycle performance and specific energy of the electrodes, (c) $x = 0$ and (d) $x = 0.15$ between 4.8-2.0 V at the rate of 0.1 C, where 1C is 200 mA g^{-1} .

Figure 4 Cycled charge/discharge curves and $\text{d}q/\text{d}v$ plots of Li-rich layered electrodes, (a, c) $x = 0$, and (b, d) $x = 0.15$. (e) Comparative discharged voltage of the electrodes.

Figure 5 (a) Voltage decay of Co-doped and Co-free electrode as cycling. (b) Typical voltage *vs.* capacity profiles of the electrode after the electrochemical activation. (c) Difference of average voltage between the charge and discharge in cycling. (d) Schematic migration of the transitional metal (*i.e.*, TM) ions in initial cycles (yellow arrow and area) and after the 30 cycles (light blue and area) as the charge/discharge process.

Figure List

Figure 1

Figure 2

Figure 3 **Figure 4**

Figure 5

Highlights

1. Spherical and high tap-density Li-rich cathodes with varied Co content are prepared.
2. The stepwise electrochemical activation strategy is applied to study the Li-rich cathode.
3. The differences of electrochemical behaviors are monitored as varying the Co content.
4. Co-doped cathode delivers much higher capacities and energy densities.
5. A relationship of the voltage decay, hysteresis and metallic ions migration trend is presented.