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Short communication

Correlation between transition metal ion migration and the voltage ranges of electrochemical process for lithium-rich manganese-based material

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HIGHLIGHTS

- Transition metal ion migration occurs at the potential above the activation energy.
- The charge/discharge lower-limit voltages have no impact on voltage decay.
- Voltage decay becomes severer with increased upper-limit voltages.
- Holding at high voltages for a prolonged time also accelerates voltage decay.

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ABSTRACT

Voltage decay of Li-rich cathode material is caused by migration of transition metal (TM) ions and layered phase transformation to spinel phase. Here electrochemical studies demonstrate that charge/discharge voltage ranges have a strong impact on the voltage decay. For cells cycling in the charge/discharge condition of voltage range at 2.0–4.6 V, 3.2–4.6 V and 4.2–4.6 V, voltage decay phenomena occur to the same extent. While for the serial conditions of 2.0–4.2 V, 2.0–4.4 V, 2.0–4.6 V, 2.0–4.8 V and 2.0–4.6V + hold at 4.6 V for 5 h, voltage decay starts to occur at a typical voltage when the potential is high enough, and then phase transformation becomes severer with increased potentials, or prolonged time holding at high voltages. TM ions at high voltages have high enough energy, which can be denoted as "activation energy", to stride across the transition state and migrate to Li vacancy, which results in spinel formation and voltage decay.

1. Introduction

The Li-rich Mn-based layered solid-solution system Li_2MnO_3–$LiMO_2$ (M = Co, Ni, Mn, $Mn_{1/2}Ni_{1/2}$, $Mn_{1/3}Ni_{1/3}Co_{1/3}$) has emerged as a potential next-generation cathode material for lithium ion batteries due to its high specific-capacity, high energy-density, low cost and low toxicity [1–3]. However, the voltage decay phenomenon observed in Li-rich electrodes is regarded as a huge barrier to commercialization. The main defect is making it too difficult to monitor the state-of-charge situation. Besides, the output energy density decreases with voltage decay. The origin of voltage decay is the formation of spinel phase, which has got to a common view [4,5]. Many works have focused on the voltage decay issue, including coating, transition metal ion tuning, Li_2MnO_3 activation controlling and voltage window controlling [4–6]. But voltage decay problem is not resolved by either method.

Based on this, recent studies are carried out to understand the voltage decay mechanism more deeply [7–12]. Voltage decay has been found to accelerate with increased upper cutoff voltage [7,8], however its mechanism is not clear. Furthermore the influence of lower cutoff voltage is not studied. The driving force of TM ion migration is as-applied voltage and Li ion vacancies (i.e. capacity), and TM ion inclines to migrate when its energy is above the activation energy barrier [10]. These two factors are largely changed during the whole charge/discharge voltage range.

In this work our purpose is to figure out the mechanism of how transition metal ion migrates and voltage decay occurs at different voltage stages. By tuning the charge/discharge voltage range, the TM ion migration and voltage decays at high voltage processes and low voltage processes are revealed respectively.

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2. Materials and methods

The precursor of nickel–cobalt–manganese carbonate was synthesized by a co-precipitation process, with stoichiometric amounts (4:1:1) of $Mn_2SO_4 \cdot 2H_2O$, $Ni_2SO_4 \cdot 7H_2O$ and $Co_2SO_4 \cdot 4H_2O$ being used. The targeted Li-rich material $Li_{1.14}Mn_{0.54}Ni_{0.14}Co_{0.14}O_2$ was prepared by the solid-state reaction of lithium carbonate with the precursor.

Electrochemical tests were performed using a CR2032-type coin cell. Electrode material contains 80 wt.% as-prepared material with 10 wt.% super P and 10 wt.% polyvinylidene fluoride. The counter electrode was lithium metal and the electrolyte was 1 M $LiPF_6$ dissolved in a mixed solvent of ethylene carbonate/diethyl carbonate. Galvanostatic charge/discharge experiments were performed at 0.2 C.

In order to study the voltage decay mechanism on how the transition metal ion migration and phase transformation occur at different charge/discharge voltage ranges, the Li-rich samples are tested for 50 cycles as following: Sample A: 2.0–4.6 V; Sample B: 3.2–4.6 V; Sample C: 4.2–4.6 V; Sample D: 2.0–4.2 V; Sample E: 2.0–4.4 V; Sample F: 2.0–4.8 V; Sample G: 2.0–4.6V + hold at 4.6 V for 5 h; then all the samples are tuned to 2.0–4.6 V potential range for another 10 cycles.

3. Results and discussion

Fig. 1(a) shows the 51st cycle's charge/discharge curves of Li-rich materials after various pre-charge/discharge treatments with different lower-limit voltages. And the potential range of the 51st cycle is tuned to 2.0–4.6 V for each sample. Comparing the curves for the 1st and 51st cycle of Sample A, the discharge voltage decreases significantly, i.e. voltage decay. The 51st cycle's charge/discharge curves of Sample B and C are very close to that of Sample A, which verifies that the phase transformation and voltage decay extent of these two samples are similar with Sample A. Thus it can be seen that different low voltage processes, including experience at 2.0–3.2 V, 3.2–4.2 V voltage ranges, have no impact on voltage decay. Fig. 1(b) gives the corresponding dQ/dV plots of these samples. The R1 peak is attributed to the reduction reaction of nickel and cobalt ions in the $LiMO_2$ component [6,13]. The individual peaks from their contributions are not distinguishable in these

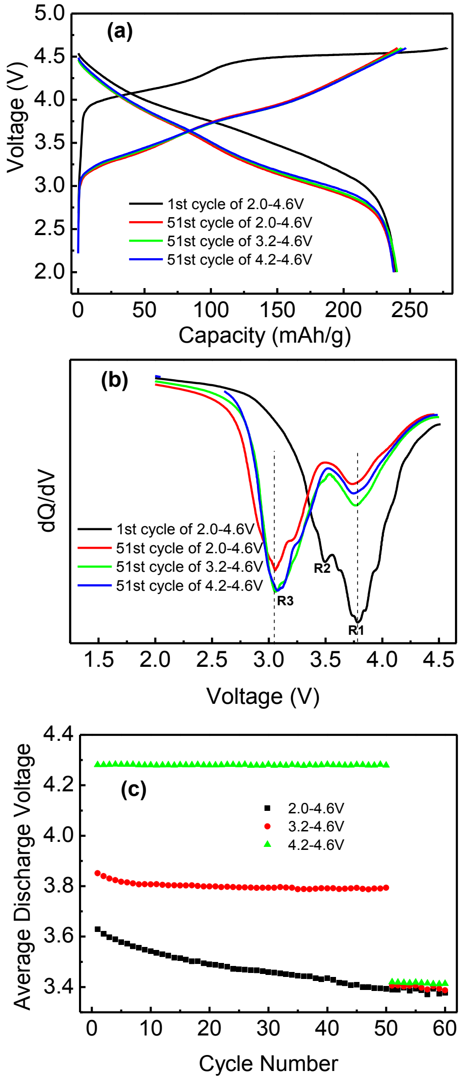

Fig. 1. (**a**) charge/discharge curves of the 1st cycle of 2.0–4.6 V and the 51st cycles of 2.0–4.6 V, 3.2–4.6 V and 4.2–4.6 V; (**b**) the corresponding discharge dQ/dV plots; (**c**) the average discharge voltages of cells charged/discharged at different lower-limit voltages.

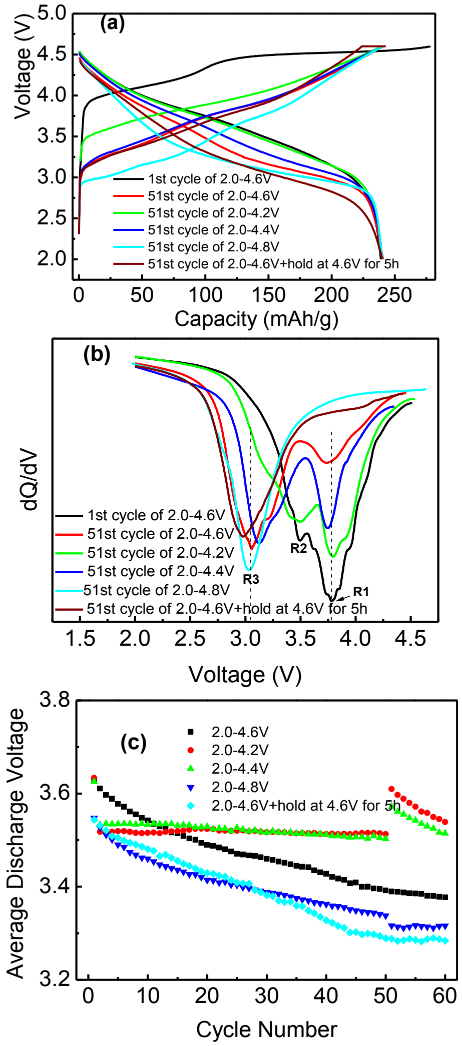

Fig. 2. (**a**) charge/discharge curves of the 1st cycle of 2.0–4.6 V and the 51st cycles of 2.0–4.6 V, 2.0–4.2 V, 2.0–4.4 V, 2.0–4.8 V and 2.0–4.6 V + hold at 4.6 V for 5 h; (**b**) the corresponding discharge dQ/dV plots; (**c**) the average discharge voltages of cells charged/discharged at different upper-limit voltages.