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A comparative study of overdischarge behaviors of cathode materials for lithium-ion batteries

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Abstract The overdischarge behaviors of LiFePO$_4$, LiNiO$_2$, and LiMn$_2$O$_4$ are thoroughly studied in different overlithiation voltage limitations. The results showed that LiFePO$_4$ and LiMn$_2$O$_4$ cathode materials show high structure stability under the overdischarge process to 1.0 V. The microstructure of LiNiO$_2$ is vulnerable to breakdown under the same testing condition. Fe-based olivine and Mn-based spinel cathode materials show better cyclic calendar life than that of Ni-based layered material. When an extreme overdischarge parameter (down to 0.0 V) is applied, all three samples experience an electrochemically driven irreversible solid-state amorphization process. Due to this overlithiation reaction, the host structure is totally destroyed. Therefore, it is harmful to experience deep overdischarge behaviors for most cathode materials.

Keywords Overdischarge · Voltage limitation · Solid-state amorphization · Cathode materials · Lithium-ion batteries

Introduction

With the development of portable electronic devices and electric vehicle, lithium-ion batteries become the main energy storage and conversion among all the chemical power sources. However, the battery safety becomes one of the most important problems of lithium-ion batteries which

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impedes them from application. In 2006, millions of laptop batteries were large scale as recalled by Sony Corporation because small metal particles were accidentally incorporated into battery cells during manufacturing. These metal particles can penetrate into the separator and make the positive touching negative electrodes within a cell. As a result, the cathode materials touching with the negative electrode are probably overdischarged with the application of large current density from short circuit. This overdischarge can generate heat during the operation, resulting in more shorting, overheating, burns, and even an explosion. Thus, the mechanism of the safety problems becomes the prerequisation for the application of lithium-ion batteries. Lots of efforts have been devoted to investigate the reasons caused the safety problem of the batteries. It has been found that, under overcharge condition, metal oxide-based cathode materials are prone to breakdown and then release oxygen [1, 2]. The released oxygen can cause the decomposition of organic electrolyte, which generates more heat, and flammable gases, finally leading to thermal runaway of the batteries. Iriyama et al. [3] showed that LiFePO$_4$ cathode could maintain its structure during an overcharge process to high voltage, even at 5.0 V, while the phosphate host suffers severe irreversible process after it was discharged to 0.0 V [4]. We have made a clear description about the overlithiation behavior of LiCoO$_2$ [5]. It is found that the reduction mechanism of LiCoO$_2$ with lithium is associated with the irreversible formation of metastable phase Li$_{1+x}$CoO$_{2-y}$, and then the final products of Li$_2$O and Co metal. During charging process to 4.3 V, Li$_2$O/Co mixture can be oxidized into CoO, Co$_3$O$_4$, and Li$_x$CoO$_y$. Nevertheless, the structural transformation of the cathode materials is scarcely studied, and thus the mechanism of the battery safety problem is still unclear yet. Usually, LiFePO$_4$ and LiMn$_2$O$_4$ are used as important candidate materials for high-

power lithium-ion batteries, while $LiNiO_2$ is a potential high-capacity cathode material for energy storage and conversion. To obtain higher safety lithium-ion batteries, the structural transformation of the cathode materials under different overdischarge processes should be concerned. In this paper, the various overdischarge behaviors of $LiFePO_4$, $LiNiO_2$, and $LiMn_2O_4$ down to 1.0 and 0.0 V were studied. It is found that $LiFePO_4$ and $LiMn_2O_4$ cathode materials show higher structure stability than that of $LiNiO_2$ in 1.0–4.3 V, whereas all the three cathode materials experience electrochemically driven solid-state amorphization when they are cycled between 0.0 and 4.3 V.

Experimental

Synthesis of materials

$LiFePO_4$ was obtained by firing the mixture of acetylene black (AB), $LiOH \cdot H_2O$, $FeC_2O_4 \cdot H_2O$, and $(NH_4)_2HPO_4$ at 700 °C for 10 h with an argon (Ar) atmosphere. $LiNiO_2$ was synthesized from a solid-state reaction with $LiOH \cdot H_2O$ and $Ni(OH)_2$ as precursors under calcination condition of 650 °C for 10 h. Reactants were surrounded with an oxygen stream. $LiMn_2O_4$ was prepared by the direction reaction of $LiOH \cdot H_2O$ and MnO_2 at 750 °C for 12 h in air. All the precursors used in the experiments were mixed by high energy ball milling for 5 h before solid-state reaction at high temperature. After the preparation of products, all the samples were also ball milled for 30 min to obtain small-sized particles.

Preparation of electrodes and batteries

The composition of positive electrodes is 85 wt.% active material, 8 wt.% AB, and 7 wt.% polyvinylidene fluoride, and the slurry for positive electrodes was achieved by the mixing of them in N-methylpyrollidone. The slurry was uniformly spread on Ti foil and dried at 120 °C for 12 h, then cut into discs. The electrodes for repeated cycling were assembled with Swagelok cells in Ar-filled glove box (M. Braun, Germany). The batteries were composed of the Ti piece with objective material as working electrode, Whatman glass fiber filter as separator, lithium metal disc as counter electrode, and 1 mol L^{-1} $LiPF_6$ dissolved in a mixture of ethylene carbonate and dimethyl carbonate (1:1; v/v) as electrolyte.

Electrochemical testing and physical characterization

The X-ray diffraction (XRD) pattern collected on sample was recorded with a Bruker D8 X-ray diffractometer (Bruker, Germany) using nickel-filtered Cu Kα radiation

($\lambda = 1.5418$ Å). The surface morphology for the sample was characterized by means of a Philips XL 30 scanning electron microscopy (SEM; Philips, Netherlands).
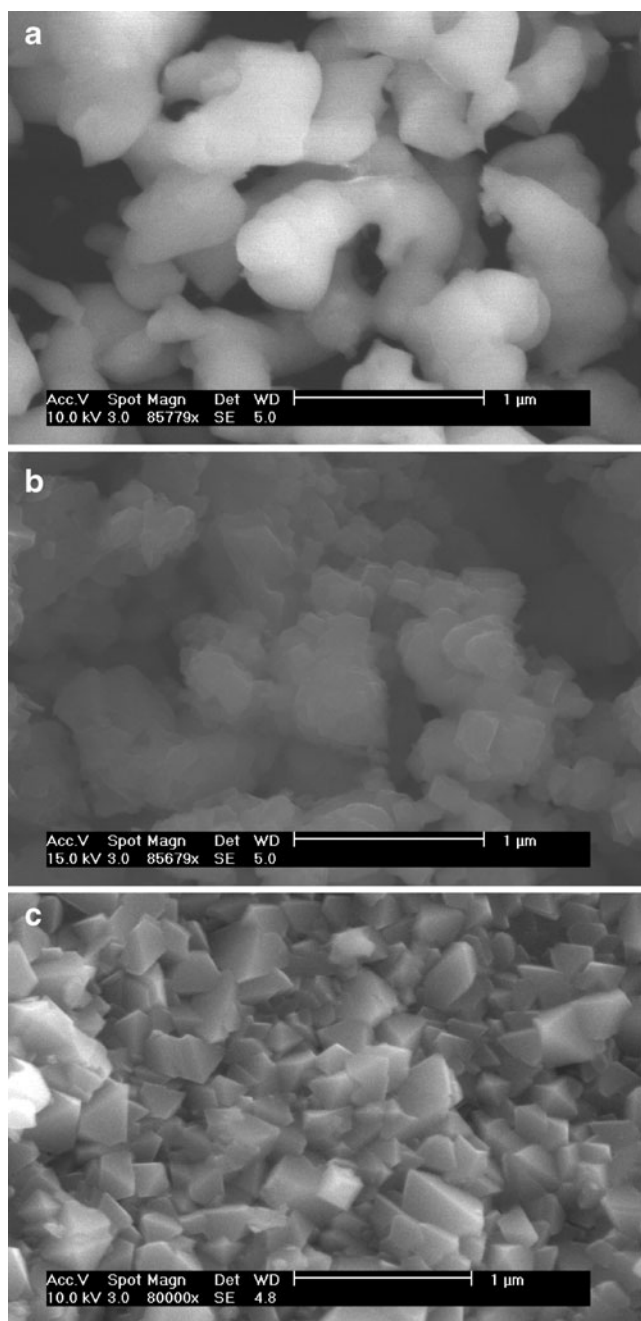
Galvanostatic charge–discharge cycling was tested on Land Battery Test System (Wuhan Jinnuo, China). Swagelok cells were charged and discharged at a constant current of 30 mA g^{-1}. All the tests were carried out at room temperature.

Results and discussion

The SEM images of $LiFePO_4$, $LiNiO_2$, and $LiMn_2O_4$ powders are shown in Fig. 1. It is clear that the surface morphologies of these three samples are quite different. The pristine $LiFePO_4$ is composed of particles with a very smooth surface and the average particle size of approximately 500 nm (Fig. 1a). Similarly, wide variation of the individual $LiNiO_2$ particle can also be observed from Fig. 1b, ranging from large irregular particles (1 μm) to small smooth platelets (200 nm). While, for the $LiMn_2O_4$ powders seen in Fig. 1c, all particles with regular shape are uniformly distributed. Spinel materials have a measured size of about 300 nm. The phase characterizations of these prepared samples are well in agreement with previously reported patterns. They are well-crystallized grains with high phase purity.
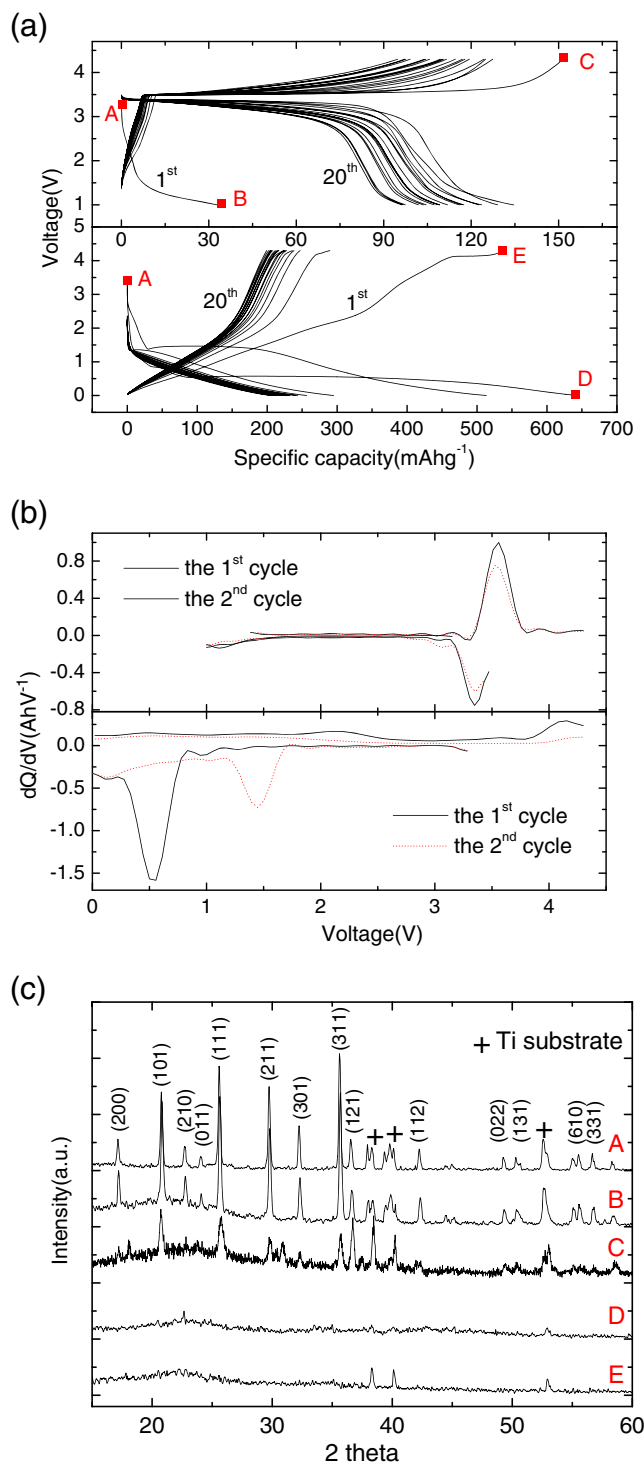
Overdischarge behavior of $LiFePO_4$

Figure 2a shows the charge–discharge curves of $LiFePO_4$ under different overdischarge conditions (1.0–4.3 and 0.0–4.3 V). When the electrode is overdischarged to 1.0 V, it is obvious that the phosphate host can uptake a specific capacity of 34 mAh g^{-1} (0.2 Li), corresponding to the slope in dQ/dV profiles (Fig. 2b). Seen from Fig. 2c, it is also found that no other new phase can be observed during the overdischarge reaction to 1.0 V. However, the intensity ratio of I(311)/I(301) of $LiFePO_4$ is increased with the lithium-ion insertion. It indicates that it is feasible to form the possible new phase, such as the postulated $Li_{1+2x}Fe_{1-x}PO_4$, which is similar to the formation of $LiFeO_2$ from the reaction between $CuFeO_2$ and Li [6]. Nevertheless, it cannot exclude the possibility of partial capacity attributed to organic solvent decomposition above 1.0 V [7]. Recharged to 4.3 V, ex-situ XRD shows that the sample transforms into $FePO_4$-type compound. With repeated cycles, the discharged and charged products can maintain their structures well. Therefore, although $LiFePO_4$ is overdischarged to 1.0 V, it is known that the Li insertion/extraction process is still a reversible reaction as the result obtained from the excellent cyclic performance in Fig. 2a.

Fig. 1 SEM images of LiFePO$_4$ (**a**), LiNiO$_2$ (**b**), and LiMn$_2$O$_4$ (**c**)

Fig. 2 Charge–discharge profiles of LiFePO$_4$ in different working voltage regions (**a**), corresponding dQ/dV curves (**b**), and corresponding XRD patterns (**c**)
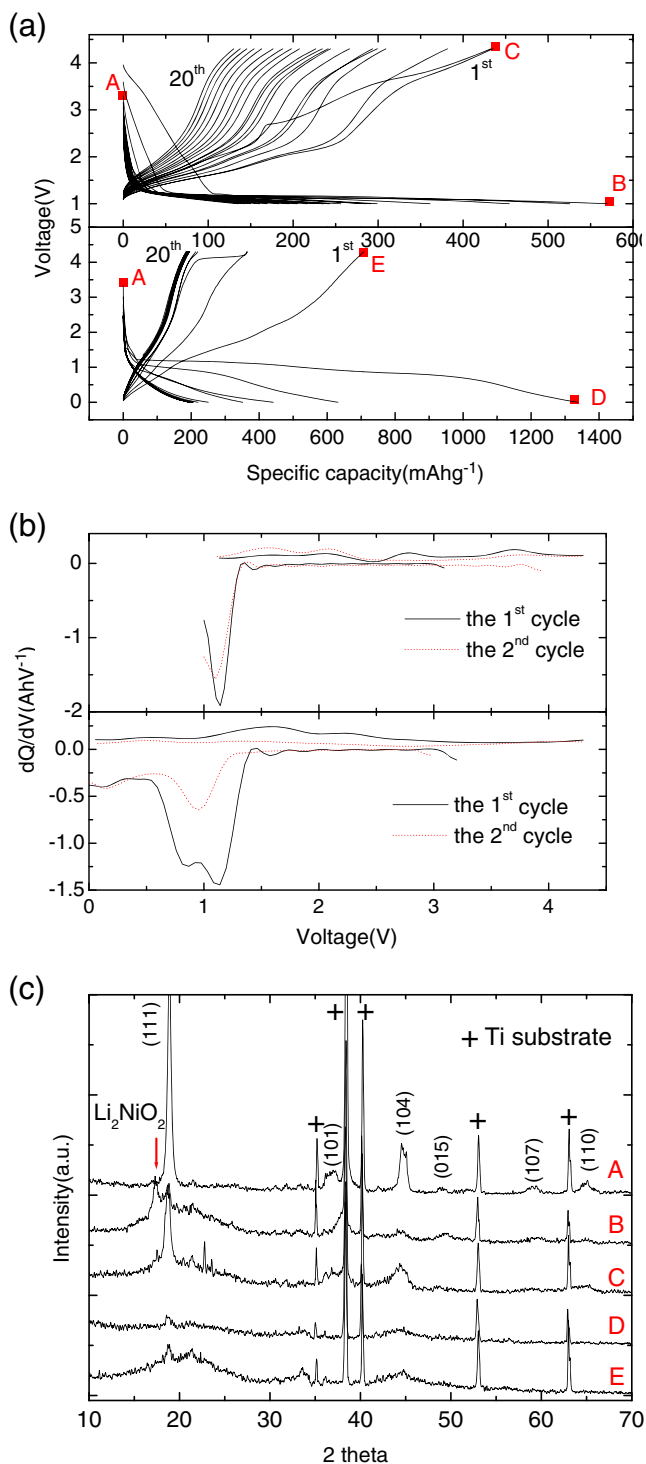
When the phosphate host is overdischarged to 0.0 V, a long plateau at 0.5 V is observed during the initial discharge as shown in Fig. 2a, corresponding to a capacity of 642 mAh g^{-1} (3.78 Li) and sharp dQ/dV reduction peak in Fig. 2b. XRD result reveals that the further electrochemical reaction of lithium iron phosphate with Li leads to the breakdown of pristine structure and the formation of amorphous compounds, which are probably the X-ray undetectable mixture of nano-sized products as the pattern D shown in Fig. 2c [8]. Although an extraction capacity of 536 mAh g^{-1} (3.15 Li) can be delivered upon recharge

process, no other diffraction peak appears in the diffraction pattern for delithiation sample (pattern E in Fig. 2c), except Ti metal. Moreover, the electrochemical property degrades rapidly in the subsequent cycles. All these evidences indicate that the structure of LiFePO$_4$ is thoroughly

destroyed with the insertion of 3.78 Li. Therefore, it is impossible to rebuild the compound as cathode material for high-performance lithium-ion batteries after a deep over-discharge process to 0.0 V.

Overdischarge behavior of LiNiO₂

Overdischarge behavior of $LiNiO_2$

For $LiNiO_2$, an overdischarge plateau is observed down to 1.0 V as displayed in Fig. 3a. This platform reveals a possible phase transformation reaction mainly involving the formation of spinel Li_2NiO_2, corresponding to the

Fig. 3 Charge–discharge profiles of $LiNiO_2$ in different working voltage regions (**a**), corresponding dQ/dV curves (**b**), and corresponding XRD patterns (**c**)
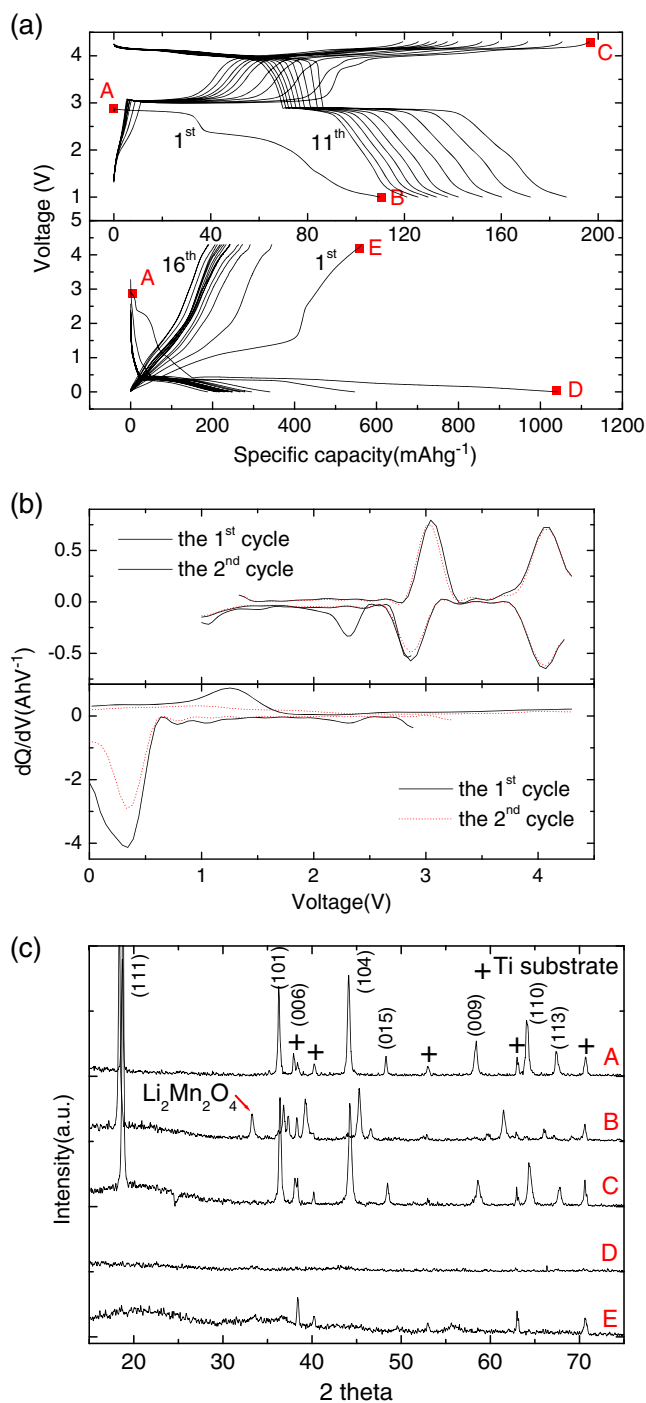
Fig. 4 Charge–discharge profiles of $LiMn_2O_4$ in different working voltage regions (**a**), corresponding dQ/dV curves (**b**), and corresponding XRD patterns (**c**)

appearance of characteristic Bragg peak at 17.45°. The XRD pattern B in Fig. 3c for moderate overdischarge sample agrees with that of the JCPDS file no.81-2411 (Li_2NiO_2) well. Different with the behavior of $LiFePO_4$, this moderate overdischarge and recharge reaction is a partially reversible process. cExtra-Bragg peaks appear at 21.45°, 22.83°, and 23.71° in the delithiation XRD pattern, and these may be ascribed to the unknown compound so far, which will be discussed elsewhere. However, this result is inconsistent with the previous report [9], in which case they found that the initial long plateau involving the formation of Li_2NiO_2 was observed near 1.75 V. The different preparation techniques or experimental conditions for $LiNiO_2$ may be possible reasons for the distinct results.

Upon extreme overdischarge to 0.0 V, another peak centered at 0.85 V can be observed from dQ/dV profile in Fig. 3b. It probably results from the destruction of Li_2NiO_2, the growth of surface film and organic polymers [10, 11]. Therefore, this extreme overdischarge reaction leads to the electrochemically driven solid-state amorphization of $LiNiO_2$. In addition, the microstructure of sample cannot get back after being recharged to 4.3 V, which is demonstrated by the XRD pattern shown in Fig. 3c. The deep lithiation sample is also an X-ray undetectable product. It indicates that extreme overdischarge behavior can wreck havoc with the performance of the lithium-ion batteries. As a result, the cycleability is unfavorable for battery abuse in 0.0–4.3 V as shown in Fig. 3a. According to the results mentioned above, it can be concluded that the structure of $LiNiO_2$ is vulnerable to collapse in various overdischarge regions. Whether the overdischarge behavior is moderate or deep, the Swagelok cell of $LiNiO_2$ cannot work again after abuse.

Overdischarge behavior of $LiMn_2O_4$

As well-known, an overlithiation of $LiMn_2O_4$ to 2.0 V will bring forth tetragonal $Li_2Mn_2O_4$ [12], which is a one-electron reaction. In our experiments, more serious over-discharge process is undertaken to test the abuse behavior of the spinel as shown in Fig. 4a, b.

Overdischarged to 1.0 V, a total number of 0.75 Li per formula unit inserts into the structure of $LiMn_2O_4$, leading to the spinel structure transform into the tetragonal one (JCPDS file no.84-1523, $Li_2Mn_2O_4$) as shown in Fig. 4c. Not only the collected XRD pattern for delithiation sample but also the charge–discharge curves confirm the revers-ibility of phase transformation between $LiMn_2O_4$ and $Li_2Mn_2O_4$. Upon cycles, a little capacity loss is observed for the existence of Jahn–Teller distortion as shown in Fig. 4a. Therefore, the reconstruction of spinel is feasible under a one-electron lithiation process.

Under an extreme overdischarge process to 0.0 V, an insertion reaction occurring at 0.33 V is characterized by dQ/dV profiles (Fig. 4b) along with the structural destruction. However, large hysteresis and low coulombic efficiency are recorded in the subsequent recharge process as exhibited in Fig. 4a, b. Apparently, it is also an irreversible solid-state amorphization process, which is approved by the results from electrochemical and physical characterizations in Fig. 4a, c. It indicates that the lower working voltage cutoff for $LiMn_2O_4$ cathode should be 1.0 V or higher. Hence, it is infeasible to recover the active materials after extreme overdischarge abuse.

Conclusions

The structural stability and reversibility of three cathode materials, $LiFePO_4$, $LiMn_2O_4$, and $LiNiO_2$, for overdi-scharge were investigated. It is found that $LiFePO_4$ and $LiMn_2O_4$ are more stable than $LiNiO_2$ when the Swagelok cells are cycled between 1.0 and 4.3 V. The former two cathode materials show reversible phase transformation behaviors during lithium insertion/extraction reaction in this electrochemical region. While, the overlithiation reaction of $LiNiO_2$ is partially reversible with the lower working voltage cutoff set at 1.0 V. In contrast, for all these active materials, an extreme overdischarge reaction to 0.0 V will lead to the electrochemically driven solid-state amorphiza-tion of the transition metal compounds. As a result, the cathode materials fail to work continually after a deep overdischarge process.

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