Journal of Power Sources 363 (2017) 168-176



Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

The high-temperature and high-humidity storage behaviors and electrochemical degradation mechanism of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode material for lithium ion batteries



Zhiqiang Chen, Jing Wang, Jingxin Huang, Tao Fu, Guiyan Sun, Shaobo Lai, Rong Zhou, Kun Li, Jinbao Zhao^{*}

State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

HIGHLIGHTS

• NCM622 stored in high-temperature and high-humidity was deteriorated in structure.

• A delithiation layer at the near-surface region was formed after storage.

• The adsorbed species contributed a large proportion in electrochemical degradation.

• The heat-treating process under oxygen flow can recover the stored degraded material.

A R T I C L E I N F O

Article history: Received 27 March 2017 Received in revised form 30 June 2017 Accepted 22 July 2017 Available online 27 July 2017

Keywords: LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ Cathodes Storage deterioration Lithium-ion batteries

ABSTRACT

The high-temperature and high-humidity storage behaviors and electrochemical degradation mechanism of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ cathode material are investigated systematically. After stored at 55 °C and 80% relative humidity, three kinds of changes are observed compared to the fresh materials. The first change is adsorbed species on the surface of the materials caused by atmospheric H₂O and CO₂. The second is a layer of impurities consisting of LiOH and Li₂CO₃ coated on the surface of the materials non-uniformly. The third is a delithiation layer directly contacting with the bulk materials in the near-surface region, which is believed to be formed by lithium-ions migrating out from the lattice accompanied by the generation of the impurities. A different combination of heating temperature, heating time and heating atmosphere is performed to achieve the separation of the adsorbed species and the delithiation layer (together with the impurities) and study the role of different part in electrochemical degradation, respectively. For the first and the following cycles, the effect of the adsorbed species on the electrochemical properties takes a larger proportion than that of the delithiation layer and impurities.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Since lithium-ion batteries (LIBs) successfully commercialized in 1990s, they are widely used in various applications, such as portable mobile devices (computer, cell phone, ipad, etc.), electric vehicle (EV), hybrid electric vehicle (HEV), stationary energy storage and smart grid [1-4]. The conventional LiCoO₂ has been considered as one of the most important cathode materials for lithium-ion

* Corresponding author. E-mail address: jbzhao@xmu.edu.cn (J. Zhao). batteries because of its high working voltage, outstanding rate performance and good cycling performance even at elevated temperatures [5,6]. However, the intrinsic defects of LiCoO₂, such as low practical specific capacity, high cost and high pollution to the environment, have limited the large-scale use, which promotes the massive exploration on the other layered cathodes [7–10]. The LiNi_xCo_yMn_zO₂(NCM, $0 \le x, y, z \le 1$) firstly synthesized and reported by Liu et al. [11] in 1999 was considered to be one of the most important and promising cathode materials for the large capacity LIBs by the reason of larger reversible capacity, lower cost and environment-friendly [12,13]. However, if the Ni content is higher in the molecular formula, the NCM oxides suffer from cycle instability

and chemical instability, especially in ambient air, which severely confine the prospect for the industrial use.

To date, both the NCM333 and the NCM523 have been successfully used in commercial LIBs, but the NCM with Ni > 60% has limited use in LIBs. One of the most notable factors is the attacking from air components such as CO₂ and H₂O, resulting in the formation of Li₂CO₃ and LiOH impurities coated on the surface of NCM, thus causing severe electrochemical performance degradation [4,14–20]. When LiNiO₂ is immersed in water, the lithium ion would be extracted from the surface layers with the formation of LiOH, accompanied by the loss of lattice oxygen, which leads to the defect of NiO₆ octahedra, but this process is not with the electron exchange [21]. These extractions of Li also plague the high Ni-content layered cathodes and cannot be avoided when exposed to the ambience. Moreover, the reaction between LiNiO₂ and CO₂ was investigated by Liu et al. [22]. They indicated that LiNiO₂ would get deteriorated under pure CO₂ atmosphere due to the formation of Li_2CO_3 , the transformation from Ni^{3+} to Ni^{2+} and the loss of lattice oxygen in the near-surface region. When stored in air, the LiNiO₂-based materials are contacted with air directly, so the reactions with H₂O and CO₂ proceed simultaneously and cannot be interdicted. Shizuka et al. [16] have suggested that the $Li_{1+z}Ni_{(1-x)/2}Co_xMn_{(1-x)/2}O_2$ has better storage performance compared with the $Li_{1+z}Ni_{1-x-y}Co_xM_yO_2$ (M = Mn, Al), which means that the materials with the same Ni and Co content, such as LiNi_{0.33}Co_{0.33}Mn_{0.33}O₂ [16] and LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ [4], have better stability when stored in air, but the Ni content in the molecular formula must be less than 0.5 due to the total content limitation of Ni. Co and Mn. The LiNiO₂-based materials with Ni > 80% have poor storage properties. Matsumoto et al. [18] reported that there was 8% Li₂CO₃ coated on the surface of LiNi_{0.81}Co_{0.16}Al_{0.03}O₂ at room temperature for 500 h and the quantity of Li₂CO₃ was proportional to the square root of storage time at 55% relative humidity (RH) and 25 °C. Zhang et al. [12] found that the LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ electrodes were coated with a dense Li₂CO₃ in long-time air exposure, which caused active materials isolated and further led to capacity loss because of the low electronic and ionic conduction of Li₂CO₃.

However, the LiNiO₂-based material with Ni content between 60% and 80% has been rarely reported on its storage properties especially at harsh condition, and this kind of material also has a great advantage in industrial use of the high-capacity and highvoltage LIBs over LiCoO₂, LiFePO₄, LiMnO₂ and low Ni content LiNiO₂-based materials. In this work, we have investigated the storage properties of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (622) materials at 80% RH and 55 °C, simulating extreme environmental conditions, as the function of storage times, through a detailed study of the surface changes and the structural changes both for the nearsurface and bulk region. Then, we explored the role of different components in degradation process. Our results indicate that the structure degradation in the surface of the material during the storage derives from strong adsorption of air components and then gradually chemical delithiation in the near-surface region, as a result of the formation of the impurities. In the traditional perspective, only the impurities adsorbed on the surface of the materials contribute to the loss of the electrochemical performance due to the inferior ionic and electronic conductivity as well as the isolation of the active particles. In our view, both the adsorbed species and the impurities (Li₂CO₃ and LiOH) as well as the delithiation layer in the near-surface region together deteriorate the electrochemical properties of the storage material through a systematic study and analysis, and the total structure degradation in the surface can be compensated at high temperature under oxygen flow.

2. Experimental section

2.1. Storage of the materials

The LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (622) sample was supplied by Beijing Easpring Material Technology Co., Ltd. (China). The storage test was carried out under 55 °C and 80% RH in a constant temperature and humidity chamber (SANTN, China), and the material was taken out every 7 days for the physical characterization and electrochemical test. In a recalcination process, the stored materials were heated up to 500 or 800 °C and maintained for 1 or 3 h under argon or oxygen flow.

2.2. Physical characterization

The quantity of the sample was determined by one over tenthousand analytical balance (Mettler-Toledo AG, Switzerland). Powder X-ray diffraction (XRD) was performed on a Rikagu Miniflex 600 (Rikagu, Japan) with Cu Ka radiation operated at 40 kV and 15 mA. Data collection was recorded with 0.02° step size in the 2θ range between 10° and 90° at 2° min⁻¹. Moreover, 15% graphite were added into the samples to ensure peak position accuracy. The morphologies and structures of the samples were captured by scanning electron microscope (SEM) S-4800 (Hitachi Corporation, Japan) and transmission electron microscope (TEM) G2 F30 (Tecnai, USA). The Fourier transform infrared (FT-IR) spectra were recorded by the Xplora (Horiba Corporation, Japan) in transmittance mode using KBr pellet method over the range of 400-4000 cm⁻¹. A microscopic Raman instrument (Renishaw, UK) was used to obtain the Raman spectra of the sample by a 0.5 mW helium/neon laser at 532 nm excitation. The thermogravimetry (TG) and the differential scanning calorimetry (DSC) curves were recorded between 35 and 850 °C at the heating rate of 5 °C/min under argon atmosphere.

2.3. Electrochemical measurements

The coin cell was fabricated as follow. A mixture of 80% $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$, 8% acetylene black, 2% conductive graphite and 10% polyvinylidene fluoride (PVDF) binder was firstly dissolved in N-methyl-1,2-pyrrolidne (NMP) to get a uniform slurry, then the slurry was cast onto aluminum foil using an automatic coating machine to get the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ electrode. Secondly, the electrode was put onto a heating plate for few minutes to evaporate residual NMP solvent and then dried at a vacuum oven overnight. The coin cells (CR2016) was assembled with the $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ electrode, Li metal counter electrode, a separator (Celgard 2400) and electrolyte (1M LiPF6, EC/DMC, 1: 1) in an argon-filled glove box (M. Braun, Germany). The charge/discharge profiles were recorded by the constant current and constant voltage charging and constant current discharging mode with 16 mAg⁻¹ between 3.0 V and 4.3 V by a battery testing system (Neware, China).

3. Results and discussion

To explore the effect of the storage time under hightemperature and high-humidity condition on the electrochemical performances of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ (622) cathode, we measured the electrochemical behaviors of the pristine material and the storage samples, as displayed in Fig. 1. Amazingly, all storage samples show inferior first charge/discharge specific capacity and cycle performance, with a higher charging potential plateau and a lower discharging potential plateau and a rapid decline in cycle capacity, which seriously limit the storage performance and the application of the materials, especially at high temperature and high humidity areas. However, it remains ambiguous how the



Fig. 1. First charge and discharge profile (a) and cycle performance (b) for the pristine and the storage materials.

electrochemical properties of the materials are affected after the storage. In the following work, the storage properties of the 622 cathode were studied systematically. Firstly, the macro changes in quantity were detailedly studied, including the mathematical relationship between the quantities changes and the storage time as well as the reason for the quantity changes, followed by the investigation on the structure changes for the stored materials. Finally, the different changes observed in the stored materials were separately studied to understand the different role in the electrochemical properties deterioration.

3.1. The changes during the storage

The relationship between weight increasing rate and storage time is plotted in Fig. 2a, with the $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ (333) given as a comparison. The specific data of weight increasing rate is listed in Table S1. Firstly, it is clear that the guality of the 333 is almost constant with the storage time, while the weight increasing rate of the 622 shows an obviously upward trend, which is mainly due to the absorbed air components and impurities on the surface of the materials [23]. The significant difference of quality increasing rate between the 333 and the 622 may be affected by Ni/Mn ratio in the molecule, which determines the oxidation state of Ni to a great extent. It has been previously concluded that the oxidation states of Ni are +2 in the LiNi_xCo_{1-2x}Mn_xO₂ (Ni/Mn = 1: 1) series [24,25], +2and + 3 in the LiNi_{1-x-y}Co_xMn_yO₂ (Ni/Mn > 1) series [26], and +3 in the LiNi_{0.80}Co_{0.15}Al_{0.05}O₂ [26], respectively. As reported by Shizuka et al., the reactivity of cathode material with CO₂ depends on Ni³⁺ content in the LiNi1-x-vCoxMnvO2 series, and the NCM cathodes with more Ni³⁺ content suffer from more weight growth and more severe degradation in the air storage [26]. According to reference [18], the conversion quantity of Li_2CO_3 was in proportion to the square root of exposure time at 55% RH and 25 °C for the LiNi_{0.81-} Co_{0.16}Al_{0.03}O₂ cathodes. Although Li₂CO₃ is not the only factor causing mass gain after the exposure in our experiments, we suggest that the conversion of Li₂CO₃ is just one part of the entire degradation reactions, which were closely related to each other and cannot be separated. Thus similarly, we explore the mathematical relationship between the mass gain rate and the exposure time. Fig. 2b shows the linear fitting curve between the weight increasing rate and the square root of the storage time, $y = -0.0979 + 2.1345t^{1/2}$ 2 (t > 0), where y is the weight increasing rate (%), t corresponds to the storage time (weeks). Furthermore, it is worth mentioning that the coefficient before $t^{1/2}$ has a kinetic significance for the total degradation reaction under certain storage condition.

To further study the reason of quality changes, the DSC&TG synchronization test for the pristine and the stored materials is performed, as displayed in Fig. 2c and d and Table S2. Firstly, in the temperature range of 35-800 °C, 622-28days show a larger drop in mass (3.9731%) than that of the 622-pristine (0.2557%), thereby 4.1394% weight loss (relative to the pristine material, 3.8837% when deducting the loss of the pristine material) of the stored material elaborates the change of the quality in the heating process, comparable to the weight increasing rate in the storage process (4.1850%). Secondly, in contrast to the 622-pristine (Fig. 2c), two main drops in mass are observed in the temperature range of 35–800 °C. On the basis of Liu et al. [23], the quality losses below 100 °C, in the temperature range of 200–400 °C and 680–780 °C were corresponding to the removal of the superficial water, the desorption of the adsorbed species and the decomposition of Li₂CO₃, respectively, and the weight loss beyond 800 °C is attributed to the decomposition of the material. Accordingly, the thermogravimetric curve of the 622-28days is summarized as two intervals, respectively adsorbed species (200-500 °C) and impurities (mainly Li₂CO₃, 668–780 °C), and the two intervals respectively account for 72.59%, 16.42% of the total loss (the remaining proportion in 500-668 °C and 780-800 °C may be also related to the adsorbed species and the impurities). Thus, the adsorbed species, caused by the ambient H₂O and CO₂, are the most important factors in weight increasing after stored at 55 °C and 80% RH.

To investigate the impurities on the surface of the stored materials, the FT-IR spectra of the pristine and stored materials were presented in Fig. 3. Clearly, there appears three new adsorbed peaks at 865, 1435 and 1496 cm⁻¹ after the storage, and the weak adsorbed band at 3200–3600 cm⁻¹ exists both for the pristine material and the storage materials. According to the previous reports, the band at $3200-3600 \text{ cm}^{-1}$ is considered as the stretching vibration of O-H from LiOH in the stored materials [12]. The absorption peaks at 1435 and 1496 cm⁻¹ are assigned to the antisymmetric and symmetrical stretching vibration modes of C-O from Li_2CO_3 , respectively, and the peak at 865 cm⁻¹ are attributed to the bending vibration absorption of CO₃ group [15,27]. Furthermore, the absorption peaks at 1435, 1496, and 865 cm⁻¹ show an increasing trend with the extension of storage time, indicating an increasing amount of Li₂CO₃ in the materials. Thus, the impurities on the surface are mainly Li₂CO₃ and LiOH. Fig. S1 presents the SEM images of the 622 pristine and the storage materials. Notably, the primary particles of the pristine materials have a clear profile without other impurities on the surface (Figs. S1a and S1b). However, after being stored for 28 days, part of the primary particles



Fig. 2. Weight increasing rate of the storage materials as a function of storage time (a); linear fit between weight increasing rate and square root of the storage time of the 622; TG and DSC test for the 622-pristine (c) and the 622-28days (d).

was covered by impurities (dark parts in the particle), giving rise to the original morphology disappearing in some extent (Figs. S1i and S1j). Pilgun et al. [14] also found that the surface of



Fig. 3. FT-IR spectra of the 622 pristine and the stored materials.

LiNi_{0.7}Co_{0.15}Mn_{0.15}O₂ was covered with a layer of other substances after stored in air for 3 months, which was considered to be a mixture of LiOH, LiHCO₃, and Li₂CO₃ [23]. Moreover, the coverage on the material surface gradually increased with the extension of storage time, indicating a more serious degradation state with the storage time increasing.

In order to study the structural information, we performed XRD test on the pristine and storage materials, as compared in Fig. 4. Before the test, we add 15% natural graphite into the samples for peak position summit correction to eliminate instrumental and operational errors, as shown in Fig. 4f. It is obvious that all samples show a typical pattern of the α -NaFeO₂ structure in the R-3m space group [6,13], which suggests the storage process has no serious impact on the bulk structure (Fig. 4a). The clear peak splitting of (006)/(102) (Fig. 4d) and (108)/(110) (Fig. 4e) indicates a good hexagonal ordering of the LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ before and after the storage [13]. However, after the storage, a new phase appears at 21.26, 30.46 and 31.94°, which are indexed to crystalline Li₂CO₃ [15,23], as shown in Fig. 4b. Furthermore, the peak intensity of Li₂CO₃ increases along with the storage time growing, which is consistent with the results of FT-IR and SEM. The position of (003) is partially enlarged for a more detailed study of the structural changes, as presented in Fig. 4c. Clearly. there is a tendency that the peak summit positions of (003) for all stored samples tend to shift to a low angle, which seems not



Fig. 4. XRD patterns of the pristine and the storage materials: global patterns between 10 and 90° (a), partially enlarged patterns of Li₂CO₃ (b), (003) profiles (c), (006) and (102) profiles (d), (108) and (110) profiles (e) and graphite calibration (f).

obvious to the time dependence. To clarify this issue and understand the process more deeply, a 70-day storage sample is employed in Fig. 4c, named as 622-70days. As we inferred, the (003) position of 622-70days shifts to a lower angle compared with the short-term storage samples. Thus, there is a tendency for the (003) position of the stored materials to move toward a lower angle. It was also demonstrated by the in-situ XRD and neutron diffraction studies [28–32] that the (003) Bragg angles of layered cathode continuously moved to a lower angle during the initial period of electrochemical delithiation, which is due to an increasing electrostatic repulsion of the oxygen layers that is partly impaired when lithium sites are mostly occupied. Thus similarly, we speculate that the (003) peak position of the storage materials shifting to a lower angle is resulted from the lithiumions migrating out from the lattice to form the impurities in the storage process, making the electrostatic repulsion between the oxygen layers more intense and finally resulting in a lower Bragg angle of (003), leaving the material in a delithiation state to some extent.

Fig. 5 displays the visible Raman spectra of the 622-pristine, the 622-28days, and the 622-70days after normalization. After the storage, the peaks of LiOH and Li₂CO₃ are observed near 200 cm⁻¹ and 1100 cm⁻¹ [13], respectively, which once again confirm the presence of LiOH and Li₂CO₃ on the surface of the storage materials. In addition, the rapid increase of the peak intensity, from the 622-



Fig. 5. Raman spectra of the pristine and the stored materials.

pristine to the 622-28days and then to the 622-70days, indicates an increasing content of LiOH and Li₂CO₃ along with the storage time growing. The Raman bands at around 600 cm⁻¹ and 500 cm⁻¹ belong to the A_{1g} and E_{g} vibration mode of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂,



Fig. 6. HRTEM and FFT images and of the 622-pristine (a) and the 622-28days (b).

respectively. The A_{1g} mode originates from M - O symmetrical stretch, in which two oxygen atoms from two neighboring oxygen layer vibrate in the opposite direction parallel to the c-axis of $LiMO_2$, while the E_g mode dates from O-M-O bending vibrations, where two oxygen atoms vibrate by turn perpendicular to the caxis of LiMO₂ [13,33,34]. In the charging step of half batteries, the A_{1g} band decreased rapidly with the lithium de-intercalation through affecting the local symmetry of v (MO_6) [35], while the E_g band continued exist, which gave rise to a decline in the ratio of A_{1g}/E_g . Clearly, the ratio of A_{1g}/E_g shows a downward trend with the extension of storage time in Fig. 5. In our view, forming LiOH and Li₂CO₃ promotes lithium ions de-embedding from the layered 622 materials in the storage process, leaving the material in a delithiation state to some extent, thus causing the A_{1g}/E_g ratio decrease. However, this process only occurs at the surface and near-surface region of the material as the incident signal of the Raman spectrum cannot reach the bulk of the material. Moreover, the ratio of A_{1g}/E_g decreases greater along with the storage time, as shown in Fig. 5, which further suggests the more deintercalation along with the storage time growing.

Fig. 6 shows the high resolution transmission electron microscopy (HRTEM) images and fast Fourier transformation (FFT) of the 622-pristine (Fig. 6a) and the 622-28days (Fig. 6b). Obviously, the pristine material shows a good structural consistency from the surface area to the bulk area, acquired from the HR-TEM (Fig. 6a) and the FFT image of area 1 in Fig. 6a, and the interplanar distance (d) is 2.40 Å, corresponding to the (101) plane of the NCM layered cathodes. After stored for 28 days (Fig. 6b), the bulk of the 622 primary particle remains the rhombohedral phase as concluded from Fig. 6b and the FFT of region 3, while the near-surface region transforms into a polycrystal area according to the region 4 and the FFT of region 2. These HRTEM and FFT images directly reveal that the structure evolution after the storage mainly occurred at the surface and the near-surface region of the materials, and the polycrystal area in the near-surface region must get great associated with the extraction of lithium-ions observed in the aforementioned studies of XRD and Raman.

Hence, there are three kinds of changes for the stored $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ under 55 °C and 80% RH compared to the fresh materials. The first change is adsorbed species on the surface of the material caused by atmospheric H₂O and CO₂. The second is a layer of impurities consisting of LiOH and Li₂CO₃ non-uniformly coated on the surface of the materials. The third is a delithiation layer directly contacting with the bulk materials in the near-surface region, which is believed to be formed due

to lithium-ions migrating out from the lattice accompanied by the generation of the impurities. In our view, these three changes together affect the electrochemical properties of the materials.

3.2. The adsorbed species

To investigate the effect of adsorbed species on the electrochemical performance of the materials, a calcination process at 500 °C under argon flow towards the 622-28days is performed, as shown in Fig. 7. In this temperature, the adsorbed species can be removed, while the extracted Li cannot be restored to the nearsurface region. After calcination, the adsorbed species disappear because the TG curve shows few changes compared to the 622pristine and the DSC curve has no endothermic peak (Fig. 7a). However, the absorption peaks of Li₂CO₃ and LiOH still exist in FT-IR spectra (Fig. 7b), and the (003) Bragg angle still shifts to the similarly low position as the 622-28days (Fig. 7c and Fig. S2), which indicate that the Li₂CO₃, LiOH and thus formed delithiation layer remain on the surface of the material after the calcination. Therefore, it is feasible to suppose the effect of the adsorbed species on the electrochemical performance of the 622-28days after this heat-treatment. The first charge and discharge profiles of the sample are presented in Fig. 7d, with the 622-pristine and the 622-28days listed as a comparison. Clearly, the charge/ discharge specific capacities of the first cycle get recovered at a great extent, in spite of a slightly higher charge plateau and a hugely lower discharge plateau, which may be caused by the remaining impurities and structure changes in the near-surface region. The cycle capacity has also been greatly improved, coming to 100.8837, 101.7634 and 98.9076 mAhg⁻¹ for the 20th, 50th and 100th cycle, respectively, as shown in Fig. 7e and Table 1. Thus, the adsorbed species caused by atmospheric H₂O and CO₂ have a great impact on the electrochemical performance of storage degradation materials. In our view, the adsorbed species coated on the surface of the material deteriorates the electrochemical performance through several ways as follows. First, the Li-ion transport channel between the electrolytes and active material particles is cut off and a new interface between the cathode and electrolyte is formed, which is nonconductive or weakly conductive to Li-ions and electrons. Second, the adsorbed species react with the components in the electrolyte to form an insulting layer covering on the surface of the material, which is also low conductive to li-ions and electrons.



Fig. 7. TG and DSC test (a), FT-IR spectra (b), (003) XRD profiles (c), initial charge-discharge profiles (d), cycle performances (e) of the 622-28days-500-1h-Ar.

3.3. Li₂CO₃, LiOH and delithiation layer

To the best of our knowledge, the formation of Li₂CO₃ and LiOH is due to lithium-ion migrating out from the lattice, which promotes the formation of delithiation layer in the near-surface area, and these two parts cannot be considered separately. Thus, the calcination of the 622-28days sample at 800 °C under oxygen flow for 3 h is employed to understand Li₂CO₃, LiOH and delithiation layer in the role of electrochemical properties degradation, and the sample is named 622-28days-800-3 h-O₂. Fig. 8a presents the TG and DSC curves of the 622-28days-800-3 h-O₂. Compared with the 622-prestine in Fig. 2c, the TG curve shows few changes between 200 and 500 °C and no endothermic peak is observed in DSC curve, which indicates that the adsorbed species are removed from the surface after calcination under oxygen flow. The absorption peaks of Li₂CO₃ disappear from the FTIR spectra (Fig. 8b), and the (003) Bragg angle goes back to the initial position as the 622-pristine (Fig. 8c), indicating that the lithium-ions in the Li₂CO₃ and LiOH reversibly return back to the lattice under oxygen flow at 800 °C, and thus the delithiation layer gets recovery.

To confirm this statement, 5% more Li₂CO₃ is added to the 622-28days and the calcination process is executed similarly, named 622-28days-5%Li₂CO₃-800-3 h-O₂, as shown in Fig. 8c and Fig. S3. Firstly, the Li₂CO₃ crystalline in the storage sample disappear after calcination both for the 622-28days-800-3 h-O2 and the 622-28days-5%Li₂CO₃-800-3 h-O₂ sample (Fig. S3b). As shown in Fig. 8c, the (003) position of the 622-28days-5%Li₂CO₃-800-3 h-O₂ moves to a higher angle after calcination compared to the 622-pristine, the 622-28days and the 622-28days-800-3 h-O2, which further prove the reinsertion of lithium-ions after heat-treatment at 800 °C under oxygen atmosphere and the extract of lithium-ions during the storage. Hence, the heat-treatment under oxygen flow can effectively make the lithium-ions in Li₂CO₃ and LiOH re-intercalate into the frame structure, and thus cause the (003) Bragg angle moves back to the initial position. Furthermore, the (003) position in the calibration XRD pattern represents the amount of embedded Li in the layered cathodes.

The SEM and TEM are performed to further verify our abovementioned inference, as shown in Fig. S4. Obviously, the morphology of the 622-28days-800-3 h- O_2 is restored and no

Table 1

Electrochemical data of the 1st, 20th, 50th, and 100th for the 622-pristine, 622-28days, 622-28days-500-1 h-Ar, and 622-28days-800-3 h-O2.

Sample	1st charge specific capacity (mAhg ⁻¹)	1st discharge specific capacity (mAhg ⁻¹)	1st coulomb efficiency (%)	20th discharge specific capacity (mAhg ⁻¹)	50th discharge specific capacity (mAhg ⁻¹)	100th discharge specific capacity (mAhg ⁻¹)			
622-pristine 622-28days 622-28days -500-1 h-Ar 622-28days -800-3 h-O ₂	195.8614 119.1527 183.9801 195.4114	163.3794 12.7524 128.2789 160.4434	83.42 10.70 69.72 82.11	157.6286 1.3774 100.8837 154.9178	152.1776 1.2441 101.7634 148.6781	144.1194 1.1997 98.9076 139.4592			



Fig. 8. TG and DSC test (a), FT-IR spectra (b), (003) XRD profiles (c), initial charge-discharge profiles (d), cycle performances (e) of the 622-28days-800-3 h-O2.

impurities appear (Figs. S4a and 4b). The polycrystal area in the near-surface region of the storage particle disappears and the crystalline structure in the near-surface region and bulk area returns to a consistent status, concluded from the HR-TEM images and FFT of selected area in Fig. S4c, which indicates the delithiation layer is compensated after a calcination process at 800 °C and oxygen flow.

The morphology and structure in the near-surface region are all restored after heat-treatment at 800 °C under oxygen flow. Also, the electrochemical performance of the sample gets a striking improvement, where the first charge and discharge specific capacity almost gets totally recovered with the same charge/ discharge potential plateaus as that of the pristine samples, implying the same bulk and surface status as the pristine material. Furthermore, the capacity retentions of the 20th, 50th, and 100th cycle reach to 96.56%, 92.67% and 86.92% of the first cycle, respectively, comparable to the pristine material, as dedicated in Fig. 8d and e and Table 1. Therefore, impurities (LiOH and Li₂CO₃) together with the delithiation layer in the near surface region also deteriorate electrochemical performances of the material in a certain degree. Moreover, it is worth mentioning that firing treatment under oxygen flow can compensate almost the total loss in

electrochemical performance after the storage, while the temperature and time of firing treatment depend on the molecular constitution of the materials and the deterioration degree, which is related to the storage time and the storage conditions.

In brief, the adsorbed species caused by ambience H_2O and CO_2 and the delithiation layer accompanied by the forming of the impurities (LiOH and Li₂CO₃) together affect the electrochemical performance of the storage 622 materials, and the respective degree of impact is listed in Table 2 obtained from Figs. 7 and 8. For the first cycle, the adsorbed species account for 78% of the specific capacity loss, and impurities together with delithiation layer take for 22% of the loss, indicating that the adsorbed species are the main factor causing electrochemical properties loss of the first cycle. In the following cycles, the impact of the adsorbed species to the electrochemical properties still takes a larger proportion than that of the delithiation layer and impurities.

4. Conclusion

The LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ cathode suffers from a great degradation in electrochemical performance after stored at 55 °C and 80% RH. There are three kinds of changes, which are adsorbed species,

IdDIC 2	Та	ble	2
---------	----	-----	---

The degree that electrochemical properties are affected.

	1st discharge specific capacity	20th discharge specific capacity	50th discharge specific capacity	100th discharge specific capacity
Adsorbed species	78%	65%	68%	71%
Delithiation layer and impurities	22%	35%	32%	29%

LiOH and Li₂CO₃ impurities, and delithiation layer, respectively, being observed after the storage. The TG test proves the existence of adsorbed species, the SEM and FTIR make sure that the main impurities are LiOH and Li₂CO₃, and the XRD, Raman and HRTEM observe delithiation layer at the near-surface region after the storage. These three kinds of changes together take responsibility for the deterioration of the electrochemical properties. For the first cycle, the adsorbed species account for 78% of the specific capacity loss, and impurities together with delithiation layer take for 22% of the loss. In the following cycles, the impact of the adsorbed species to the electrochemical properties still takes a larger proportion than that of the delithiation layer and impurities. Furthermore, the firing treatment at high temperature under oxygen flow is an easy and effective way to recover the electrochemical performance of the storage deteriorated materials.

Acknowledgements

This work was financial supported by National Natural Science Foundation of China (21603179), the Fundamental Research Funds for the Central Universities (20720170021) and National Natural Science Foundation of China (21321062). The authors also wish to express their gratitude to Prof. Daiwei Liao for his valuable suggestions.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/i.jpowsour.2017.07.087.

References

- [1] K. Xu, Chem. Rev. 104 (2004) 4303-4417.
- [2] W. Liu, P. Oh, X. Liu, M.J. Lee, W. Cho, S. Chae, Y. Kim, J. Cho, Angew. Chem. Int. Ed. 54 (2015) 4440-4457.
- [3] A. Manthiram, J.C. Knight, S.-T. Myung, S.-M. Oh, Y.-K. Sun, Adv. Energy Mater.

6 (2016), 1501010.

- J. Li, J.M. Zheng, Y. Yang, J. Electrochem. Soc. 154 (2007) A427.
 S.-C. Park, Y.-S. Han, Y.-S. Kang, P.S. Lee, S. Ahn, H.-M. Lee, J.-Y. Lee, J. Electrochem. Soc. 148 (2001) A680.
- [6] S.-K. Jung, H. Gwon, J. Hong, K.-Y. Park, D.-H. Seo, H. Kim, J. Hyun, W. Yang, K. Kang, Adv. Energy Mater. 4 (2014), 1300787.
- [7] Y.-K. Sun, D.-H. Kim, C.S. Yoon, S.-T. Myung, J. Prakash, K. Amine, Adv. Funct. Mater. 20 (2010) 485-491.
- [8] J.-Z. Kong, H.-F. Zhai, C. Ren, M.-Y. Gao, X. Zhang, H. Li, J.-X. Li, Z. Tang, F. Zhou, J. Alloys Compd. 577 (2013) 507–510.
- [9] C.-T. Hsieh, Y.-F. Chen, C.-T. Pai, C.-Y. Mo, I. Power Sources 269 (2014) 31–36. [10] S. Liu, L. Xiong, C. He, J. Power Sources 261 (2014) 285-291.
- [11] Z. Liu, A. Yu, J.Y. Lee, J. Power Sources 81 (1999) 416-419.
- [12] X. Xiong, Z. Wang, P. Yue, H. Guo, F. Wu, J. Wang, X. Li, J. Power Sources 222
- 2013) 318-325.
- [13] X. Zhang, W.J. Jiang, X.P. Zhu, A. Mauger, Qilu, C.M. Julien, J. Power Sources 196 (2011) 5102-5108.
- [14] P. Oh, B. Song, W. Li, A. Manthiram, J. Mater. Chem. A 4 (2016) 5839-5841.
- [15] G.V. Zhuang, G. Chen, J. Shim, X. Song, P.N. Ross, T.J. Richardson, J. Power Sources 134 (2004) 293–297.
- [16] K. Shizuka, C. Kiyohara, K. Shima, Y. Takeda, J. Power Sources 166 (2007) 233-238
- [17] J. Eom, M.G. Kim, J. Cho, J. Electrochem. Soc. 155 (2008) A239.
- [18] k. Matsumoto, R. Kuzuo, K. Takeya, A. Yamanaka, J. Power Sources 81-82 (1999)
- [19] W. Liu, G. Hu, K. Du, Z. Peng, Y. Cao, J. Power Sources 230 (2013) 201-206. X. Zheng, X. Li, Z. Wang, H. Guo, Z. Huang, G. Yan, D. Wang, Electrochim. Acta [20]
- 191 (2016) 832-840.
- [21] R. Moshtev, P. zlatilova, S. Vasilev, J. Power Sources 81 (1999) 434-441.
- [22] H. Liu, Y. Yang, J. Zhang, J. Power Sources 173 (2007) 556–561.
- [23] H. Liu, Y. Yang, J. Zhang, J. Power Sources 162 (2006) 644-650.
- [24] Z. Lu, D.D. MacNeil, J.R. Dahn, Electrochem. Solid-State Lett. 4 (2001) A200.
- [25] D.D. MacNeil, Z. Lu, J.R. Dahn, J. Electrochem. Soc. 149 (2002) A1332.
- [26] K. Shizuka, C. Kiyohara, K. Shima, K. Okahara, ECS Trans. 11 (2008).
- [27] D. Ostrovskii, F. Ronci, B. Scrosati, P. Jacobsson, J. Power Sources 103 (2001).
- [28] J.R. Dahn, J. Electrochem. Soc. 139 (1992). [29] J.R. Dahn, W. Li, Solid State Ionics (1993) 123-130.
- [30] M. Balasubramanian, X. Sun, J. Power Sources 92 (2001).
- [31] X.-Q. yang, J. McBreen, Electrochem. Commun. 4 (2002) 649–654.
- [32] O. Dolotko, A. Senyshyn, M.J. Mühlbauer, K. Nikolowski, H. Ehrenberg, J. Power Sources 255 (2014) 197-203.
- [33] A. Rougier, C. Julien, Ionics 3 (1997).
- [34] C. Julien, L. EL-FARH, J. Sol-Gel Sci. Technol. 15 (1999) 63-72.
- [35] P. Lanz, C. Villevieille, P. Novák, Electrochim. Acta 130 (2014) 206-212.