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Structural evolution of NM (Ni and Mn) lithium-rich layered material revealed by in-situ electrochemical Raman spectroscopic study



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HIGHLIGHTS

- A sophisticate air-tight in-situ electrochemical Raman spectroscopic cell was developed.
- In-situ Raman spectral analysis of the structural evolution was given.
- In-situ Raman spectra shows Li₂MnO₃ activation changes ionic local coordination structure.

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G R A P H I C A L A B S T R A C T



1. Introduction

ABSTRACT

Li-rich layered materials are one of promising candidates of cathode materials for energy storage in electric vehicles (EVs) due to their high energy density. The practical application of these materials relies on the in-depth understanding of the crystal structures and reaction mechanisms during the electrochemical processes to overcome the potential decay issue. In this work, in-situ electrochemical Raman spectroscopy has been developed and used to investigate the structural evolution of the Li-rich layered material ($0.5LiNi_{0.5}Mn_{0.5}O_2 \cdot 0.5Li_2MnO_3$). An electrochemical Raman spectroscopic cell with an excellent air-tightness and optical signal collection efficiency has been designed and used for in-situ investigation of the NM Li-rich material during the very first two electrochemical cycles. We found that the reactions of Ni²⁺ to Ni³⁺ and Ni³⁺ to Ni⁴⁺ appearing in the potential range of from 3.70 V to 4.45 V show a good reversibility. The in-situ Raman spectra after the first two electrochemical cycles also indicate the activation of Li₂MnO₃ changes the ionic local coordination structure and increases the ionic disorder of the pristine NM Li-rich layered material. This structural change has a great impact on the subsequent electrochemical cycles. The in-situ Raman spectroscopy results can help to improve the performance of NM Li-rich layered materials.

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Secondary lithium (Li) ion battery is one of the most promising energy storage devices and has been developed for several decades. The capacity is one of the most important factors in evaluating a Li ion battery. Li-rich layered structure materials [1-3] have attracted

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worldwide interests, thanks to their large discharging capacity up to around 250 mAh g^{-1} that exceeds the capacity of most of other metal-oxide cathode materials [1,4–6]. However, the application of this kind of materials is limited by potential decay [7-11] and bad rate capability [12], as a result of the structural instability of the material during the electrochemical charging and discharging processes. One of the structural problems is the migration of Ni^{2+} to the vacant sites left by the de-intercalated Li⁺ from the lavered structure, which will increase the disorder of the ionic arrangement in the material [2,7]. Moreover, the activation of Li₂MnO₃ in the material will result in a loss of the oxygen atom from the lattice [13,14] and reduce the stability of the material structure. Therefore, it is important to figure out the structural features and reveal the mechanism of the structural evolution of the material during the electrochemical charging and discharging processes, so that measures can be taken to improve the stability of the material.

In-situ characterization methods are indispensable in obtaining the reaction mechanism, because the intermediates, such as Ni³⁺, Ni⁴⁺ and Mn³⁺ in most of the cathode materials produced during the battery cycling are easy to be hydrolyzed or oxidized in atmosphere. Furthermore, it is well-known that the electrode may experience a potential relaxation or self-discharge under the open circuit condition. Therefore, the materials characterized by ex-situ methods could be in a state very different from that at the desired potential. A reliable correlation of the electrochemical charging or discharging states of the material with potentials can be well established by a well-designed in-situ measurement.

Up to now, various techniques have been used to investigate the structure and the structural evolution of the Li-rich layered material, such as (S)TEM, XRD, EXANES, and Raman spectroscopy. The transformation of the material from the layered structure to the spinel-like phase has been evidenced by (S)TEM [8]. The valence change of Ni, Mn and Co has been observed by EXANES [12,15]. The mechanism of the lattice inter-layer space change has been investigated by in-situ XRD, and the migration of Ni²⁺ to the Li⁺ vacant site has been evidenced [7]. All these techniques have provided important information toward the understanding of the structural evolution of the electrode material.

Different from XRD (providing the information of long-range order structures), X-ray techniques (based on the synchrotron sources), and TEM (based on high vacuum systems), Raman spectroscopy is a more convenient in situ tool to obtain the short range as well as long-range order structural information as it works usually in the visible light range. In fact, it is a powerful technique for characterizing the material structure by providing the fingerprint vibrational information from molecular or lattice vibrations [16]. Raman spectroscopy can sensitively detect the local coordination structural change as a result of different coordination configurations and indirectly reflect the valence change of metal cations in metal oxides. For example, Both Mn^{3+} and Mn^{4+} exist in the form of MO6 (M = metal) octahedral cages, but they will give different Mn–O vibrational frequency values due to their different local coordination structures, which can be sensitively used to identify Mn³⁺ and Mn⁴⁺ in spinel LiMn₂O₄ [17,18]. More recently, Raman spectroscopy has been used to study the different behavior of Li₂MnO₃-like and LiMO₂ components in NCM (Ni, Co and Mn) Lirich material under the ex-situ condition [19].

In-situ Raman spectroscopy has been used to investigate the NCM Li-rich layered material during the first electrochemical cycle [5,20,21]. In comparison, the study on NM Li-rich material is much less. NM Li-rich material has a relative simple composition and contains only two kinds of transition metal cations [22]. During the activation of Li₂MnO₃ in the first electrochemical cycle, the lattice oxygen will release and the lattice framework will change [13], leading to the instability of the material and deterioration of its

electrochemical performance. However, the deterioration of the electrochemical performance of the NM Li-rich materials becomes significant in the subsequent electrochemical cycles, especially in the second electrochemical cycle. The potential decay is the most significant in the second cycle. Therefore, it is highly important to investigate the structural evolution of the materials also in the subsequent electrochemical cycles in order to understand the impact of the Li₂MnO₃ activation on the structure of the NM Li-rich materials.

In this work, we used in-situ electrochemical Raman spectroscopy to investigate the local coordination structural evolution during the first and second electrochemical cycles. In this way, we will be able to understand the deterioration mechanism of the electrochemical performance of the NM Li-rich material (0.5LiNi_{0.5}Mn_{0.5}O₂·0.5Li₂MnO₃). Such a detailed molecular level understanding of the correlation between the structures and electrochemical performance may help figure out the key factors influencing the electrochemical performance and guide the design of electrode materials.

2. Experimental

2.1. Material synthsesis

The metal salt solution was prepared by mixing $MnSO_4 \cdot 6H_2O$ (>99%) and $NiSO_4 \cdot 6H_2O$ (>99.5%) at a concentration ratio of Mn:Ni = 3:1. The total concentration of the metal salt solution was 1 M. Then the solution was co-precipitated by adding 1 M Na₂CO₃ solution (with a pH of 7–8 adjusted with ammonia aqueous solution) at 55 °C while stirring at 500 rpm. The precipitate was filtered, washed with de-ionized water, and dried at 80 °C. The product was then mixed with LiOH (5% excess of the stoichiometric amount). The mixture was then transferred to a muffle oven for calcination at 480 °C for 4 h and then at 800 °C for 10 h.

2.2. Electrode preparation

The active materials, acetylene black, and polyvinylidene fluoride (PVDF) were mixed at a weight ratio of 8:1:1 in *N*-methyl-2pyrrolidone (NMP). The slurry was coated on an Al foil with a thickness of 0.015 mm, which was vaccum dried at 80 °C for 10 h. The sheet was then punched into a round discs (12 mm diameter) and pressed at 16 MPa, followed by vaccum drying at 120 °C for 4 h. The disc was used as the cathode. A metallic lithium foil with the thickness of 1 mm was used as the anode.

The electrochemical properties of the NM Li-rich material were measured using CR2016 coin cells. The electrolyte was 1.0 M LiPF₆ in mixed organic solvents of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) (EC:DEC:DMC = 1:1:1, volume ratio). A Celgard[®] membrane was used as the separator.

2.3. Physical characterization

XRD (Powder X-ray diffraction) characterization of the NM Lirich material was performed on MiniFlex600 X'pert diffractometer (Rigaku corporation, Japan) using Cu K α radiation ($\lambda = 0.154$ nm) and the scan rate was 1° min⁻¹. The morphology of the sample was measured on scanning electron microscope (SEM) S-4800 (Hitachi, Japan). The elemental composition of the materials were determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES) on IRIS intrepid II XSP (Thermo Electron Corporation, US).

2.4. In-situ electrochemical Raman spectroscopic measurement

Different from that working in aqueous solutions, the electrochemical Raman spectroscopic cell for Li ion batteries has a much stricter requirement on the air and water tightness to ensure the normal working of the Li ion batteries. Furthermore, the optical throughput should be maximized to ensure a high detection sensitivity. The configuration of the in-situ electrochemical Raman cell is shown in Fig. 1. The commonly used CR2016 coin cell was chosen to hold the cathode, separator and Li foil. The stainless steel mesh grid coated with the material slurry was used as the cathode, which ensures the normal electrochemical cycling and the acquisition of Raman signals [21,23]. The stainless steel cap in the cathode side of the coin cell was drilled with a hole with a diameter of ~1 mm. A 0.5 mm thick guartz window was sealed to the stainless steel plate with epoxy resin to keep the air and water tightness and allow the light transmission. The window and the top cap of the CR2016 coin cell are compressed together to minimize the thickness of the electrolyte layer in order to minimize the distortion of the optical path due to the mismatch of the refractive index [24] and to improve the collecting efficiency of Raman signals. The assembly of the electrodes and the component of the insitu Raman cell was performed in the argon-filled glove box (Labstar, Mbraun, Germany). The electrochemical charging and discharging tests were performed galvanostatically between 2.0 V and 4.8 V with a current density of 30 mA g^{-1} using a Landian CT2001A (Wuhan, China) battery testing system at room temperature.

A microscopic Raman instrument XploRa (Horiba-Jobin Yvon, Japan) with a water immersion objective (numeric aperture of 1.0 and working distance of 2.0 mm, Olympus, Japan) were used to conduct the in-situ electrochemical Raman measurement. The use of the water immersion objective not only increases the numerical aperture but also minimizes mismatch of the refractive index (the difference in the refractive indexes between water and quartz is less than that between air and quartz), which can significantly improve the collection efficiency of the Raman signal. The Raman measurement was performed while the cell was electrochemically cycled. The laser wavelength was 785 nm and the laser power was



Fig. 1. Exploded view of the configuration of the in-situ electrochemical Raman spectroscopic cell for studying Li-rich layered materials: a) water sink for the water immersion objective, b) stainless steel plate as the current collector for the working electrode, c) quartz window of 0.5 mm thickness, d) CR2016 coin cell with a drilled hole (diameter: 1 mm), e) spring, f) O-ring, g) the PTFE base, h) the counter electrode wire.

set to 0.04 mW. The use of a low laser power is to guarantee no laser-induced heating and photochemical reaction at the laser spot [25]. Due to the use of a low laser power, we increase the acquisition time to 900 s for each spectrum to ensure the reasonable signal to noise ratio. The interval between two acquisitions was 300 s. In fact, because the current used for electrochemically cycling is small enough that the material change can be negligible even in such a long acquisition time.

3. Results and discussion

3.1. Structure

The SEM images of the synthesized material are shown in Fig. S1. The experimentally determined sample composition by ICP is Li:Mn:Ni = 1.22:0.6:0.20, which agrees well with the designed value (1:20:0.6:0.2). It indicates we have successfully synthesized the desired material. The SEM images of the material reveal that they are aggregates formed by small particles with a diameter of 100-300 nm.

The crystal structure of the material was further characterized by both XRD and normal Raman spectroscopy. It can be seen in Fig. 2 that the material consists of two components, belonging to the R-3m and C2/m space groups. The result agrees well with the literature [26].

The diffraction peaks show a similar feature to that of a hexagonal α -NaFeO₂ structure (space group: 166, R-3*m*), with a few broad peaks between $2\theta = 20$ and 25° . It is worth emphasizing some features in the XRD data. First, the diffraction peaks between 2θ = 20 and 25° are known to be caused by the super-lattice ordering of Li and Mn in the transition metal layers in the Li-rich layered oxides, which confirms the existence of Li₂MnO₃ [1]. Second, the formation of ordered lamellar structures in the hexagonal structure can be confirmed by the appearance of the (018) and (110) doublet [27]. The good separation of the (018)/(110) doublets indicates the formation of highly ordered lamellar structures. Last, the intensity ratio of (003) over (104) peaks is around 1.6, indicating that the sample is free or has a low level of cations-mixing. It is known that a well-ordered sample should have a value larger than 1.2, while a heavily ion-mixed sample should have a value smaller than 1.2 [28].

The normal Raman spectrum of NM Li-rich layered material



Fig. 2. The XRD patterns (Cu Ka, $\lambda=0.154$ nm) of the NM Li-rich material (0.5LiNi_{0.5}Mn_{0.5}O_2\cdot 0.5Li_2MnO_3).



Fig. 3. (a) The normalized Raman Spectrum of the NM Li-rich material 0.5LiNi_{0.5}M- $n_{0.5}O_2 \cdot 0.5Li_2MnO_3$. The Raman spectrum of Li₂MnO₃ (b) is also given for comparison. Excitation laser: 785 nm.

(0.5LiNi_{0.5}Mn_{0.5}O₂•0.5Li₂MnO₃) is shown in Fig. 3a. For comparison, the Raman spectrum of pure Li₂MnO₃ powder, one component of the NM Li-rich layered material [1], is shown in Fig. 3b. The NM Li-rich material shows two peaks belonging to the *R*-3*m* space group at 610 and 496 cm⁻¹ [29], which can be assigned to v_{MO6} vibration (M = Ni, Mn cations, A_{1g} mode) and δ_{O-M-O} vibration (Eg mode), respectively. The peaks at 569, 440, 416, and 330 cm⁻¹ are clearly from Li₂MnO₃ [30], indicating the presence of Li₂MnO₃-like structure belonging to the *C*2/*m* space group in the NM Li-rich layered material [21,31].

3.2. Electrochemistry

The electrochemical performance of the NM Li-rich layered material was tested in the CR2016 coin cell. Fig. 4a shows the electrochemical charging and discharging curves of the first and second electrochemical cycles for the NM Li-rich layered material. The material gave charging and discharging capacity of around 343 and 267 mAh g⁻¹ in the first electrochemical cycle, and 278 and 270 mAh g^{-1} in the second electrochemical cycle, respectively. To clearly see the features during the electrochemical reaction, we present in Fig. 4b the differential capacity (dQ/dV) curves with the data of Fig. 4a. We see obvious differences for the two cycles in the whole electrochemical charging curves and the discharging curves in the potential region more negative than 3.50 V. A detailed analysis of the reason for the differences in dQ/dV curves on the molecular level by in-situ Raman spectroscopy will be indispensable to the understanding of the correlation between the structural evolution of the local coordinates and the deterioration mechanism of the electrochemical performance of the material.

3.3. In-situ electrochemical Raman spectroscopic measurement

Fig. 5a shows the simultaneously obtained in-situ Raman data and electrochemical data during the first electrochemical cycle. As can be seen in Fig. 5a, the 610 cm⁻¹ peak related to v_{MO6} gradually decreases from 3.70 to 4.30 V, which can be related to the Li⁺ deintercalation from the material [6,32]. With the increase of the voltage, the peak at 496 cm⁻¹ (δ_{O-M-O}) shifts to 489 cm⁻¹, and meanwhile a new peak at around 545 cm⁻¹ grows after 3.8 V. In



Fig. 4. The galvanostatic charging and discharging curves (a) and the differential capacity (dQ/dV) curves (b) of the NM Li-rich layered material (0.5LiNi_{0.5}M- $n_{0.5}O_2 \cdot 0.5Li_2MnO_3$) obtained at a current density of 30 mAh g^{-1} . The voltage is referred to Li⁺ (1 M)/Li electrode.

fact, the two peaks can be assigned to $A_{1g}~(545~cm^{-1})$ and $E_g~(489~cm^{-1})$ vibrations of the $Ni^{3+}{-}O$ belonging to R-3m space group [33] (Fig. S3 shows the Raman spectra covering these two peaks in the first and second electrochemical cycles both at around 4.45 V extracted from Fig. 5a and b). The change of these two peaks can be well correlated to the peak growing at 3.80 V in the dQ/dV curve shown in Fig. 4b. Therefore, we can assign this dQ/dV peak to the oxidation of Ni²⁺ to Ni³⁺. The Ni³⁺–O peaks decrease at voltages higher than 4.45 V, which may be due to the oxidation of Ni³⁺ to Ni⁴⁺ [6,32]. It seems that only part of the Ni³⁺ is oxidized to Ni⁴⁺ as the Ni³⁺–O signal remains observable even till the end of the first electrochemical charging process. The small peak at around 4.20 V in the dQ/dV curve shown in Fig. 4b can be assigned to the oxidation of Ni^{3+} to Ni^{4+} . When the voltage is above 4.45 V, the activation of Li₂MnO₃ occurs [13]. As a result, the ionic arrangement of the material becomes disordered and the Raman intensity of Ni^{3+} –O peaks decreases [5,20,21].

During the first electrochemical discharging process, the Raman peaks of Ni^{3+} –O changes first as a result of the reduction of Ni^{4+} and Ni^{3+} to Ni^{2+} . Such a change corresponds to the two dQ/dV



Fig. 5. Simultaneous in situ Raman and electrochemical measurements during the first(a) and second(b) electrochemical cycle of galvanostatic charging and discharging processes of the NM Li-rich layered material at a current density of 30 mAh g⁻¹ in the in-situ electrochemical Raman spectroscopic cell. The red lines in a) and b) are the electrochemical charging and discharging curves of the NM Li-rich material and the voltage axis are shown on the right with red color (The voltage is referred to Li⁺ (1 M)/Li electrode). The background images in a) and b) are the time dependent Raman spectral contour plots. The intensity color bars are shown on the right for the intensity range of 0–1000 counts. As the capacity of the second cycle is lower than the first cycle, the charging and discharging time of this cycle is shorter than that in the first cycle. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

peaks at 4.20 and 3.80 V in Fig. 4b. These two dQ/dV peaks correspond to the reverse processes of the previous two dQ/dV peaks at 3.80 and 4.20 V during the first electrochemical charging process. The Ni^{3+} –O Raman peaks disappear at around 3.70 V, indicating that most of the Ni^{3+} has been reduced to Ni^{2+} . This observation is also supported by some previous findings [26,34–37].

The ν_{MO6} and δ_{O-M-O} peaks can only be observed when the voltage is more negative than 3.50 V. The widths of these two peaks become much broader than those of the pristine material. For a clear comparison, the Raman spectrum of the pristine material was plotted in Fig. 6 together with that obtained after the first electrochemical cycle. The peaks at 440 and 416 cm⁻¹ related to the Li₂MnO₃ have evolved into a broad peak together with the 496 cm⁻¹ of δ_{O-M-O} Such a broadening reflects a wide distribution of vibration modes and may be correlated with the increased local structural disorder as a result of the Li₂MnO₃ activation The potential range for such an obvious Raman peak change right corresponds to the dQ/dV peak below 3.50 V in the first electrochemical discharging curve in Fig. 4b. However, this dQ/dV peak has no corresponding dQ/dV peak in the first electrochemical charging process. Meanwhile, as can be seen in Fig. 4b, in the electrochemical charging curve of the second electrochemical cycle, a new shoulder peak appears at around 3.50 V and can is related to the dQ/dV peak below 3.50 V in the electrochemical discharging process. This pair of dQ/dV peaks have been related to the reaction of Mn^{4+}/Mn^{3+} redox couple as a result of the activation of Li₂MnO₃ in the materials [32,37]. They keep changing even at the eighth electrochemical cycle (see Fig. S2), indicating the instability of the material structure after the Li₂MnO₃ activation and that the electrochemical performance has been affected by this unstable structure. A clear



Fig. 6. The in-situ Raman spectra acquired in the in-situ electrochemical Raman cell of the NM Li-rich layered material a) at the pristine state before the electrochemical cycling (black line); b) after the first electrochemical cycle (red line); c) after the second electrochemical cycle (blue line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

understanding of the local structural feature related to this pair of dQ/dV peaks requires the further in-situ Raman characterization of the second electrochemical cycle.

The simultaneously obtained in-situ Raman and electrochemical data for the second electrochemical cycle are shown in Fig. 5b. In the electrochemical charging process, the 610 (ν_{MO6}) and 496 cm⁻¹ (δ_{O-M-O}) Raman peaks decrease gradually from 3.00 to 3.50 V, which can be related to the dQ/dV shoulder peak ranging from 3.00 to 3.50 V in Fig. 4b. It indicates that this reaction may be related to the Li₂MnO₃ activation, considering that there is no reaction before 3.50 V in the first electrochemical charging process. It has been pointed out that the activation of Li₂MnO₃ may change the local coordination structure of the material and increase the disorder of the ionic arrangement. Such a structural change can lead to a decrease in the structural stability of the material and impact the electrochemical performance in subsequent electrochemical cycles of the material [6,13].

Then, the 545 cm⁻¹ (Ni³⁺–O A_{1g}) Raman peak appears again at the same voltage around 3.80 V as that in the first electrochemical charging process. At more positive voltages, the changing process of this Raman peak is similar to that in the first electrochemical charging process. However, at voltages more positive than 4.45 V, the decreasing trend of this Raman peak is less obvious than that in the first electrochemical charging process, which may also be caused by the disordering of the ionic arrangement as a result of the activation of Li₂MnO₃ [20].

In the beginning of the second electrochemical discharging process, the change of the Ni³⁺–O Raman peaks is related to the electrochemical reduction of Ni⁴⁺ and Ni³⁺ to Ni²⁺. This phenomenon can be related to the dQ/dV peaks at 4.20 and 3.80 V in Fig. 4b, corresponding to the reactions of Ni⁴⁺ to Ni³⁺ and Ni³⁺ to Ni²⁺, respectively. These two dQ/dV peaks overlap well with those in the first electrochemical discharging process, which indicates a good electrochemical reversibility of the Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ reactions.

The v_{MOG} and δ_{O-M-O} peaks appear at 3.50 V, showing similar changing trends to that in the first electrochemical discharging process. However, it can be clearly seen in Fig. 6 that these two Raman peaks become broader after the second discharging process compared with that after the first discharging process, indicating a

more disordered structure. On the basis of this phenomenon, it seems like that the structure of the material after the activation of Li₂MnO₃ in the first electrochemical charging is unstable and experiences a structural evolution. In contrast to the broader Raman peaks in Fig. 6, the dQ/dV peak in the second electrochemie Fig. 4b), cal discharging process is sharper and stronger than that in the first electrochemical discharging process (se which may indicate a kinetic improvement of the reaction from 3.50 V to 2.00 V [36]. Both Raman and the differential capacity data infer the close correlation between the structural instability and the unstable electrochemical performance.

As mentioned above, the most distinct difference between the first and second electrochemical cycles is in the potential range from 3.50 to 2.00 V after the first electrochemical charging process. In the NM Li-rich layered material, there are only two transition metal cations. The Ni cations (Ni⁴⁺ and Ni³⁺) already show two pairs of reversible dQ/dV peaks at 4.20 and 3.80 V, respectively (see Fig. 4b). Whereas the reaction related to the dQ/dV peak at 3.20 V only occurs after the activation of Li₂MnO₃. Therefore, it seems that the reaction may not be related to Ni cations and rather may be related to Mn cations. Such an assumption is supported by some reports, in which they pointed out the possible involvement of the Mn^{3+} in the subsequent electrochemical cycles after the first electrochemical charging of the pure Li₂MnO₃ [32,38], NM Li-rich layered material [32,37], and NCM Li-rich layered material [12,15]. Using the electrochemical data alone is not sufficient to exclude the possibility of the Ni cations that are located in different local coordination structures after the Li₂MnO₃ activation. However, according to the similar evolution trends of both the dO/dV peaks at 3.20 V in Fig. 4b and in Fig. S2, and the Raman peaks of M–O related to Li₂MnO₃ in Fig. 6 during the electrochemical cycling, it is still possible for us to assign the dQ/dV peak at 3.20 V to the Mn cation. With this understanding, we can conclude that the activation of Li₂MnO₃ can provide more capacity meanwhile also decreases the stability of the structure, leading to the unstable cycling performance of the material [32].

4. Conclusion

In summary, we have designed a cell with a good air-tightness and high throughput for in-situ electrochemical Raman spectroscopic study of the electrochemical charging and discharging processes of the NM Li-rich layered material. We have been able to obtain Raman signals with minimum interference from laser illumination. We found that the dQ/dV peak at 3.20 V after the first electrochemical charging process may be caused by the activation of Li₂MnO₃, which also indicates that both of the structure and the electrochemical behavior of the material have changed after the activation of Li₂MnO₃. The in-situ Raman spectra revealed the structural evolution of the local coordination structure and the increased disorder of the ionic arrangement. Such a structural evolution leads to the deterioration of the stability of the material and the electrochemical performance. According to this finding, it may be meaningful to design a material with a structure that can only be activated in a designed degree or that has a solid framework to stabilize the material. This work also demonstrates that in situ electrochemical Raman spectroscopy can really reflect the dynamic local coordination structural information and is a powerful tool in exploring the underlying mechanisms of the structural evolution in metal oxide materials of Li ion batteries, which may also be applied in other types of Li-related battery system.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jpowsour.2016.01.065.

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