Distribution of relaxation times investigation of Co^{3+} doping lithium-rich cathode material $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.1}\text{Mn}_{0.5}\text{Co}_{0.2}]\text{O}_2$

WANWAN LI, YUE LI, XIAOLIN YAO, MINHUA FANG, MIAO SHUI*, JIE SHU
and YUANLONG REN

The State Key Laboratory Base of Novel Functional Materials and Preparation Science, The Faculty of Materials Science and Chemical Engineering, Ningbo University, Ningbo 315211, People's Republic of China

*Author for correspondence (shuimiao@nbu.edu.cn)

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Abstract. The element Co^{3+} was introduced into lithium-rich material $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by a polyacrylamide-assisted sol–gel method to form $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.1}\text{Mn}_{0.5}\text{Co}_{0.2}]\text{O}_2$ and better electro-chemical performances were observed. Electrochemical impedance spectroscopy spectra were measured on 11 specific open circuit voltage levels on the initial charge profile. Then they were converted to the distribution of relaxation times (DRTs) $g(\tau)$ by self-consistent Tikhonov regularization method. The obtained DRTs offered a higher resolution in the frequency domain and provided the number and the physical origins of loss processes clearly. Through the analysis of DRTs, the rapid augmentation of resistance to electronic conduction and charge transfer within the voltage range 4.46–4.7 V where the removal of Li_2O from Li_2MnO_3 component took place was the most remarkable phenomenon and the Co^{3+} doping greatly reduced the resistance to electronic conduction R_e . This gave us more evidence about the complicated ‘structurally integrated’ composite character of the material.

Keywords. Electrochemical impedance spectroscopy; DRTs; lithium rich; cathode material; Tikhonov regularization.

1. Introduction

Nowadays, commercially available cathode materials for lithium ion batteries are increasingly falling short of the demands of miniaturization and light weight of electric energy-consuming devices, like electric vehicles (EVs) and other mobile facilities. The finding and application of high-capacity cathode material ($>200 \text{ mAh g}^{-1}$) thus always pose a challenge for us. Recently, the appearance of Mn-, Ni- or Co-based multi-component solid solutions or complicated ‘structurally integrated compounds’ surprised us [1–3]. Material with nominal composition $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ showed amazingly high discharge capacity more than 200 mAh g^{-1} . However, some aspects of this lithium-rich material still bewildered us. Firstly, this material still suffered greatly from serious capacity fading at higher C-rates and the poor reproducibility probably caused by the extremely low electron conductivity of $\text{Li}(\text{Mn})_6$ local domain in the structure. Secondly, there is some debate, however, as to whether the structure of the material shall be considered to be a kind of true solid solution where the lithium and transition metal ions were randomly and homogeneously distributed within the M layers [4] or complicated ‘structurally integrated’ material, where nanometer regions with Li_2MnO_3 - and LiMO_2 -like features merged together [5–8]. Therefore, the capacity degeneration of the lithium-rich material was

normally attributed to the dynamic factors, for example, the electrochemical polarization resulting from the poor electron or lithium ion transportation speed, the delayed redox reaction etc. Thus, analysing the resistance of the underlying physical and chemical processes while the charge/discharge of the electrode occurred will help us understand the origin of the poor electro-chemical performance of the material, pin down the rate-determining step, tailor the material to mitigate the kinetically unfavourable factors and also help to obtain structural information. To accomplish this, electrochemical impedance spectroscopy (EIS), which contains information about the physico-chemical processes within the cell, is the most frequently used method. However, to analyse the electro-chemical dynamics by this method, two points usually bewilder us. One is that the knowledge about the number and the physical origins of all processes, which contribute to the cumulative impedance, are required. Another is that the equivalent circuit that seems to be the best fit of the experimental EIS profile is usually not unique. This is most likely caused by the overlapping of the different loss processes with different time constants in the frequency domain. Therefore, the explanation of kinetics is thus perplexing.

This perplex can somewhat be solved by a deconvolution method of the impedance with the distribution of relaxation times (DRTs). Compared to the traditional impedance spectra, the DRTs method offered a higher resolution in the frequency

domain, the outstanding potential to resolve polarization process with time constants close to each other, allowing a clearer identification of the loss processes and the determination of electro-chemical mechanisms.

In our previous report, a detailed EIS investigations of lithium-rich cathode material $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ on the possible electro-chemical mechanisms and charge carrier transportation kinetics by measuring the EIS spectra at different open circuit voltage (OCV) levels in the charge process for the initial two cycles were presented [9]. It was found that the rapid augmentation of resistance to electronic and ionic conduction within the voltage range 4.45–4.6 V where the removal of Li_2O from Li_2MnO_3 component took place was the main factor that was responsible for the capacity decay. Owing to the structural complexity of the material and the multiple species capable of electro-chemical reactions, a variety of loss processes overlapping with each other in the frequency domain were presented on the EIS spectra. Although we managed to identify all the loss processes, because of the drawbacks of the traditional equivalent circuit method, the number and the physical origins of loss processes were possibly still controversial.

Here, in this paper, Co^{3+} element was further introduced into $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ by a polyacrylamide (PAM)-assisted sol-gel method and the enhanced electro-chemical performances were observed. To clarify the number and the physical origins of loss processes, the EIS spectra measured at a series of given state of charges for the first charge process were measured and were then transformed to DRTs by a self-consistent Tikhonov regularization method. This method separated the loss processes with different time constants at a satisfactory level and gave us the sound information for the determination of the physical origins of the loss processes. The result showed that Co^{3+} doping greatly reduced the resistance to electronic conduction R_e .

2. Theories

EIS $Z(\omega)$ in frequency domain is related to the normalized DRTs function $g(\tau)$ by the following equation:

$$Z(\omega) = R_0 + R_{\text{pol}} \int_0^\infty \frac{g(\tau)}{1 + j\omega\tau} d\tau \quad (1)$$

where R_0 means the ohmic resistance and R_{pol} is the polarization part.

Many researchers have demonstrated that compared to the traditional impedance spectra, the DRTs have offered a higher resolution in the frequency domain. Therefore, it is helpful in the determination of electro-chemical mechanisms as well as the detailed analysis of loss processes. However, the application of DRTs method may encounter the following difficulties.

1. The DRTs $g(\tau)$ is expressed in equation (1) as an integral from zero to infinity. However, the measurement in mHz frequency range is extremely time consuming and extending the testing frequency to infinity is also unachievable. Therefore, the low-frequency branch shall be physically reasonably modelled and afterwards excluded. Levi and Aurbach [10] supposed that the low-frequency resistance response was comprised of a finite length Warburg element and a series capacity and was expressed as

$$\begin{aligned} Z_{\text{Diff}} &= Z_{\text{FLW}} + Z_c \\ &= R_w \cdot \frac{\tanh([j\tau_w\omega]^{P_w})}{[j\tau_w\omega]^{P_w}} + \frac{1}{j\omega C_0}. \end{aligned} \quad (2)$$

Therefore, subtraction of the low-frequency branch from $Z_{\text{tot}}(\omega)$ allows the evaluation of the resulting spectra by DRTs approach.

$$\begin{aligned} Z_{\text{sub}}(\omega) &= Z_{\text{tot}}(\omega) - Z_{\text{Diff}} \\ &= R_0 + R_{\text{pol}} \int_0^{\tau_{\text{cut off}}} \frac{g(\tau)}{1 + j\omega\tau} d\tau. \end{aligned} \quad (3)$$

2. This relationship is given by a typical Fredholm integral equation of the first kind. The solution to a Fredholm integral equation of the first kind is an ill-posed problem and a simple least-squares method is not appropriate for the solution of such a problem. Tikhonov regularization is the best-known method to solve the Fredholm integral equation of the first kind. However, whether the result obtained by a regularization method is good or not depended mostly on a value called regularization parameter. The procedure for the determination of this regularization parameter is also the main difference between the different solution methods like the implementation of an edge-preserving technique and stochastic algorithm. The procedure used here is the self-consistent method [11]. References [12,13] also contain a comparison of the self-consistent with other procedures, which are often used for the determination of the regularization parameter. This comparison leads to the conclusion that the results obtained with the self-consistent method are much better and more reliable than the other procedures. A kind of generalized [14] singular-value decomposition is also used to prevent the enormous computational effort by matrix inversions.

3. Experimental

A stoichiometric amount of $\text{C}_2\text{H}_7\text{LiO}_4$, $\text{C}_4\text{H}_6\text{NiO}_4 \cdot 4\text{H}_2\text{O}$, $\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ were dissolved in distilled water with 10% excess of $\text{C}_2\text{H}_7\text{LiO}_4$. After 10 min

Figure 1. Schematic illustration of the preparation of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$.

stirring, 50 wt% citric acid solution (citric acid/metal ions = 1:1) was dipped into the solution under strong stirring at 50 °C for 4 h for the complete chelating reaction. Then, acrylamide (6 g/100 ml) and *N,N'*-methylene-bis-acrylamide (1 g/100 ml) were dissolved in the solution. The solution was heated to 85 °C and a few milligrams of α, α' -azoisobutyronitrile (AIBN) in acetone was introduced. Once the initiator was added, a transparent hydrogel formed instantly and lithium, manganese, nickel and cobalt cations were trapped homogeneously and simultaneously throughout the polymer matrix. Figure 1 shows the detailed synthesizing procedure of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$. After ageing at room temperature for 10 h, the hydrogel was dried overnight at 160 °C followed by grinding in a pestle for 30 min, calcinating at 500 °C for 4 h in order to ensure total decomposition of reagents, and finally sintering at 900 °C for 2 h. Cooled down to room temperature, the mixture was again ground for 20 min in an agate mortar.

The powder X-ray diffraction (XRD) measurements were recorded on a Bruker AXS D8 FOCUS X-ray diffractometer operated at 36 kV and 20 mA using $\text{Cu K}\alpha$ radiation. The patterns were obtained at a scanning velocity of $0.029^\circ \text{ s}^{-1}$ over an angle range from 10 to 70°. The surface morphology was investigated by a Hitachi S4800 scanning electron microscope (SEM).

The cathode was prepared by coating the slurry consisting of 80 wt% active material, 10 wt% acetylene black and 10 wt% polyvinylidene difluoride (PVDF) binder onto the Al foil, followed by drying at 120 °C under vacuum overnight. A three-electrode simulation cell was fabricated in the argon-filled glove box with the as-prepared cathode, metallic lithium foils as reference electrode and counter electrode, Celgard 2300 polypropylene membrane as separator and 1 M LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate (1:1 volume ratio) as electrolyte. CHI660D Electrochemical WorkStation was employed for the electrochemical impedance measurement. The cell was firstly maintained at a constant given state of charge for 2 h with the aim that the electrode was equilibrated at that potential. The EIS was carried out by applying an ac amplitude of 5 mV on that equilibrium potential in the frequency range of 10 mHz to 100 kHz.

4. Results and discussion

The powder XRD pattern of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ is shown in figure 2a with Miller indices indicated. All of the diffraction peaks could be indexed by the layered $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ (R-3m) and localized monoclinic Li_2MnO_3 (C2/c, marked by a red circle). Based on this, the

Figure 2. (a) XRD pattern and (b) SEM image of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$.

compound can be characterized as a combination of two phases, namely, a trigonal R-3m phase ($\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$) and a monoclinic C2/m phase (Li_2MnO_3). These results were consistent with the previously reported references [3–5]. The SEM image of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ is shown in figure 2b. Clear-edged particles with average size of about 150–250 nm were observed. Some of the granules merged together and formed larger agglomerates.

Figure 3a illustrated the charge/discharge profiles for the first 50 cycles of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$. Except for the unique initial charge profile with a long platform characteristic of the simultaneous leaving of Li_2O and O_2 , all the subsequent charge/discharge profiles were very similar. The capacity fading was trivial from the 10th cycle. Over 200 mAh g^{-1} discharge capacity was still delivered after 50 cycles. Figure 3b showed the rate capability of cathode material $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$. The battery was cycled at different current densities, namely, 0.1, 0.2, 0.5, 1, 2 C and back to 0.1 C, for 5 charge/discharge cycles each. Nearly all coulomb efficiencies were more than 95% except the relatively low efficiency of 0.78 for the first cycle. This can be explained by the removal of Li_2O from Li_2MnO_3 component within a voltage range of 4.45–4.6 V for the initial charge process. The discharge capacity of the battery at 0.1 C current density degenerated quickly from near 270 mAh g^{-1} of the first cycle to ca. 230 mAh g^{-1} of the fifth cycle. With the augment of charge/discharge current, the released capacity decreased slowly. The discharge capacity at the end of each C-rate was estimated to be ca. 230, ca. 201,

Figure 3. (a) Fifty charge/discharge cycles and (b) rate capability at 0.1, 0.2, 0.5, 1, 2 C and back to 0.1 C of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$.

Figure 4. First charge profile of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode material and the open red circle represented the given state of charge where EIS was measured.

ca. 170, ca. 140 and ca. 105 mAh g^{-1} , respectively. When the current density was back to 0.1 C, nearly 225 mAh g^{-1} was

Figure 5. EIS spectra of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode material measured at OCV levels from 3.4 to 3.8 V (top left), 4.0 to 4.2 V (top right) and 4.46 to 4.70 V (bottom left).

regained. The electro-chemical performance of the material $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ showed significant improvement.

Figure 4 showed the first charge profile of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode and the open red circle represented the given state of charge where EIS was measured. A capacity of ca. 350 mAh g^{-1} was released. Altogether, 11 EIS spectra, which are shown in figure 4, were measured at the marked OCV levels. The 11 EIS profiles, presented in figure 5, can be roughly classified into three groups according to the appearance of the profile. The first category included three profiles measured at OCV levels 3.4, 3.6 and 3.8 V. It featured the remarkable long tail in low-frequency range and the relatively small semi-circle in high- and medium-high-frequency range. With the elevation of OCV levels, the complex resistance decreased quickly. The second category consisted of three profiles measured at OCV levels 4.0, 4.2 and 4.4 V. In this category, the complex resistances in both high- and low-frequency range remained low. However, they had the tendency of growing higher with the increasing of OCV levels. The third category included five profiles measured at OCV levels 4.46, 4.52, 4.58, 4.64 and 4.7 V. The EIS profiles changed much in this narrow 0.2 V voltage interval. Both the spans of the

semi-circle within the high-frequency range and the complex resistances at lower end frequency grew rapidly.

On the basis of the deconvolution method described above, the DRTs was calculated. DRTs for equilibrium potential 3.4–3.8 V is illustrated in figure 6, where the high-frequency part was magnified in the inset. For DRT at 3.4 and 3.6 V, there were four major loss processes (or polarization processes) marked by red arrows. According to the common agreement about the most prominent loss processes that took place in a lithium ion battery and their characteristic frequencies, the assignment of the four loss processes are given as follows.

The loss process at ca. $2.0 \times 10^{-5} \text{ s}$ (ca. 50 kHz) was related to the lithium ion transportation across the solid electrolyte inter-phase (SEI) or surface insulating layer combined with electrical double-layer capacitive behaviour and designated as P_{SEI} . The loss process at ca. $3.5 \times 10^{-4} \text{ s}$ (ca. 2.9 kHz) was supposed to be connected with the electron transportation in the particles of active cathode material, which was not necessarily resolved, but usually would be the limiting kinetic step for those cathode materials with low electronic conductivity like LiFePO_4 and FeF_3 , etc. As a consequence and the followed-up procedure of ionic transportation through SEI, this loss

Figure 6. DRT of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode material measured at OCV levels from 3.4 to 3.8 V.

process was considered to show up between the relaxation responsible for the ionic transportation through SEI and the relaxation responsible for the charge transfer. Here again, it was designated as P_E . The loss process at ca. 0.1 s (ca. 10 Hz) was connected with the charge transfer. Sometimes, multiple charge transfer processes will present simultaneously in the electro-chemical system.

As described above, $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ was complicated structurally integrated composite material where nanometer regions with Li_2MnO_3 - and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ -like features intermingled with each other. According to reference [8], in the first charge process of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$, in the wake of the oxidation of Ni^{2+} to Ni^{4+} via Ni^{3+} at voltages 3.2–4.4 V, Li_2O in Li_2MnO_3 local domains would be partially removed to produce $\gamma\text{-MnO}_2$ (structurally integrated $\beta\text{-MnO}_2$ and ramsdellite- MnO_2) where the valence state of Mn^{4+} remained unchanged. When Co^{3+} was introduced in

Figure 7. DRT of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode material measured at OCV levels from 4.0 to 4.2 V.

the matrix $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, the substitution of Co^{3+} most likely took place according to the following relationship:

The substitution of Co^{3+} in crystal lattice for Mn^{4+} in the $\text{Li}(\text{Mn})_6$ structure lowered the ordering of $\text{Li}(\text{Mn})_6$ domain. Therefore, the electro-chemical reactions taking place in the cathode material was somewhat different with those of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ in the first charge process at low equilibrium potentials. In this process, two metal ion species, namely, Co^{3+} and Ni^{2+} , were able to be oxidized within their individual electrode potential range. With the increasing potential level, Ni^{2+} was first oxidized, and then Co^{3+} oxidation followed. Therefore, here, the loss process at ca. 8.4 s (ca. 0.1 Hz) was supposed to be responsible for the oxidation of Co^{3+} -substituted Li_2MnO_3 domain. Because of the insulating character of Li_2MnO_3 domain, the polarization of this process was estimated to be as high as $1100\ \Omega$. Therefore, the mobility of lithium ion was greatly depressed in such complicated ‘structurally integrated’ compound. Accordingly, particularly low lithium ion diffusion

Figure 8. DRT of $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$ cathode material measured at OCV levels from 4.46 to 4.7 V.

Figure 9. Variation of resistance R_{SEI} vs. OCV.

coefficient and poor rate capability were anticipated [15]. Here, the last two consecutive loss processes were designated as $P_{\text{CT-Ni}}$ and $P_{\text{CT-Co}}$, respectively.

With the increase in equilibrium potential, the most remarkable change was the gradual attenuation of the resistance of

$P_{\text{CT-Co}}$ and the increase in the corresponding time constants. At the equilibrium potential 3.8 V, $P_{\text{CT-Co}}$ disappeared in that at this equilibrium potential, the $\text{Co}^{3+} \rightarrow \text{Co}^{4+}$ transformation in $\text{Li}(\text{Mn})_6$ structure almost completed. The DRTs for equilibrium potential 4.0–4.4 V is illustrated in figure 7. Basically, only three loss processes are observed here. These loss processes are also designated as P_{SEI} , P_{E} and $P_{\text{CT-Ni}}$, respectively. In this potential range, the oxidation of Ni^{2+} to Ni^{4+} via Ni^{3+} took place and the valence state of Mn^{4+} remained unchanged. Therefore, the oxidation of Ni^{2+} to Ni^{4+} was the only charge transfer loss. Also, we can observe that this charge transfer loss gradually aggrandized and the DRT obviously broadened over the increasing equilibrium potential. When the equilibrium potential fell within a voltage range of 4.46–4.7 V presented in figure 8, the prominent loss processes were still supposed to be 3. The magnitude of the resistance and the time constant of the high frequency P_{SEI} changed a little compared with other equilibrium potential regions. However, the polarization of second loss process P_{E} gradually increased from ca. 60 Ω in the case of 4.46 V to ca. 600 Ω in the case of 4.7 V. This enlarged resistance was supposed to come from the electronic conduction through the particles. However, in view of the extraordinary large

Figure 10. Variation of resistance R_E vs. OCV.

resistance to electronic conduction ca. 2000 Ω in the case of OCV 4.6 V in our recent report [9], the electronic conduction of Co^{3+} -substituted Li_2MnO_3 domain was improved substantially. The outstanding loss process at low frequency at this equilibrium potential was supposed to come from the charge transfer of Li_2O removal from Li_2MnO_3 domain and referred to as $P_{\text{CT-Li}_2\text{O}}$. Unlike the behaviour of LiCoO_2 , when charged above 4.5 V, lithium was extracted from the Li_2MnO_3 component of this material concomitant with oxygen released. Taking into consideration the electronic insulating character of Li_2MnO_3 domain, it was understandable that the resistance to charge transfer of Li_2O removal reaction increased rapidly. With the uprising of equilibrium potential from 4.46–4.7 V, the loss of charge transfer of Li_2O removal reaction increased quickly from 400 to 1600 Ω .

The integral of the individual DRT peak was supposed to be the polarization (resistance) of the loss process. The variation of the resistance of the loss process P_{SEI} was thus calculated and presented in figure 9. Basically, it remained low, ca. 15–40 Ω in the whole voltage coverage. With the increasing equilibrium potential, R_{SEI} increased slowly at first, and then more quickly when the potential exceeded by 4.4 V indicating the gradual formation of SEI film at the particle/electrolyte interface. The variation of the resistance of the loss process R_E is illustrated in figure 10. The resistance R_E remained almost unchanged within the range 30–40 Ω below equilibrium potential 4.2 V. However, a sudden sharp rise was observed near OCV 4.5 V and a seemingly abnormal resistance as high as ca. 600 Ω was observed near 4.7 V, indicating the inhomogeneous phase distribution in crystal lattice of Co^{3+} -substituted $\text{Li}[\text{Ni}_{0.1}\text{Li}_{0.2}\text{Co}_{0.2}\text{Mn}_{0.5}]\text{O}_2$. This also demonstrated the rationality of the hypothesis that Li_2MnO_3 domains were structurally integrated into $\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ layers proposed by M. M. Thackery considering the electric insulating character of Li_2MnO_3 phase.

The characteristic frequencies (or time constants) of those loss processes vs. equilibrium are illustrated in figure 11. Basically, the variations of both time constants of P_{SEI} and

Figure 11. Variation of time constants of the loss processes R_{SEI} and R_E vs. OCV levels.

Figure 12. Variations of charge transfer resistances vs. OCV levels for the first charge.

P_E described almost the same trend as the variations in their resistance. A turning point at about 4.5 V was observed. When the equilibrium potential was below 4.5 V, the change of time constant was a little and they increased rapidly with a further elevation of equilibrium potential above 4.5 V. Basically, τ (time constant) varied within the range 1.5×10^{-5} – 6.0×10^{-5} s. The charge transfer resistance R_{CT} was depicted against equilibrium potential in figure 12. The sudden rise in the resistance even to 5500 Ω within the voltage level 4.46–4.7 V marked by red circles was observed indicating the slow extraction rate of Li_2O from Li_2MnO_3 domains. The line marked by red triangles represented the charge transfer of Ni^{2+} oxidation and it increased slowly from dozens of ohms at low equilibrium potential level to more than 200 Ω at 4.4 V. Charge transfer related to Co^{3+} was limited to voltage range 3.4–3.6 with a quick plunge from over 1200 Ω at 3.4 V to less than 40 Ω at 3.6 V. The characteristic frequencies of the charge transfer processes are depicted in figure 13. Again here, the variation of τ (time constant) with the equilibrium potential resembled that of resistance very much. The relaxation time of Li_2O removal was estimated to be 120 s at 4.7 V indicating the low characteristic frequency and the extremely high resistance to the Li_2O removal reaction.

Figure 13. Variations of time constants of charge transfer resistances vs. OCV levels for the first charge.

Figure 14. Equivalent circuit model derived from the DRTs method. The open black circles denote the measured EIS data and the thick purple line was the calculated cumulative impedance by the combination of the individual loss processes, including R_{SEI} (painted in red), R_E (painted in blue), R_{CT} (painted in olive), lithium ion diffusion resistance (painted in green).

Finally, the identification of all relevant loss processes and the determination of their electrode origin led to an equivalent circuit. Furthermore, based on the obtained polarization and characteristic frequency of a particular loss process, the EIS can be recovered. To test the validity and the accuracy of the deconvolution method, taking the EIS spectrum measured at 3.6 V for example. Three R-Q elements in serial, representing the three major loss processes P_{SEI} , P_E and P_{CT-Ni} in ascending order of the time constant, as well as a serial finite-length-Warburg element, were constructed as the equivalent circuit according to the parameters determined by DRTs analysis. Therefore, the EIS profile was retrieved in figure 14. Three consecutive flattened semicircles represented the individual loss processes. The line marked with green circles at the end of the three consecutive semicircles

represented the solid-state diffusion of lithium ions modelled by finite-length-Warburg element. The black circles were measured data points and the purple line was the summation of the equivalent circuit $R_S(R_{SEI}Q_{SEI})(R_EQ_E)(R_{CT-Ni}Q_{CT-Ni}) \times Z_{flw}$. The purple line matched the experimental data points pretty well.

5. Conclusion

1. Co^{3+} -substituted lithium-rich cathode material $Li[Ni_{0.2-x}Li_{0.2}Co_{2x}Mn_{0.6-x}]O_2$ ($x = 0.1$) was successfully synthesized by an easy PAM-assisted sol-gel method. It showed improved rate capability and cycling performance compared with those of $0.5Li_2MnO_3 \cdot 0.5LiNi_{0.5}Mn_{0.5}O_2$ matrix.
2. A reliable deconvolution method was put forward and EIS profiles were transformed to DRTs function. The DRTs method offered a higher resolution in the frequency domain, allowing a clearer identification of the loss processes and the determination of electrochemical mechanisms. For the initial charge process, the rapid augmentation of resistance to electronic conduction and charge transfer within the voltage range 4.46–4.7 V where the removal of Li_2O from Li_2MnO_3 component takes place is the most remarkable. This gives us more evidence about the complicated ‘structurally integrated’ composite character of the material. The results also showed that Co^{3+} doping greatly reduced the resistance to electronic conduction R_e .
3. The variations of time constant of P_{SEI} , P_E and P_{CT} exhibited the same trend as the variations of their resistances.

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