Exploring the Effect of a MnO₂ Coating on the Electrochemical Performance of a Li₁₂Mn₀.₅₄Ni₀.₁₃Co₀.₁₃O₂ Cathode Material

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Abstract: The effect of electrochemically active MnO₂ as a coating material on the electrochemical properties of a Li₁₂Mn₀.₅₄Ni₀.₁₃Co₀.₁₃O₂ (LTMO) cathode material is explored in this article. The structural analysis indicated that the layered structure of the LTMO was unchanged after the modification with MnO₂. The morphology inspection demonstrated that the rod-like LTMO particles were encapsulated by a compact coating layer. The MnO₂ layer was able to hinder the electrolyte solution from corroding the LTMO particles and optimized the formation of a solid electrolyte interface (SEI). Meanwhile, lithium ions were reversibly inserted into and extracted from MnO₂, which afforded an additional capacity. Compared with the bare LTMO, the MnO₂-coated sample exhibited enhanced electrochemical performance. After the MnO₂ coating, the first discharge capacity rose from 224.2 to 239.1 mAh/g, and the initial irreversible capacity loss declined from 78.2 to 46.0 mAh/g. Meanwhile, the cyclic retention climbed up to 88.2% after 100 cycles at 0.5 C, which was more competitive than that of the bare LTMO with a value of 71.1%. When discharging at a high current density of 2 C, the capacity increased from 100.5 to 136.9 mAh/g after the modification. These investigations may be conducive to the practical application of LTMO in prospective automotive Li-ion batteries.

Keywords: lithium-rich cathode material; surface modification; manganese dioxide; electrochemical performance

1. Introduction

Developing high-energy-density secondary batteries to appease the increasing consumption of electronic apparatuses and electric vehicles is the responsibility of battery researchers [1,2]. In the last two decades, Li-rich Mn-based solid-solution cathode materials of nLi₂MnO₃·(1−n)LiTMO₂ (0 < n < 1, TM = Mn, Ni, Co, Mn₀.₅Ni₀.₅, Mn₀.₃₃₃Ni₀.₃₃₃Co₀.₃₃₃, etc.) with a layered structure have drawn much attention, which has been ascribed to their outstanding specific capacity [3–5]. The nLi₂MnO₃·(1−n)LiTMO₂ materials are made up of a monoclinic Li₂MnO₃ component (C2/m) and a layered LiTMO₂ component (R-3m) [6,7]. Usually, the two-component notation nLi₂MnO₃·(1−n)LiTMO₂ can be denoted as a layered type of Li₁₄₊ₙTM₁−ₙO₂ [8]. The cutoff voltage of Li₁₊ₙTM₁−ₙO₂ is high—up to 4.6–4.8 V—because the Li₂MnO₃ component must undergo an activation over 4.5 V to generate an extra reversible capacity, enabling Li₁₊ₙTM₁−ₙO₂ to achieve a much higher specific capacity than that of the LiTMO₂ component [4,9].

As one of the most representative types of Li₁₊ₙTM₁−ₙO₂, Li₁₂Mn₀.₅₄Ni₀.₁₃Co₀.₁₃O₂ (LTMO, or denoted as 0.5Li₂MnO₃·0.5LiMn₀.₃₃₃Ni₀.₃₃₃Co₀.₃₃₃O₂) can release a competitive capacity of 220–280 mAh/g at 2.0–4.8 V [10–12], and it is considered to be one of the preferred cathode materials for prospective automotive Li-ion batteries. However, LTMO still suffers from several shortcomings that limit its practical application [8–11]. During the first charge, the movement of transition metal ions eliminates oxide ion vacancies generated by the deintercalation of lithium as Li₂O in the Li₂MnO₃ over 4.5 V, which gives rise to a decrease in lithium-ion sites for Li⁺ to be reinserted during the first discharge [3,13].
The reduced insertion of lithium ions, along with the growth of a thick solid electrolyte interface (SEI) layer caused by the side reaction between the LTMO particles and electrolyte, brings about a large initial irreversible capacity loss for the LTMO [4,6]. Meanwhile, the continuous corrosion of the electrolyte on the LTMO surface at a high cut-off voltage of 4.8 V severely deteriorates the cyclic performance [9,14]. Moreover, the LTMO demonstrates an unsatisfied rate capability, which is ascribed to the poor conductivity for the electrons and lithium ions of the Li$_2$MnO$_3$ component [7,11].

Currently, many approaches have been implemented to upgrade the electrochemical properties of LTMO, including morphology optimization [15–17], ion doping [18–22], surface coating [10,11,13,14,23–34], and special treatment [35–38]. Among the above-mentioned strategies, modification of the surface of LTMO particles with inert metal oxides has been testified to remarkably enhance the cyclic performance, such as with ZrO$_2$ [10], TiO$_2$ [25], Al$_2$O$_3$ [23,26], MgO [27], ZnO [28], Pr$_6$O$_{11}$ [29], and Er$_2$O$_3$ [30]. The above chemically stable metal oxides not only stabilize the interface of LTMO particles, but also act as an effective barrier in order to inhibit the etching by the electrolyte [10,23,25–30]. Nevertheless, owing to the electrochemical inertness properties of these metal oxides, the coating layer will reduce the initial specific capacity of LTMO to some extent [10,25–30].

MnO$_2$ is a well-known electrochemically active oxide that has been widely applied as an active material for the research fields of supercapacitors [39], electrocatalysis [40], and lithium-ion batteries [41]. Recently, the function of MnO$_2$ has extended to become a surface modification material on cathode materials, such as LiMn$_2$O$_4$ [42], Li$_3$V$_2$(PO$_4$)$_3$ [43], and LiMn$_{0.333}$Ni$_{0.333}$Co$_{0.333}$O$_2$ [44], in order to obtain a better electrochemical performance. Firstly, the stable MnO$_2$ protective layer can hinder the electrolyte from corroding the cathode particles and can optimize the formation of the SEI layer [42–44]. Furthermore, lithium ions can be inserted into and extracted from the electrochemically active MnO$_2$ under 3 V, which affords an additional capacity and benefits the Li$^+$ transfer from the interface of the cathode particle to the electrolyte [44].

Inspired by such research, this article explores the impacts of MnO$_2$ as a surface modification material on LTMO particles. The structures and morphologies of LTMO before and after MnO$_2$ modification are thoroughly examined. In addition, the electrochemical properties, such as the specific capacity, initial irreversible capacity loss, cyclic stability, rate capability, and electrochemical impedance spectroscopy, are systematically investigated and discussed.

2. Materials and Methods

2.1. Preparation of Bare LTMO

The bare LTMO cathode material was synthesized as follows: Firstly, stoichiometric amounts of manganese sulfate monohydrate, nickel sulfate hexahydrate, and cobalt sulfate heptahydrate were put into distilled water and stirred continuously to generate a homogeneous solution (1 mol/L). Then, 1 mol/L sodium carbonate solution and 0.3 mol/L ammonium hydroxide were slowly dropped into the above solution. After being stirred at 60 $^\circ$C for 0.5 h and 30 $^\circ$C for 12 h, the coprecipitated carbonate precursor was filtered and then rinsed with distilled water. After drying at 80 $^\circ$C for one day, the filtered powder was thoroughly blended with lithium carbonate, then heated at 500 $^\circ$C for 5 h and calcined at 900 $^\circ$C for 15 h in air atmosphere to form LTMO.

2.2. Preparation of MnO$_2$-Coated LTMO

The MnO$_2$-coated LTMO was prepared as follows: Initially, the LTMO was put into the manganese sulfate solution and stirred vigorously for 0.5 h. Then, an aqueous solution of sodium carbonate was dropped slowly into the above suspension to precipitate manganese carbonate. The obtained slurry was filtered and rinsed with distilled water, subsequently dried at 80 $^\circ$C for 2 days, and then heated at 400 $^\circ$C for 2 h in air atmosphere to get the MnO$_2$-coated LTMO material with 3 wt % MnO$_2$. 
2.3. Material Characterization

The materials were characterized by using X-ray diffraction (XRD, D8-Advance, Bruker, Karlsruhe, Baden-Württemberg, Germany) (2θ degree: 10–70°, operating rate: 4°/min). The particle micro-morphologies were inspected by using field-emission scanning electron microscopy (FESEM, Sirion 200, FEI, Hillsboro, OR, USA), and the elemental distribution was probed with energy-dispersive spectroscopy (EDS, SU8010, HITACHI, Tokyo, Japan). The specific amounts of transition metal ions were determined by using inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 7000 DV, PerkinElmer, Waltham, MA, USA). The MnO$_2$ coating layer on the LTMO particles was surveyed by using transmission electron microscopy (TEM, Philips CM12, Philips, Amsterdam, Noord-Holland, Netherlands).

2.4. Electrochemical Evaluations

CR2016 coin cells were fabricated to evaluate the electrochemical properties. To prepare the LTMO (bare and MnO$_2$-coated) electrodes, active cathode powder (85 wt %), conductive carbon (10 wt %), and polytetrafluoroethylene (PTFE) (5 wt %) were mixed and continuously rolled to obtain a thin sheet. Subsequently, the thin sheet was separated into several circular films and dried at 120 °C in a vacuum to produce the electrodes. The diameter and mass loading of the LTMO (bare and MnO$_2$-coated) electrodes were 8 mm and 5–6 mg/cm$^2$. The cells were fabricated with the electrodes, metallic lithium sheet, separator (Celgard 2400), and carbonate-based electrolyte (1 mol/L LiPF$_6$ in the solvents consisting of ethylene carbonate and dimethyl carbonate with the volume ratio of 1:1) under an argon atmosphere. The galvanostatic charge/discharge evaluations were implemented at ambient temperature on an electrochemical test system (CT2001A, Wuhan Land) at 2.0–4.8 V with various current densities (1 C = 250 mA/g). Electrochemical impedance spectroscopy (EIS) was assessed by utilizing a CorrTest electrochemical workstation (frequency: 100,000–0.01 Hz, amplitude: 10 mV).

3. Results and Discussion

3.1. Structures of Bare and MnO$_2$-Coated LTMO

The XRD results for the bare and MnO$_2$-coated LTMO are exhibited in Figure 1. All of the diffraction peaks (excluding the peaks from 20° to 25°) of both samples belonged to the layered LiMn$_{0.333}$Ni$_{0.333}$Co$_{0.333}$O$_2$ component with a hexagonal α-NaFeO$_2$ structure (R-3m) [13]. The weak peaks (020) and (110) located at the degree of 20–25° indicate the existence of the monoclinic Li$_2$MnO$_3$ component (C2/m) [27]. The (006)/(012) and (018)/(110) peaks displayed obvious separation in the bare and MnO$_2$-coated LTMO, proving the excellence of the layered structure [15,20].

The lattice parameters of the bare and MnO$_2$-coated LTMO from XRD patterns are presented in Table 1. Since the ion radii of Ni$^+$ and Li$^+$ were very close, cation mixing may have occurred in the preparation process of the materials. If the values of $c/a$ and $I_{(003)}/I_{(104)}$ of 4.96 and 1.2 cannot be achieved, this implies that partial cation mixing exists in a material [16]. Notably, the $c/a$ and $I_{(003)}/I_{(104)}$ of both materials demonstrated values higher than 4.99 and 2.2, respectively, indicating the low degree of cation mixing for the bare and MnO$_2$-coated LTMO. Furthermore, no distinct XRD peaks were indexed to MnO$_2$ in the MnO$_2$-coated LTMO, which may have been caused by the low amount and poor crystallinity of MnO$_2$ [42–44]. The XRD results illustrate that the MnO$_2$ coating did not damage the lattice structure of the LTMO.


3.2. Microscopic Morphologies of Bare and MnO$_2$-Coated LTMO

The field-emission scanning electron microscopy (FESEM) images of the LTMO particles before and after the MnO$_2$ modification are shown in Figure 2 with different magnifications. The images in Figure 2a,c show that both samples comprised well-crystallized particles, and the particles presented a rod-like morphology with lengths in the range of 300–1000 nm. The bare LTMO particles all displayed clean and smooth surfaces at high magnification (Figure 2b). In contrast, the MnO$_2$-coated LTMO particles exhibited ambiguous and rough surfaces, which were ascribed to the coarse coating layer (Figure 2d).

The elemental distributions of Mn, Ni, and Co in the bare and MnO$_2$-coated LTMO particles are shown in Figure 3. For both samples, the transition metal elements were uniformly dispersed in the particles. Moreover, the ICP-AES test was applied to examine the elemental composition of transition metal ions in the two samples, and the measured values are presented in Table 2. The atomic ratio in the bare LTMO was almost identical to the theoretical stoichiometric ratio of Mn, Ni, and Co (0.54:0.13:0.13). It should be noted that the content of the Mn element in the MnO$_2$-coated LTMO was 3.327%, which was higher than in the bare simple. This result originated from the added MnO$_2$ coating layer and was very close to the designed amount of the coated Mn element (3 wt %) in this article.

![Figure 1. XRD results of bare and MnO$_2$-coated LTMO.](image)

Table 1. Lattice parameters of the LTMO before and after the MnO$_2$ modification.

| Sample          | $a$ (Å) | $c$ (Å) | $c/a$ | $I_{(003)}/I_{(104)}$ |
|-----------------|---------|---------|-------|-----------------------|
| Bare            | 2.8501  | 14.2384 | 4.9958| 2.24                  |
| MnO$_2$-coated  | 2.8508  | 14.2364 | 4.9938| 2.26                  |

Table 1. Lattice parameters of the LTMO before and after the MnO$_2$ modification.

The XRD results of bare and MnO$_2$-coated LTMO are shown in Figure 1. The lattice parameters are presented in Table 1. The atomic ratio in the bare LTMO was almost identical to the theoretical stoichiometric ratio of Mn, Ni, and Co (0.54:0.13:0.13). It should be noted that the content of the Mn element in the MnO$_2$-coated LTMO was 3.327%, which was higher than in the bare simple. This result originated from the added MnO$_2$ coating layer and was very close to the designed amount of the coated Mn element (3 wt %) in this article.
Figure 3. The elemental distributions of Mn, Ni, and Co in the bare and MnO$_2$-coated LTMO particles.

The ICP-AES test was applied to examine the elemental composition of the bare and MnO$_2$-coated LTMO determined with ICP-AES. The measured atomic ratio values are presented in Table 2. The atomic ratio in the bare LTMO was noted to the theoretical stoichiometric ratio of Mn, Ni, and Co values are presented in Table 2. The atomic ratio in the bare LTMO particles are shown in Figure 3.

Moreover, compared to the smooth surface appearing in the bare sample at high magnification (Figure 4b), it can be seen that the MnO$_2$-coated LTMO in Figure 4d was coated with a compact and distinguishable layer with a thickness from 10 to 50 nm. The compact coated layer was able to encapsulate the LTMO particles to constrain the side reaction and erosion caused by the electrolyte [42–44].
Figure 4. TEM images of the (a,b) bare and (c,d) MnO₂-coated LTMO particles.

3.3. The Electrochemical Characteristics of Bare and MnO₂-Coated LTMO at 0.05 C

Figure 5 displays the electrochemical characteristics of the bare and MnO₂-coated LTMO at 0.05 C for the first two cycles. The first charge curve shows no evident change after MnO₂ coating. Both curves have an inclined plateau at less than 4.5 V and a gentle plateau over 4.5 V (Figure 5a,b), which always appears in LTMO [3,4]. The inclined voltage plateau is derived from the variations of Ni²⁺ to Ni⁴⁺, as well as Co³⁺ to Co⁴⁺, in the LiMn₀.₃₃₃Ni₀.₃₃₃Co₀.₃₃₃O₂ component [31]. The gentle plateau emerged only in the first charge process, reflecting the activation of the Li₂MnO₃ component, and was accompanied by the removal of Li₂O [3,7,13,17]. As for the first discharge curves, the MnO₂-coated LTMO exhibited a small potential plateau around 2.8 V, but not in the bare sample. Meanwhile, an additional corresponding charge plateau around 2.9 V occurred in the second charge curve for only the MnO₂-coated sample.

The dQ/dV profiles for the first two cycles of the LTMO before and after MnO₂ coating are depicted in Figure 5c,d. For the dQ/dV profiles of the bare and MnO₂-coated LTMO during the initial charge, the anodic peak at 4.0 V was correlated to the inclined plateau in the charge curve (Figure 5a,b), and another peak at 4.5 V was associated with the gentle plateau. Moreover, a cathodic peak at 2.8 V and an anodic peak at 2.9 V appeared in the dQ/dV profiles of the MnO₂-coated LTMO (Figure 5d), while these two peaks could not be found for the bare sample (Figure 5c), which is in keeping with the information in Figure 5a,b. According to the previous literature [44], these phenomena could stem from the insertion of Li⁺ into the coated MnO₂ in the first discharge process and reversible extraction in the following charge process. The results prove that the MnO₂ layer with electrochemical activity was well coated on the surface of the LTMO.
The charge and discharge capacities of the bare LTMO were 302.4 and 224.2 mAh/g, respectively (Figure 5a). In contrast, although the charge capacity of the MnO$_2$-coated LTMO decreased to 285.1 mAh/g, the discharge capacity climbed up to 239.1 mAh/g (Figure 5b). Consequently, after surface coating, the irreversible capacity loss fell from 78.2 to 46.0 mAh/g, while the coulombic efficiency rose from 74.1% to 83.9%. The electrochemical redox process of the MnO$_2$ coating layer could be partially responsible for the enhanced first discharge capacity and the reduced initial irreversible capacity loss. Furthermore, the growth of the SEI was reduced, which was ascribed to the repression of the side reaction between the LTMO particles and electrolyte by the MnO$_2$ modification, which can be another benefit for the promoted electrochemical performance [42–44].

3.4. The Cyclic Performance of Bare and MnO$_2$-Coated LTMO

Figure 6 displays the cyclic performance of the bare and MnO$_2$-coated LTMO at 0.5 C for 100 cycles after an activation process at 0.05 C for two cycles. The cyclic performance at 0.5 C of the LTMO cathode was remarkably enhanced after the MnO$_2$ coating (Figure 6a). Specifically, the bare LTMO delivered 145.6 and 103.5 mAh/g for the first and 100th cycles, and the corresponding retention was 71.1%. In contrast, the MnO$_2$-coated LTMO released a higher capacity of 181.5 mAh/g at the first cycle and retained 160.1 mAh/g at the end with a retention rate of 88.2%. In addition, the MnO$_2$-coated sample exhibited less polarization compared to the bare one as the cycle proceeded (Figure 6b,c). Since MnO$_2$ can hinder the direct contact between the LTMO particles and the electrolyte [42–44], the superior cyclic stability after the surface coating was due to the inhibition of electrolyte corrosion on the surface of LTMO at high potential. Similarly to the metal oxides reported in previous
studies (Table 3), MnO$_2$ can evidently improve the electrochemical performance of LTMO, and especially has the advantage of reducing the initial irreversible capacity loss.

Figure 6. (a) Cyclic performance at 0.5 C. Charge and discharge curves of the (b) bare LTMO and (c) MnO$_2$-coated LTMO for different cycles.

Table 3. Comparison of the data of MnO$_2$ with other metal oxides reported as coating materials for LTMO.

| Coating Material [References] | Initial Irreversible Capacity Loss (mAh/g) | Cyclic Retention |
|------------------------------|------------------------------------------|-----------------|
|                              | Bare Sample | Coated Sample | Bare Sample | Coated Sample |
| This work MnO$_2$ (3 wt %)   | 78.2        | 46            | 85.4% (50 cycles) | 94.3% (50 cycles) |
| ZrO$_2$ (1 wt %) [10]        | ~70.3       | ~71.9         | 87.5% (50 cycles) | 94.9% (50 cycles) |
| Al$_2$O$_3$ (3 wt %) [23]    | 75          | 41            | 89.5% (50 cycles) | 94% (50 cycles) |
| TiO$_2$ (3 mol %) [25]       | 75.5        | ~60           | 63% (90 cycles) | 87% (90 cycles) |
| MgO (2 wt %) [27]            | 74.1        | 73.7          | 70.7% (100 cycles) | 96.4% (100 cycles) |
| ZnO (20 ALD layers) [28]     | 77.5        | 50.8          | 85.3% (100 cycles) | 97.5% (100 cycles) |
| Pr$_6$O$_{11}$ (3 wt %) [29] | 73.1        | 47.8          | 79.2% (50 cycles) | 97.9% (50 cycles) |
| Er$_2$O$_3$ (4 wt %) [30]    | 64          | 55            | 84% (300 cycles) | 89% (300 cycles) |

3.5. The Rate Capabilities of Bare and MnO$_2$-Coated LTMO

The bare and MnO$_2$-coated LTMO were successively tested at 0.05, 0.5, 1, 2, and 0.5 C to evaluate their rate capabilities. As exhibited in Figure 7a, the MnO$_2$-coated LTMO delivered an elevated capacity in comparison with the bare sample at all C rates. Moreover, as the C rate increased, the discharge midpoint voltage difference between the MnO$_2$-coated LTMO and the bare LTMO showed an upward tendency (Figure 7b), and the discharge
curves of the bare sample (Figure 7c) exhibited more polarization compared to the MnO$_2$-coated sample (Figure 7d). The detailed discharge capacities of the bare LTMO at 0.05, 0.5, 1, and 2 C were 221.7, 143.7, 125.0, and 100.5 mAh/g, respectively. In contrast, the MnO$_2$-coated LTMO was able to deliver improved capacities of 242.8, 178.3, 161.8, and 136.9 mAh/g under identical test conditions.

![Figure 7](https://example.com/figure7.png)

**Figure 7.** The electrochemical properties of the bare and MnO$_2$-coated LTMO evaluated at various C rates. (a) The rate capabilities. (b) The discharge midpoint voltage. (c,d) Discharge curves.

### 3.6. The EIS Measurements of Bare and MnO$_2$-Coated LTMO

To seek the origin of the enhanced electrochemical properties, EIS experiments were conducted on the bare and MnO$_2$-coated LTMO. Before the EIS tests, both the bare and MnO$_2$-coated samples were charged to 4.6 V after 40 cycles at 0.5 C to achieve an identical status. Figure 8 demonstrates the obtained and fitted Nyquist plots, as well as the equivalent circuit. Similarly, the EIS spectra of the bare and MnO$_2$-coated LTMO exhibited a pair of well-defined semicircles and a short, straight line that rose slowly. The intersection between the left side of the initial semicircle and the x-axis reflects the total ohmic resistance ($R_o$) [45]. The initial semicircle in the high frequency reflects the impedance ($R_{sd}$) for Li$^+$ transmission through the interfacial film (SEI layer) of the cathode particle, and the subsequent semicircle in intermediate frequency indicates the resistance of the charge transfer reaction ($R_{ct}$). The short line in the low frequency is relevant with the Warburg impedance ($Z_w$), which reflects Li$^+$ diffusion inside the cathode particles [28,46].
3.6. The EIS Measurements of Bare and MnO$_2$-coated LTMO

To seek the origin of the superior electrochemical performance of the MnO$_2$-coated LTMO, a Li-rich layered cathode material, LTMO, was prepared and then successfully coated with MnO$_2$. Firstly, the MnO$_2$ coating layer can inhibit the electrolyte from corroding the LTMO surface and can optimize the formation of SEI. Moreover, lithium ions are reversibly inserted into/extracted from MnO$_2$, which affords an additional capacity. Compared with the bare LTMO, the MnO$_2$-coated sample displayed a better first discharge capacity, lower initial irreversible capacity loss, superior cyclic performance, and promoted rate capability. After the MnO$_2$ coating, the first discharge capacity rose from 224.2 to 239.1 mAh/g, and the initial irreversible capacity loss fell from 78.2 to 46.0 mAh/g. Furthermore, the MnO$_2$-coated LTMO delivered a cyclic retention of 88.2% after 100 cycles at 0.5 C, which is more competitive than that of the bare LTMO with a value of 71.1%. At a high current density of 2 C, the discharge capacity increased from 100.5 to 136.9 mAh/g after the modification with MnO$_2$. The EIS results illustrate that the electrochemically active MnO$_2$ can enhance the transmission kinetics of lithium ions through the interfacial film and can speed up the charge transfer reaction. Therefore, MnO$_2$ should be a beneficial surface modification material for promoting the electrochemical properties of LTMO.

Figure 8. Nyquist plots of the bare and MnO$_2$-coated LTMO and the equivalent circuit for fitting.

The fitted values of $R_a$, $R_{sf}$, and $R_{ct}$ are listed in Table 4. $R_a$, which contains the impedance of the two electrodes, separator, and electrolyte, showed close values for the two samples. Nonetheless, the values of $R_{sf}$ and $R_{ct}$ for the MnO$_2$-coated sample were 39.7 and 167.8 $\Omega$, exhibiting values that remarkably declined compared to those of the bare one (94.5 and 422.6 $\Omega$). The side reaction occurring on the cathode surface with the electrolyte was significantly impaired after the MnO$_2$ modification, leading to a decrease in $R_{sf}$ [42]. Furthermore, the electrochemically active MnO$_2$ coating layer was conducive to Li$^+$ transport [43,44], together with the reduced $R_{sf}$, which accounted for the decrease in $R_{ct}$ for the coated sample. The EIS results demonstrate that the coated MnO$_2$ was able to accelerate the transmission kinetics of Li$^+$ through the interfacial film and speed up the charge transfer reaction, revealing the origin of the superior electrochemical performance of the MnO$_2$-coated LTMO.

Table 4. Lattice-fitted values of the parameters according to the equivalent circuit.

| Sample          | $R_a$ ($\Omega$) | $R_{sf}$ ($\Omega$) | $R_{ct}$ ($\Omega$) |
|-----------------|------------------|---------------------|---------------------|
| Bare            | 10.3             | 94.5                | 422.6               |
| MnO$_2$-coated  | 9.6              | 39.7                | 167.8               |

4. Conclusions

In summary, a Li-rich layered cathode material, LTMO, was prepared and then successfully coated with MnO$_2$. Firstly, the MnO$_2$ coating layer can inhibit the electrolyte from corroding the LTMO surface and can optimize the formation of SEI. Moreover, lithium ions are reversibly inserted into/extracted from MnO$_2$, which affords an additional capacity. Compared with the bare LTMO, the MnO$_2$-coated sample displayed a better first discharge capacity, lower initial irreversible capacity loss, superior cyclic performance, and promoted rate capability. After the MnO$_2$ coating, the first discharge capacity rose from 224.2 to 239.1 mAh/g, and the initial irreversible capacity loss fell from 78.2 to 46.0 mAh/g. Furthermore, the MnO$_2$-coated LTMO delivered a cyclic retention of 88.2% after 100 cycles at 0.5 C, which is more competitive than that of the bare LTMO with a value of 71.1%. At a high current density of 2 C, the discharge capacity increased from 100.5 to 136.9 mAh/g after the modification with MnO$_2$. The EIS results illustrate that the electrochemically active MnO$_2$ can enhance the transmission kinetics of lithium ions through the interfacial film and can speed up the charge transfer reaction. Therefore, MnO$_2$ should be a beneficial surface modification material for promoting the electrochemical properties of LTMO.
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