Improved electrochemical performance of LiMn_2O_4 surface-modified by a Mn^{4+} -rich phase for rechargeable lithium-ion batteries

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Abstract

The surface of spinel LiMn_2O_4 is modified with different quantities of a Mn^{4+} -rich phase prepared by a facile sol-gel method to improve electrochemical properties at elevated temperatures. Impurity-free and uniform morphologies for the LiMn_2O_4 particles are demonstrated from the X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The Mn^{4+} -rich phase modified on the surface of the LiMn_2O_4 alleviates the dissolution of manganese in the electrolyte, thus improving the cycling performance and rate capability relative to the bare LiMn_2O_4 . 1 wt.-%-modified LiMn_2O_4 delivers a capacity retention of 92.7% and a discharge capacity of 113.5 mAhg^{-1} after 200 cycles at 1 C and 25°C , compared with that of 83.1%, and 100.8 mAhg^{-1} for the bare LiMn_2O_4 . In addition, after 100 cycles, a capacity retention of 88.6% at 1 C is achieved for 1 wt.-%-modified LiMn_2O_4 at 55°C , which is higher than the 76.0% for the bare LiMn_2O_4 . Furthermore, this sample shows the best rate capability among all samples. The Mn^{4+} -rich phase is an appropriate candidate for modifying surfaces to suppress dissolution of manganese, thereby improving the electrochemical properties of LiMn_2O_4 .

Keywords: Li-ion battery, LiMn_2O_4 , Mn^{4+} -rich phase, surface modification

1. Introduction

Lithium manganese oxide, LiMn_2O_4 , having a spinel structure is an attractive cathode material for rechargeable Li-ion batteries because of its low cost, environmental friendliness, natural abundance, and good safety compared with commercialized LiCoO_2 [1–3]. LiMn_2O_4 cathode materials undergo severe capacity fading during repeated cycling, particularly at elevated temperatures, which restricts its commercial usage for rechargeable Li-ion batteries [4]. Capacity fading in the 4-V (versus Li/Li^+) region is connected with the following factors: structural instability induced by the Jahn-Teller distortion and manganese dissolution via the Mn^{3+} disproportionation reaction ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$). The latter is caused by a trace of hydrofluoric acid present in the electrolyte, which is the most important cause of capacity fading [5–8].

Two mainstream strategies have been proposed by academic and industrial scientists to overcome the capacity fading issue. First, cationic doping of a small fraction at the manganese sites has been investigated to stabilize the spinel structure. Single-doping of Ni^{2+} [9], Al^{3+} [10], Cr^{3+} [11], Sm^{3+} [12], Ru^{4+} [13] has been reported. Co-doping with Ni-Cu [14], Cr-Fe [15], Mg-Si [16], and La-Bi [17] has also been carried out. The results have shown that these doped LiMn_2O_4 spinel materials display enhanced stabilization of their structure and improved cycling performance compared with non-doped LiMn_2O_4 materials. However, this doping method could not eliminate the irreversible capacity loss associated with the dissolution of manganese at the cathode/electrolyte interface, especially at elevated temperatures [18].

The second approach is surface modification, which can minimize direct contact between the cathode and electrolyte interfaces, thereby effectively suppressing the dissolution of manganese [7,19]. Recently, Huang et al confirmed that the presence of Mn^{4+} on the surface of Mn-surface-modified $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$, synthesized by an in situ oxidizing-coating method, can suppress capacity fading during charge-discharge cycles at room and elevated temperature [20]. Jeong et al pointed out that the average Mn oxidation of ~ 3.69 on the surface of $\text{Li}_{1.15}\text{Co}_{0.32}\text{Mn}_{1.53}\text{O}_4$ -coated LiMn_2O_4 resulted in superior rate capability and improved capacity retention at 60°C [21]. Kang et al showed that Mn^{4+} in a MnO_2 coating layer can not only effectively suppress Mn dissolution, but also provide chemical stability, thereby improving storage and rate capability for MnO_2 -coated LiMn_2O_4 [22]. Therefore, the presence of Mn^{4+} on the surface of LiMn_2O_4 particles can considerably lessen the dissolution of Mn, and maintain the stability of LiMn_2O_4 , resulting in enhanced electrochemical performance. The Mn^{4+} -rich phase in this work is embodied in the form of Li_2MnO_3 , which is based on the several factors. Monoclinic Li_2MnO_3 , with its layered structure, acts as an indispensable component of the Li-rich layered $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($\text{M}=\text{Mn}, \text{Ni}, \text{Co}$) cathode material because of its stabilization function [23,24]. The Li_2MnO_3 cathode material, where interslab octahedral sites are occupied by Li only, and the octahedral sites within the slabs are occupied by both Li and Mn in a ratio of 1: 2 [25], supplies more mobile Li ions compared with others without Li ions in the structure. These mobile Li ions accessibly transport and permeate through the interslab channel into the electrolyte solution [26,27]. In addition, Li_2MnO_3 cathode materials consisting of

only Mn^{4+} shows a more stable structure resulting from the absence of the disproportionation reaction of Mn^{3+} that occurs in LiMn_2O_4 . Nanosized Li_2MnO_3 as the modification layer becomes active compared with its inactive status existing in micro-sized particles [28]. Xiong et al [27] reported that Li_2MnO_3 as an impurity appeared in Li/F co-doped spinel LiMn_2O_4 -based composites prepared by a solid state reaction, which Li_2MnO_3 -impurity was detected at the surface of the composites in TEM images. These complicated composites exhibited excellent cycling performance and high rate capability, which results from eliminating the Jahn-Teller distortion by double-doping with Li and F, and suppressing the disproportionation reaction of Mn^{3+} on the surface caused by the coated Li_2MnO_3 impurity. Given this, Mn^{4+} -rich phase is employed to modify the surface of LiMn_2O_4 particles to improve the electrochemical performance by decreasing the direct contact area at the cathode/electrolyte interface, thereby reducing the dissolution of manganese and stabilizing the structure.

In this work, a series of Mn^{4+} -rich phase-modified LiMn_2O_4 with weight ratios of 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.% were synthesized by a facile sol-gel method to ensure uniformity of the modified layers. The electrochemical properties at both 25 °C and 55 °C were investigated in detail.

2. Experimental

2.1 Preparation and characterization of Mn^{4+} -rich phase-modified LiMn_2O_4

LiMn_2O_4 powders were prepared by solution combustion synthesis (SCS) in combination with calcination [17,29,30]. Lithium nitrate (LiNO_3 , 99.0%, Kishida Chemical Co., Ltd., Japan), lithium acetate (CH_3COOLi , 99.0%, Kishida Chemical Co., Ltd., Japan), manganese nitrate ($\text{Mn}(\text{NO}_3)_2$, 50% w/w aqueous solution, Alfa Aesar), and urea (NH_2CONH_2 , 99.0%, Chameleon Reagent, Japan) were used as the raw materials without further purification. The oxidizers, LiNO_3 and $\text{Mn}(\text{NO}_3)_2$ (mole ratio of $\text{Li}:\text{Mn}=1.05:2$), and reductant, NH_2CONH_2 (with $\varphi=0.5$, φ is the ratio of the total valence of reductants to the total valence of nitrate oxidizers), were dissolved in 5 ml of distilled water. After evaporating the water, the homogenous sol-gels were self-ignited in a homemade combustion apparatus. Following the SCS, the collected powders were further calcined at 800 °C at a rate of 5 °C/min in air for 24 h to obtain the LiMn_2O_4 powders.

A facile sol-gel method was employed to achieve the modification of a Mn^{4+} -rich phase. Stoichiometric amounts of CH_3COOLi and $\text{Mn}(\text{NO}_3)_2$, required to produce Li_2MnO_3 , were homogeneously dissolved in distilled water with stirring at room temperature. This solution was then added dropwise to a well-dispersed LiMn_2O_4 aqueous solution that had been subjected to ultrasonic treatment. After evaporating the water, the resulting powders were sintered at 600 °C for 3 h in air to obtain the final powders. The weight percent of Li_2MnO_3 to LiMn_2O_4 were 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.%. For simplicity, these samples are labeled as 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.%,

respectively.

The phase structure of Mn^{4+} -rich phase-modified LiMn_2O_4 was characterized by powder XRD ($\text{Cu K}\alpha$, Rigaku Miniflex). The morphology and size of the powders were determined using SEM (JEOL, JSM-7001FA), and TEM (JEOL JEM-2010F). The surface composition of the samples was detected by X-ray photoelectron spectroscopy (XPS, JEOL Ltd., JPS-9200) using an $\text{Mg K}\alpha$ X-ray source (1253.6 eV).

2.2 Cell assembly and electrochemical measurements

A Swagelok-type cell consisting of a working electrode and a lithium metal anode, was assembled in an Ar-filled glove box, as described in our previous reports [29,30]. The working electrode consisted of 80 wt.% active material, 10 wt.% binder (PVDF) dissolved in N-methyl-2-pyrrolidone (NMP), and 10 wt.% conductive carbon (acetylene black). The diameter of the working electrode was 10 mm and its thickness was 0.1 mm. A lithium metal disk was chosen as the counter and reference electrode. The electrolyte was a solution of 1 M lithium hexafluorophosphate (LiPF_6) in EC/DMC (1:1 in volume). The separator was a Celgard polypropylene membrane. Electrochemical measurements were galvanostatically carried out in the voltage range of 3.2–4.4 V at different current densities (a rate of 1 C corresponding to a full charge/discharge of 150 mAhg^{-1} in 1 h) at 25 °C and 55 °C using a battery tester (Arbin Instruments, MSTAT4, USA). Cyclic voltammetry (CV) was performed by a potentiostat/galvanostat apparatus (Autolab, PGSTAT128N) in the voltage range of 3.2–4.4 V at a scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$, while the electrochemical impedance spectroscopy (EIS) was

conducted by employing an Autolab instrument with the frequency response analyzer (FRA), in the frequency range from 1000 kHz to 0.01 Hz after the 5 cycles of CV measurement scanning at 0.3 mV·s⁻¹

3. Results and discussion

Figure 1 shows XRD patterns of Mn^{4+} -rich phase-modified LiMn_2O_4 samples. All the diffraction peaks are consistent with the characteristic diffraction peaks of well-defined spinel LiMn_2O_4 with a space group of $Fd3m$. The absence of an impurity phase is noticed in the XRD patterns for all modified LiMn_2O_4 samples. This absence is probably due to low coating amounts and/or an amorphous texture [18,22]. Lattice parameters and cell volumes calculated by the MDI Jade Software are listed in Table 1 for all samples. No significant changes between the bare and modified LiMn_2O_4 samples indicate that surface modification has no effect on the structure of the spinel LiMn_2O_4 phase.

Figure 2 displays SEM images of Mn^{4+} -rich phase-modified LiMn_2O_4 samples. Similar morphologies and/or particle sizes are shown from the SEM images for all samples, reflecting no big changes after modification. Primary particles, showing sizes of 200–500 nm (Fig. 2 inset), agglomerate into secondary particles with sizes of 3–7 μm . In order to compare the modified layers on the surface of LiMn_2O_4 particles, TEM images of Mn^{4+} -rich phase-modified LiMn_2O_4 samples with amounts of 0 wt.% and 2 wt.% were recorded, and are displayed in Fig. 3. A distinct layer with a thickness of ~ 3 nm is visible on the particle surface of the modified LiMn_2O_4 sample, compared with the smooth particle surface of the bare LiMn_2O_4 sample. Electron diffraction patterns of the modified layer were undetectable in the modified LiMn_2O_4 sample, which is due to its amorphous texture. A modified layer on the particle surface, unfortunately, is invisible using TEM observation for the 1 wt.%-modified LiMn_2O_4 sample, which is likely attributable to the low quantities of the

Mn⁴⁺-rich phase.

XPS has been widely employed to analyze surface compositions, and to detect whether the Mn⁴⁺-rich phase exists on the surface of the spinel structure. Figure 4 shows the Mn 2p_{3/2} XPS spectra of Mn⁴⁺-rich phase-modified LiMn₂O₄ samples. The Mn 2p_{3/2} XPS binding energy for Mn³⁺ and Mn⁴⁺ is located at 641.7 eV (Mn₂O₃) and 642.6 eV (MnO₂), respectively [31–33]. After peak-fitting, binding energy, cation distribution of Mn³⁺ and Mn⁴⁺, and average valance of Mn are given in Table 2. As modified quantities rise in the order of 0 wt.%, 1 wt.%, 2 wt.% and 4 wt.%, Mn⁴⁺ amounts are increased and displayed the value of 49.0%, 70.7%, 81.1%, and 89.6%, whereas Mn³⁺ amounts show the diminishing values of 51.0%, 29.3%, 18.9%, and 10.4%. In addition, the average valance of Mn on the surface of the LiMn₂O₄ matrix also changes from 3.490 to 3.707, and 3.811, then to 3.896. The increased amounts of Mn⁴⁺ and the average valance of Mn are a result of the existence of Li₂MnO₃ on the surface, in which only Mn⁴⁺ exists. A Mn⁴⁺-rich phase on the surface of the particles can hold the stability and alleviate the dissolution of Mn via the disproportionation reaction of Mn³⁺ ($2\text{Mn}^{3+} \rightarrow \text{Mn}^{4+} + \text{Mn}^{2+}$), thereby enhancing the cycling performance of LiMn₂O₄ cathode materials.

The discharge capacity as a function of cycle number for Mn⁴⁺-rich phase-modified LiMn₂O₄ samples at 1 C and 25 °C is presented in Fig. 5. A serious capacity fading during cycling is observed for the bare LiMn₂O₄ sample, in which the 100.8 mAhg⁻¹ discharge capacity and 83.1% capacity retention are maintained at 1 C after 200 cycles. Improved cycling performance is displayed for the modified LiMn₂O₄ samples. A discharge capacity of 113.5 mAhg⁻¹, 109.9 mAhg⁻¹, 105.6 mAhg⁻¹,

and capacity retention of 92.7%, 94.0%, and 97.6% after 200 cycles, are delivered for the 1 wt.%, 2 wt.%, and 4 wt.%-modified LiMn_2O_4 samples, respectively. In the whole cycle number, the decreased discharge capacity as rising the modified mounts from 1 wt.% to 4 wt.% is observed, which can be attributed to the electrochemical inactive of Mn^{4+} -rich phase below the voltage of 4.4 V [23,34] and the hindered Li^+ diffusion due to the expanding diffusion path by the more modified layer [35]. The improved cycling performance can be ascribed to the alleviated dissolution of Mn in the electrolyte, and enhanced stability of the surface-modified structure. On the other hand, the 1 wt.%, 2 wt.%, and 4 wt.%-modified samples manifest capacity fading of 0.045 mAhg^{-1} , 0.035 mAhg^{-1} , and 0.013 mAhg^{-1} per cycle, respectively, compared with 0.103 mAhg^{-1} per cycle for the bare LiMn_2O_4 sample. A Mn^{4+} -rich phase can benefit the cycling stability of the spinel LiMn_2O_4 material.

The charge–discharge curves at different cycle numbers are demonstrated in Fig. 6, for Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 1 C and 25 °C. The curves for all samples present two obvious charge–discharge plateaus, indicating that two oxidation/reduction reactions occur during the Li extraction/insertion process. These two plateaus at 4.0–4.1 V and 3.9–4.0 V, correspond to the two-phase transitions of $\text{MnO}_2/\text{Li}_{0.5}\text{Mn}_2\text{O}_4$, and $\text{Li}_{0.5}\text{Mn}_2\text{O}_4/\text{LiMn}_2\text{O}_4$, respectively [36,37]. The voltage difference between the charge and discharge plateaus for the modified LiMn_2O_4 samples maintains the same as the cycle number increases from the first cycle to the 200th cycle, whereas the value for the bare LiMn_2O_4 sample increases slightly. These facts demonstrate a suppressed polarization increment and inner resistance of the batteries to the modified LiMn_2O_4 samples [38,39]. The surface-

modified samples experience less loss of the initial capacity, and better cycling performance.

CV curves of the first and third cycle for Mn^{4+} -rich phase-modified LiMn_2O_4 samples are exhibited in Fig. 7. All CV curves of these samples display two pairs of well-separated peaks, which correspond to the two plateaus in the charge–discharge curves of Fig. 6. This confirms that two reversible redox reactions occur during Li-ions extraction/insertion process. Similar CV curves confirm that surface-modified technology supports the unvaried electrochemical process of spinel structure during cycling. The potential values for the CV curves at the first cycle are shown in Table 3. The 0 wt.%, 1 wt.%, 2 wt.%, and 4 wt.%-modified LiMn_2O_4 samples manifest an anodic peak of 4.07/4.20 V, 4.07/4.19 V, 4.06/4.19 V, and 4.06/4.18 V together with a cathodic peak of 3.94/4.06 V, 3.96/4.08 V, 3.96/4.09 V, and 3.97/4.10 V, respectively. The decreased anodic potential, and increased cathodic potential as increasing the modified amounts, demonstrate that Li extraction (charge process) occurs at a lower potential value, whereas Li insertion (discharge process) occurs at a higher potential value. These results show that less energy is required for Li ion diffusion during cycling for the modified samples. ΔE_p is related to the polarization degree of the battery, and is the separation between the anodic peak potential, E_{pa} , and the cathodic peak potential, E_{pc} . The value of E_{p1}/E_{p2} decreases from 0.13/0.14 V for the 0 wt.%-modified sample to 0.11/0.11 V, and 0.10/0.10 V for the 1 wt.%- and 2 wt.%-modified samples, respectively, down to 0.09/0.08 V for the 4 wt.%-modified sample. These data indicate the weak polarization of the modified samples with assistance of the modified layers [40]. The Mn^{4+} -rich phase can suppress the dissolution of Mn and maintain the stability of the spinel structure during the

charge–discharge process.

A high rate capability is always a key criterion to evaluate the performance of cathode materials used in high-power, high-energy Li-ion batteries. Figure 8 shows the rate capability of Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 25 °C. As the current densities increase from 1 C to 7 C, a large decrease in the discharge capacity is observed for the bare LiMn_2O_4 sample, which results from the increased polarization of the batteries due to limited Li ion diffusion during cycling. By contrast, an improved rate capability is noticed for the Mn^{4+} -rich phase-modified LiMn_2O_4 samples, demonstrating the enhanced diffusion of Li ions and/or the conductivity of electrons via the Mn^{4+} -rich phase modified layers. In particular, the 1 wt. %- LiMn_2O_4 sample delivers the highest discharge capacity among all samples at each current density, which 98.0 mAhg^{-1} even at 7 C is obtained in contrast with 75.8 mAhg^{-1} of the bare LiMn_2O_4 sample. Meanwhile, the improved capacity retention (relative to 1 C) of this sample is 6.3% (2 C), 13.6% (3 C), 19.0% (4 C), 22.8% (5 C), and 28.6% (7 C) higher than that of the bare LiMn_2O_4 sample, respectively. The capacity retention as discharging from 2 C to 7 C, is increased in the order of 0 wt. % < 1 wt. % < 2 wt. % < 4 wt. %- LiMn_2O_4 sample, which indicates the Mn^{4+} -rich phase can suppress dissolution of manganese and keep the structural stability of LiMn_2O_4 material. As rising the modified quantities in the order of 1 wt. %, 2 wt. % and 4 wt. %, the decreased discharge capacity is noticed for these samples, which is corresponding to the trend in Fig. 5. The modified samples manifest a remarkable increase in capacity retention compared with the bare LiMn_2O_4 sample.

The discharge capacity as a function of cycle number for the 1 wt.%-modified LiMn_2O_4 sample at 1 C, 3 C, 5 C, and 7 C at 25 °C is presented in Fig. 9. A high discharge capacity of 108.7 mAhg^{-1} (1 C), 105.8 mAhg^{-1} (3 C), 101.8 mAhg^{-1} (5 C), and 90.4 mAhg^{-1} (7 C) is maintained even after 500 cycles. And the capacity retention (with reference to the highest capacity) of 88.8% (1 C), 93.2% (3 C), 93.9% (5 C), and 95.1% (7 C) is also delivered, which demonstrates a high rate performance.

High-temperature electrochemical performance is crucial to the practical application of LiMn_2O_4 cathode materials in Li-ion batteries. The discharge capacity as a function of cycle number for Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 1 C and 55 °C is shown in Fig. 10. The bare LiMn_2O_4 sample displays serious capacity fading during cycling at 55 °C, showing a capacity retention of only 76.0% after 100 cycles. In contrast, improved cycling performance at 55 °C is observed for the modified samples. This improvement is due to the minimization of the contact area between the active material and the electrolyte solution via the modified layers, thereby suppressing the dissolution of Mn and maintaining the stability of the overall structure. A capacity retention of 88.6%, 89.5%, and 91.9% is delivered in the 1 wt.%-, 2 wt.%-, and 4 wt.%-modified LiMn_2O_4 samples, respectively. The increased capacity retention at an elevated temperature, which is consistent with that obtained at 25 °C, is observed as raising the modified amounts. The reason is that the more modified amounts of Mn^{4+} -rich phase give rise to the less dissolution of manganese in the electrolyte solution and more stable of spinel structure, thereby resulting in the increased capacity retention at elevated temperature. The rate capability measured at 55 °C for the 0 wt.%- and 1 wt.%-modified LiMn_2O_4 samples is

given in Fig. 11. Compared with the bare LiMn_2O_4 sample, a markedly increased rate capability is noticed for the 1 wt. %-modified LiMn_2O_4 sample, experiencing a discharge capacity of 122.9 mAhg^{-1} (1 C), 118.9 mAhg^{-1} (2 C), 116.1 mAhg^{-1} (3 C), 113.5 mAhg^{-1} (4 C), 111.0 mAhg^{-1} (5 C), and 106.6 mAhg^{-1} (7 C). The improved discharge capacity retention (relative to 1 C), especially the value of 86.7% at 7 C, is higher than that of 59.3% for the bare LiMn_2O_4 sample. Compared with the rate capability at 25 °C, the higher rate capability at 55 °C is observed for the 1 wt. %-modified LiMn_2O_4 sample, which is ascribed to the fast mobility of Li ions at high temperature [39, 41]. Mn^{4+} -rich phase-modified LiMn_2O_4 samples demonstrate an improved electrochemical performance at a high temperature of 55 °C, in contrast to the bare LiMn_2O_4 sample.

In order to further investigate the conductivity and the Li ions diffusion in Mn^{4+} -rich phase-modified LiMn_2O_4 samples, electrochemical impedance spectroscopy (EIS) are carried out after the 5 cycles of CV measurements at the scan rate of $0.3 \text{ mV}\cdot\text{s}^{-1}$. Fig. 12 (a) manifests the Nyquist plots of Mn^{4+} -rich phase-modified LiMn_2O_4 samples, along with the equivalent circuit in the inset used to fit the spectra. As shown in the equivalent circuit, R_s is the ohmic resistance, which includes the electrolyte and electrode resistance, R_f represent the resistance for Li ion diffusion in the surface layer (solid electrolyte interphase (SEI) film, and Mn^{4+} -rich phase modified layer), R_{ct} is the resistance of the charge transfer. Constant phase elements, CPE_1 and CPE_2 , mean the capacitance of the surface layer, and the double-layer capacitance, respectively. CPE_3 , instead of the finite Warburg element, is chosen to properly fit the inclined line of the Nyquist plots in the low frequency region [42], which

is associated to the Li-ions diffusion from the surface to the center of the cathode particles. All impedance curves display a typical semicircle in the high and medium frequency region, which are assigned to the CPE_1-R_f , and CPE_2-R_{ct} , respectively. R_f and R_{ct} values simulated by *Zsimpwin* Software for Mn^{4+} -rich phase-modified $LiMn_2O_4$ samples are listed in Table 4. In particular, the lowest value of 5.19Ω for R_f , and 49.70Ω for R_{ct} are obtained in 2 wt.%-modified $LiMn_2O_4$ sample among all samples. The larger R_f of 4 wt.%-modified $LiMn_2O_4$ than that of 1 wt.%- and 2 wt.%-modified $LiMn_2O_4$ sample, is ascribed to the predomination of the hindered Li^+ diffusion via the thick modified layer due to the expanding Li^+ diffusion path, regardless of the enhanced Li ion diffusion via the retarded SEI film. These values are far less than that of 31.41Ω for R_f , and 62.05Ω for R_{ct} in 0 wt.%-modified $LiMn_2O_4$ sample. The decreased R_f and R_{ct} values of the surface-modified $LiMn_2O_4$ samples, in compare with the bare $LiMn_2O_4$ sample, indicates that the Mn^{4+} -rich phase-modified layer restrains the side reactions of the active material with the electrolyte solution, thereby retarding the formation of SEI film [43], and meanwhile improves the electronic conductivity of the electrode and electron transport during the electrochemical process [18], resulting in the improved cycling performance.

The Li^+ ion diffusion coefficient can be calculated according to the following equation:

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

Where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of the electrons per molecule in the redox process, F is the Faraday constant, C is the

Li^+ ion concentration in electrode material, σ is the slope of the line in the curves of Z' vs. $\omega^{-0.5}$ (shown in the Fig. 12 (b)). Note that, C can be derived by the following equation [44]:

$$C = \frac{n}{V} = \frac{(\rho V/M)}{V} = \frac{\rho}{M} \quad (2)$$

Where ρ is the volume density of the spinel, $\rho = 4.4 \text{ g}\cdot\text{cm}^{-3}$, and M is the molecular weight of the active material, $M=180.813 \text{ g}\cdot\text{mol}^{-1}$ [45]. Combined with equation (1) and (2), the Li^+ ion diffusion coefficient is calculated and shown in Table 4. The D_{Li^+} of $8.71 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$, $1.49 \times 10^{-11} \text{ cm}^2\text{s}^{-1}$, and $8.80 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$ is obtained for the 1 wt.%, 2 wt.%, and 4 wt.-%-modified LiMn_2O_4 samples, respectively, compared with that of $5.65 \times 10^{-12} \text{ cm}^2\text{s}^{-1}$ for the bare LiMn_2O_4 sample. The larger Li^+ ion diffusion coefficient in the modified LiMn_2O_4 active materials is achieved, which could be responsible for the improved electrochemical performance.

The SEM of the cycled electrodes are carried out for monitoring the effect of Mn^{4+} -rich phase layer on the stability of the spinel structure. Figure 13 manifests SEM of the cycled electrodes for 0 wt.%, and 4 wt.-%-modified LiMn_2O_4 samples, (a) and (b) before cycling, (c) and (d) after 200 cycling at 1 C, respectively. Compared with Fig. 13 (a), a large crack is observed on the surface of the bare LiMn_2O_4 electrode after 200 cycling, along with a crack on the particle of the active materials in the inset, which results from the electrolyte erosion and inferior structural stability [46,47]. However, the same morphology and structure of the electrode for 4 wt.-%-modified LiMn_2O_4 sample, in Fig.13 (b) and (d), are kept before and after the cycling. This demonstrates that Mn^{4+} -rich phase acts as a protective layer to suppress the electrolyte erosion and keep the structural stability, giving rise to the

improved cycling performance.

4. Conclusions

A series of Mn^{4+} -rich phase-modified LiMn_2O_4 samples were designed and then synthesized by a facile sol-gel method. Impurity-free and uniform morphologies were confirmed by the XRD and SEM, respectively. XPS demonstrated the existence of the Mn^{4+} -rich phase on the particle surface of the modified LiMn_2O_4 samples, which was detected by TEM. The improved cycling performance and rate capability both at 25 °C and 55 °C were achieved for the modified LiMn_2O_4 samples as contrast to the bare LiMn_2O_4 sample. The reason for the enhanced electrochemical performance was attributed to the characteristic of Mn^{4+} rich phase-modified layer: (1) acting as a protecting layer for alleviating the dissolution of manganese in the electrolyte and supporting the structural stability of spinel structure; (2) an efficient migration medium for more mobile Li ions. A high discharge capacity of 113.5 mAhg^{-1} , and capacity retention of 92.7% were observed in the 1 wt.-%-modified LiMn_2O_4 sample after 200 cycles at 1 C and 25 °C, compared with 100.8 mAhg^{-1} and 83.1% for the bare LiMn_2O_4 . After 100 cycles at 1 C, the discharge capacity retention at 55 °C was remarkably improved from 76.0% for the bare LiMn_2O_4 , to 88.6% for the 1 wt.-%-modified LiMn_2O_4 sample. It also manifested the highest rate capability. Hence, modifying the Mn^{4+} -rich phase on the surface of the particles of the spinel structure, is an effective method to achieve the excellent electrochemical performance for rechargeable Li-ion batteries.

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Figure captions

Fig. 1 XRD patterns of Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Fig. 2 SEM images of Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Fig. 3 TEM images of Mn^{4+} -rich phase-modified LiMn_2O_4 samples with (a) 0 wt.%, and (b) 2 wt.%.

Fig. 4 XPS spectra of Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Fig. 5 Discharge capacity vs. cycle number for Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 1 C and 25 °C.

Fig. 6 Charge–discharge curves of Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 1 C and 25 °C.

Fig. 7 CV curves of Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Fig. 8 Rate capability of Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 25 °C.

Fig. 9 Discharge capacity vs. cycle number for the 1 wt.%-modified LiMn_2O_4 sample at 1 C, 3 C, 5 C, and 7 C at 25 °C.

Fig. 10 Discharge capacity vs. cycle number for Mn^{4+} -rich phase-modified LiMn_2O_4 samples at 1 C and 55 °C.

Fig. 11 Rate capability of the 0 wt.%- and 1 wt.%-modified LiMn_2O_4 samples at 55 °C.

Fig. 12 (a) EIS measured after the 5 cycles of CV measurements at the scan rate of $0.3 \text{ mV}\cdot\text{s}^{-1}$, and (b) Z' vs. $\omega^{-0.5}$ plots at the low frequency region for Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Fig.13 SEM of the cycled electrodes for 0 wt.%, and 4 wt.%-modified LiMn_2O_4 samples, (a) and (b) before cycling, (c) and (d) after 200 cycling at 1 C, respectively.

Fig. 1

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Fig. 9

Fig. 10

Fig. 11

Fig. 12

Fig. 13

Table 1. Lattice parameters and cell volumes for Mn⁴⁺-rich phase-modified LiMn₂O₄ samples.

Sample	a (Å)	Cell volume (Å ³)
0 wt.%	8.2268(5)	556.80
1 wt.%	8.2225(6)	555.93
2 wt.%	8.2216(6)	555.75
4 wt.%	8.2144(1)	554.28

Table 2. Binding energy, cation distribution, and average valence of Mn from XPS (Mn-2p_{3/2} spectra) of Mn⁴⁺-rich phase-modified LiMn₂O₄ samples.

Sample	Binding energy (eV)		Cation distribution		Average valence
	Mn ⁴⁺	Mn ³⁺	Mn ⁴⁺ (%)	Mn ³⁺ (%)	Mn
0 wt.%	642.6	641.8	49.0	51.0	3.490
1 wt.%	642.5	641.4	70.7	29.3	3.707
2 wt.%	642.5	641.5	81.1	18.9	3.811
4 wt.%	642.6	641.1	89.6	10.4	3.896

Table 3. Potential values of the CV curves at the first cycle for Mn^{4+} -rich phase-modified LiMn_2O_4 samples.

Sample	E_{pa1} (V)	E_{pa2} (V)	E_{pc1} (V)	E_{pc2} (V)	ΔE_{p1} (V)	ΔE_{p2} (V)
0 wt. %	4.07	4.20	3.94	4.06	0.13	0.14
1 wt. %	4.07	4.19	3.96	4.08	0.11	0.11
2 wt. %	4.06	4.19	3.96	4.09	0.10	0.09
4 wt. %	4.06	4.18	3.97	4.10	0.09	0.08

ΔE_{p} represents the separation between the anodic peak potential, E_{pa} , and the cathodic peak potential, E_{pc} .

Table 4. R_f , R_{ct} , and D_{Li+} for Mn^{4+} -rich phase-modified $LiMn_2O_4$ samples.

Sample	$R_f(\Omega)$	$R_{ct}(\Omega)$	$D_{Li+} (cm^2s^{-1})$
0 wt. %	31.41	62.05	5.65×10^{-12}
1 wt. %	6.59	60.04	8.71×10^{-12}
2 wt. %	5.19	49.70	1.49×10^{-11}
4 wt. %	27.98	60.66	8.80×10^{-12}