

Enhanced High-Temperature Cycling Stability of LiMn_2O_4 by LiCoO_2 Coating as Cathode Material for Lithium Ion Batteries

Jing Yan¹, Haohan Liu^{2,3}, Yuelei Wang¹, Xinxin Zhao¹, Yiming Mi^{1*}, Baojia Xia³

¹College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, Shanghai, China

²Shanghai Nanotechnology Promotion Center, Shanghai, China

³Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai, China
Email: *biluo1873@163.com

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Abstract

LiCoO_2 surface layer is proposed and prepared through sol-gel method. The physical and electrochemical performances of pristine LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 cathode materials were investigated by X-ray diffraction, scanning electron microscopy, transmission electron microscopy, electrochemical measurements respectively. Comparing with the pristine LiMn_2O_4 , the LiCoO_2 -coated LiMn_2O_4 phase significantly improved cycling stability, especially at 55°C. Additionally, the thermal safety of LiMn_2O_4 is greatly enhanced after being coated by LiCoO_2 . ICP-AES measurement, structural analysis, and impedance experiments indicate that the improved electrochemical property of LiCoO_2 -coated LiMn_2O_4 should be attributed to the alleviated dissolution loss of manganese, strengthened structural stability.

Keywords

LiMn_2O_4 , Sol-Gel Method, Surface Coating, Electrochemical Performance

1. Introduction

Lithium ion battery (LIB) has become the most widely used power supply for electronics. Safer electrode material has been pursued by researchers for years [1]. Spinel lithium manganese oxide (LiMn_2O_4), with the advantages of abundant, nontoxic, and inexpensive, is a promising cathode material for power lithium ion battery mainly [2]. Especially, the good stability may ensure its large-scale usage in the batteries for electric vehicle or

*Corresponding author.

energy storage [3]. However, LiMn_2O_4 shows obvious capacity fade when high-temperature working condition is applied (50°C - 60°C) [4]. The cause for the capacity degradation of LiMn_2O_4 is Jahn-Teller distortion and accepted as electrolyte decomposition, Mn^{2+} ions dissolution [5], oxygen deficiency [6] [7]. In order to solve this problem, earlier studies have been focused on a chemical modification of LiMn_2O_4 by a partial substitution of Mn with some metal ions to obtain $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M = \text{Co}, \text{Mg}, \text{Cr}, \text{Ni}, \text{Fe}, \text{Al}, \text{Ti}$ and Zn) [8]-[12]. Another effective way is surface coating on LiMn_2O_4 by oxide with high thermal and structural stability. ZrO_2 , SiO_2 , Al_2O_3 and MgO [13]-[16] have been used to coat LiMn_2O_4 by some chemical processes. LiCoO_2 coating may suppress the dissolution of Mn and with de-intercalation and intercalation of Li ions, which will enhance the capacity of LiMn_2O_4 . Therefore, it is expected that the LiMn_2O_4 by coating LiCoO_2 will show an excellent cycle performance at high-temperature. In this study, the effect of LiCoO_2 layer on the morphology and electrochemical performances of LiMn_2O_4 cathode materials were examined in detail.

2. Experimental

LiMn_2O_4 powder was purchased from Hebei Strong-Power Li-ion Battery Technology Co. Ltd. (D98, China). $\text{LiCH}_3\text{COO}\cdot 2\text{H}_2\text{O}$ (1.03 g), $\text{Co}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (2.53 g) with a stoichiometric ratio (1:1) were dissolved in distilled water. An aqueous solution of ethylene glycol and citric acid (1:4) as a chelating agent was added to the mixtures. pH value at 7.0 - 7.5 was achieved by Ammonium hydroxide. Then slowly add the LiMn_2O_4 powders (50 g) to the sol and vigorously stirred at 85°C for 5 h. As the evaporation of water proceeding, the sol was turned into a viscous transparent gel. After drying and sieving, the powder was sintering in air at 350°C for 3 h and 650°C for 3 h to obtain LiCoO_2 -coated LiMn_2O_4 . For a comparison, pristine LiMn_2O_4 was also heat-treated in the same condition.

2.1. Structure and Morphology Characterization

X-ray diffraction patterns were recorded on a DX-2700 diffract meter (Siemens D-5000, Mac Science MXP 18) equipped with $\text{Cu K}\alpha$ radiation of $\lambda = 0.154145$ nm. The diffraction patterns were recorded between scattering angles of 15° and 80° at a step of $4^\circ/\text{min}$. The morphology was studied by a scanning electron microscopy (S4700, Hitachi) and transmission electron microscope (JEOL-1200EX). After cycling, the batteries were disassembled in glove box and the electrodes and membrane were washed by EC/DMC for several times. The cathode was used to examine the changes in structure by XRD and the obtained solution was diluted to suitable concentration to detect the content of Mn element. Inductively coupled plasma atomic emission spectrometry analysis was conducted on IRIS Intrepid II XSP inductively coupled plasma emission spectrometer (THERMO).

2.2. Electrochemical and Thermal Characteristics

To obtain working electrode, 85 wt% active materials, 6 wt% polyvinylidene fluoride and 9 wt% acetylene black were homogeneously mixed in NMP. Then the resulting slurry was spread on an Al foil and thoroughly dried. The electrodes were punched in the form of 14 mm diameter disks, and the typical active material mass loading was about $6 \text{ mg}/\text{cm}^2$. The electrolyte was 1 M LiPF_6 dissolved in a mixture of ethylene carbonate and dimethylene carbonate with the volume ratio of 1:1. The anode of the battery is Li electrode. The assembly process was conducted in an argon-filled glove-box with the content of H_2O and O_2 less than 1 ppm.

Before electrochemical tests, the batteries were aged for 24 h to ensure good soakage. The cells were charged and discharged on a battery tester (CT-3008W, NEWARE) between 3.3 and 4.35 V at the rate of 2C at elevated temperatures ($55^\circ\text{C} \pm 2^\circ\text{C}$) in dry oven (A201113, Shanghai).

3. Results and Discussion

Figure 1 shows the XRD patterns. The peaks of both samples could be indexed to a cubic spinel structure with the space group $\text{Fd}3\text{m}$. There is no substantial difference between XRD patterns for LiMn_2O_4 and modified sample. The crystal lattice parameters were calculated by using the software of Jade, are 8.245 and 8.246 Å for the pristine and LiCoO_2 -coated LiMn_2O_4 , indicating that the bulk structure of LiMn_2O_4 unchange after surface modification. The characteristic peaks corresponding to LiCoO_2 are not observed because of low content (about 2.0 wt%).

Scanning electron microscopy has been shown in **Figure 2** which reveals the pristine and modified samples

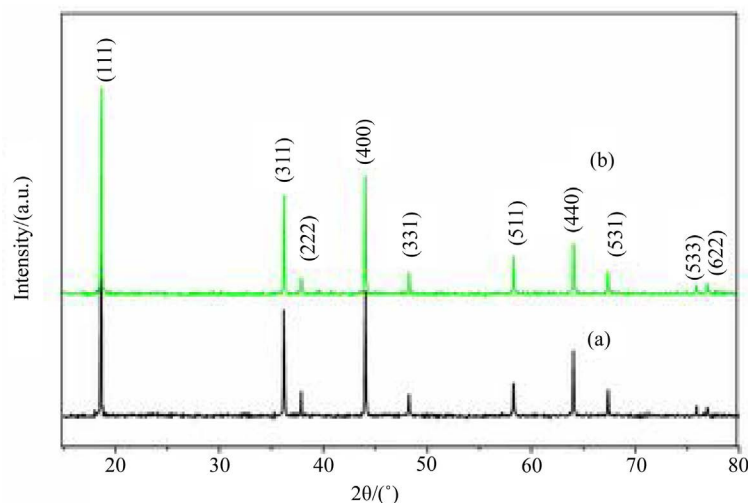


Figure 1. X-ray diffraction patterns of (a) Pristine and (b) LiCoO_2 -coated LiMn_2O_4 .

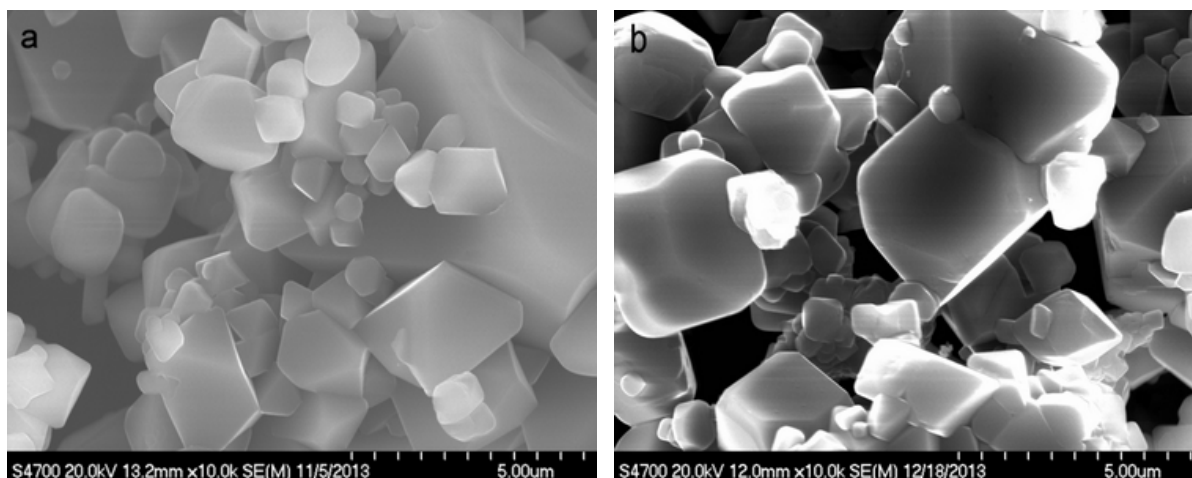


Figure 2. SEM figures of (a) Pristine and (b) LiCoO_2 -coated LiMn_2O_4 .

present a uniform particle distribution, ranging from 3 to 6 μm . The pristine spinel crystals are smooth with well-defined facets, as observed in **Figure 2(a)**. It can be seen that the morphology and particle diameter of the LiCoO_2 -coated LiMn_2O_4 powders in **Figure 2(b)**, are similar to the pristine sample. No LiCoO_2 agglomerations and obscured facets of spinel LiMn_2O_4 are observed.

The further investment of the surface of LiMn_2O_4 by transmission electron microscope is displayed in **Figure 3**. Compared to the pristine sample (**Figure 3(a)**), about 3 - 5 nm thick layer of LiCoO_2 is uniformly formed on the surface of the LiMn_2O_4 (**Figure 3(b)**). The coating layer is clearly distinguishable from the crystalline LiMn_2O_4 . This result demonstrates that sol-gel method is an effective way to coat the LiCoO_2 layer on the surface of LiMn_2O_4 .

To further identify the homogeneity of coating layer, the element distribution is determined by EDS mapping, which is displayed in **Figure 4**. The dense accumulation of Mn element is attributed to the host material of LiMn_2O_4 and there is no significant agglomeration of Co. These results indicate that LiCoO_2 is homogeneously dispersed on the surface of the LiMn_2O_4 particles.

The XPS is shown in **Figure 5**, for pristine LiMn_2O_4 sample, there is no $\text{Co}2\text{p}$ peaks. For LiCoO_2 -coated LiMn_2O_4 sample, the $\text{Co}2\text{p}$ region shows a $\text{Co}2\text{p}_{3/2}$ main peak at 780.4 eV with satellite peak at 796.8 eV. It is concluded that Co^{3+} have deposited on the surface of LiMn_2O_4 . This result is in good agreement with the

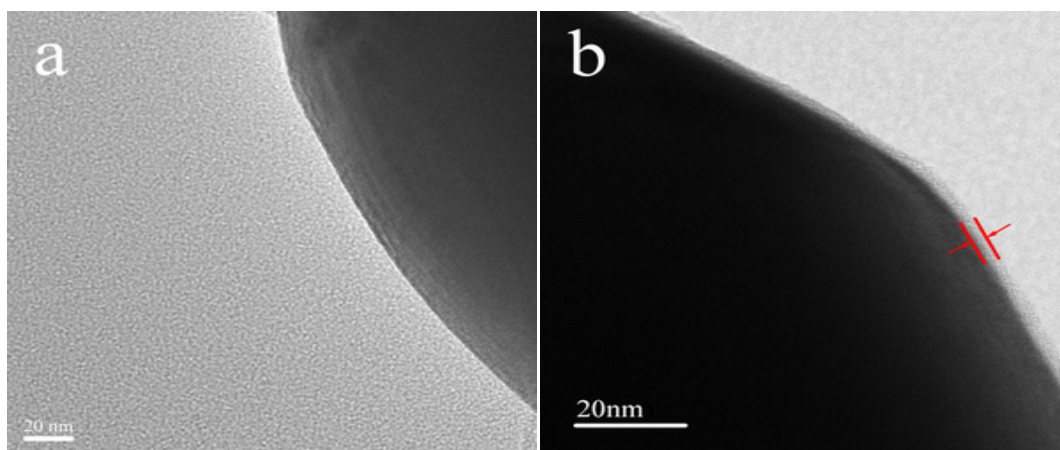


Figure 3. TEM figures of (a) Pristine and (b) LiCoO₂-coated LiMn₂O₄.

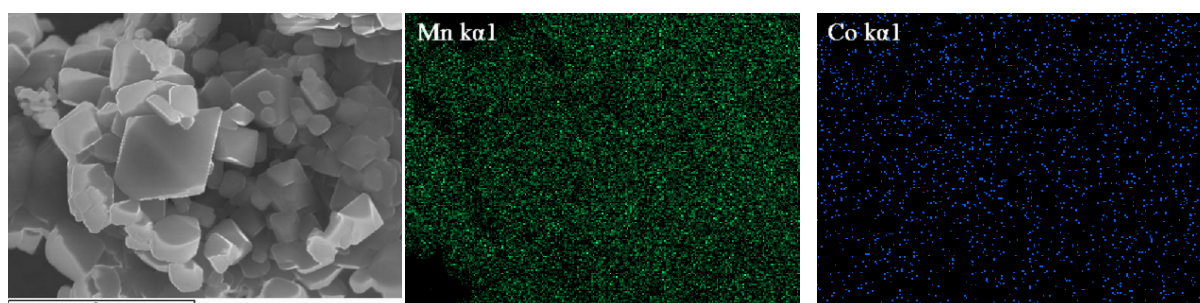


Figure 4. EDS mappings of Co and Mn elements of modified LiMn₂O₄ sample.

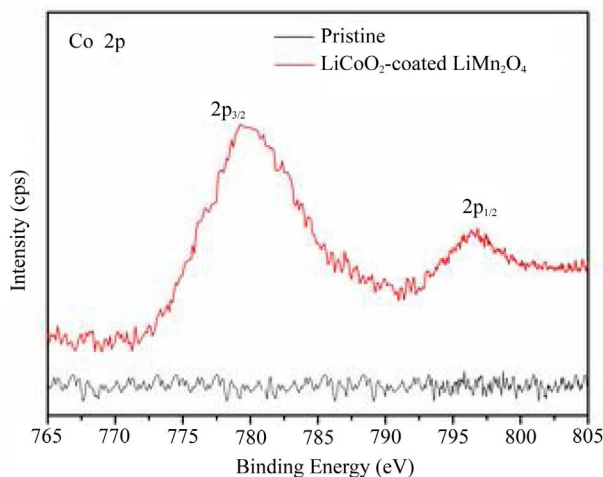


Figure 5. The Co2p X-ray photoelectron spectra of the pristine and LiCoO₂-coated LiMn₂O₄.

observation in TEM and EDS element mapping.

The structure of pristine LiMn₂O₄ and LiCoO₂-coated LiMn₂O₄ cathodes after cycling 100 times (55°C) was examined. The results are given in **Figure 6**. It can be seen that, the diffraction peaks of cycled LiMn₂O₄ cathode are widened and the peak intensity declined compared with the pristine LiMn₂O₄ cathode. In addition, some extra peaks appear in LiMn₂O₄ cathode XRD pattern after cycling, which should be assigned to Li₂Mn₂O₄. Usually, tetrahedral Li₂Mn₂O₄ can be generated at the final discharge stage of LiMn₂O₄ because of more Mn³⁺ and more significant Jahn-Teller effect. However, for the LiCoO₂-coated LiMn₂O₄ cathode, the diffraction peak width changed insignificantly before and after cycling. Comparing with cycled LiMn₂O₄ cathode, in the XRD

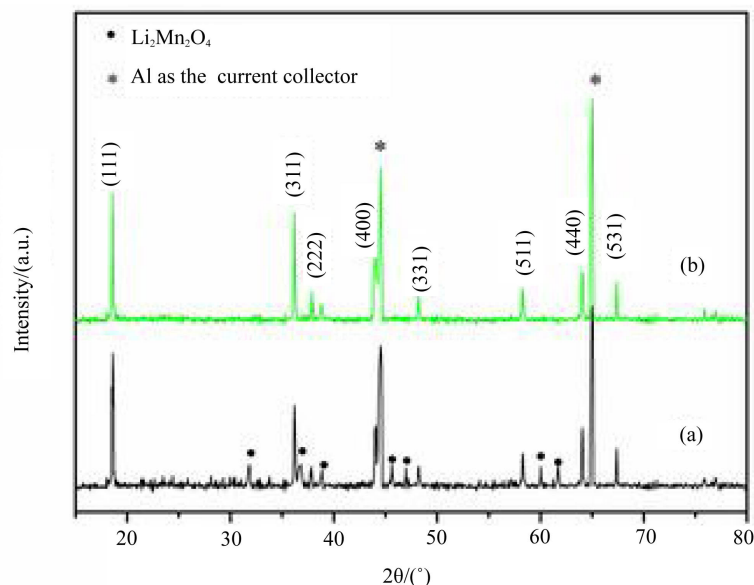


Figure 6. XRD patterns of (a) Pristine, (b) LiCoO₂-coated LiMn₂O₄.

pattern of the cycled LiCoO₂-coated LiMn₂O₄, the peak intensity declines a polarization, we still should ascribe them to the LiCoO₂ on the surface of LiMn₂O₄.

In **Figure 7**, the galvanostatic charge-discharge curves under a current rate of 2C were conducted at (a) room temperature and (b) elevated temperatures in drying oven. They shows two discharge plateaus, which should be attributed to orderly intercalating of lithium ions in the tetrahedral (8a) sites at 4.1 V and disorderly intercalating lithium ions at 3.9 V which substantially maintains the intercalation feature of LiMn₂O₄ substrate [17], indicating LiCoO₂ surface layer rather than Ni-doped LiMn₂O₄ because LiMn₂O₄ with Ni-doped spinel surface showed two ambiguously resolved discharging plateaus [18]. LiCoO₂-coated LiMn₂O₄ shows a higher discharge capacity compares to the pristine sample. The reason of high initial discharge capacity is that LiCoO₂ has capacity at this voltage range.

Figure 8 shows the cycling performance of electrodes with and without LiCoO₂ coating at (a) room temperature and (b) elevated temperatures. After 100 cycles at room temperature, the capacity retention of pristine sample (94.3%) is similar to that of modified sample (94.4%), as shown in **Figure 8(a)**. However, after 100 cycles at elevated temperature, the discharge capacity of the pristine LiMn₂O₄ drops from 115.3 to 100.6 mAh/g. In contrast, the discharge capacity of modified sample changes from 117.2 to 110.1 mAh/g. The capacity retention increases from 87.5% to 93.6% after LiCoO₂ coating. Compared with other coating materials such as Al₂O₃ [19], La₂O₃ [20], AlPO₄ [21], In these paper, surface modification by sol-gel method can improve the high-temperature cycling stability of LiMn₂O₄, because oxide layer can reduce the contact area of LiMn₂O₄ and electrolyte. However, the covering layer is not very uniform, the highest capacity retention is about 89%, coupled with the oxide itself do not have de-intercalation and intercalation of Li ions, it will result in a decrease in initial capacity.

To further verify the effects of surface coating on manganese ions dissolution, the quality of the manganese element was directly determined by using ICP-AES. Li metal anode was washed by dilute hydrochloric acid after 100th cycle at 55°C ± 2°C. It can be seen in **Table 1**, the dissolved quality of Mn²⁺ ions of the pristine and LiCoO₂-coated LiMn₂O₄ electrode was 22.54 and 10.17 μg/cm², respectively. It can be concluded that after coating by LiCoO₂ layer, the dissolution of the manganese ions was significantly reduced. Therefore, LiCoO₂-coated LiMn₂O₄ electrode had better cycle stability at elevated temperature. The reason is that the coating material will reduce the contact area of LiMn₂O₄ and electrolyte, which may decrease the dissolution of Mn. The reactivity between LiCoO₂ and electrolyte has not yet clear, which need further research in future.

4. Conclusion

In summary, the surface of LiMn₂O₄ sample was modified by LiCoO₂ using a sol-gel method. TEM and XPS results confirm the existence of LiCoO₂ layer. A uniform and dense layer about 3 - 5 nm was coating on the

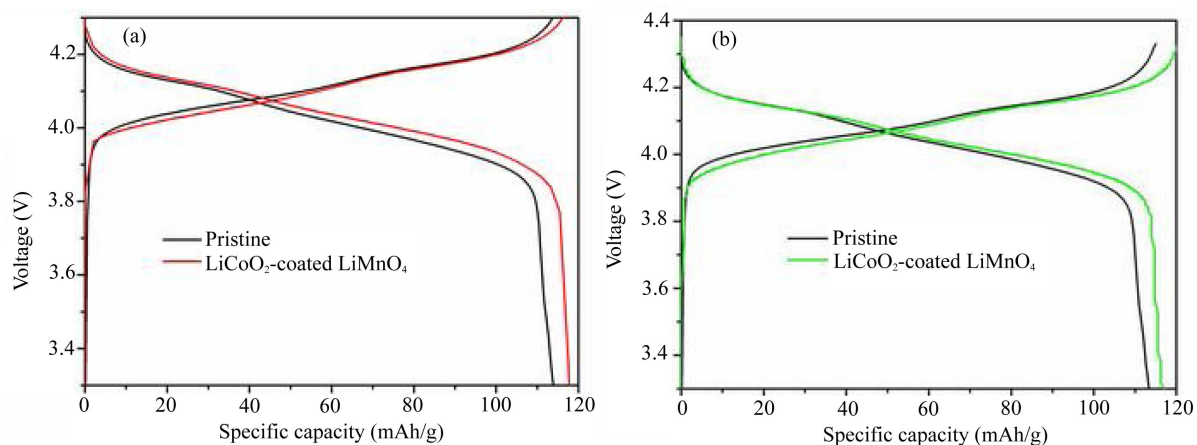


Figure 7. The first charge-discharge curves at (a) Room temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$); (b) Elevated temperature ($55^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

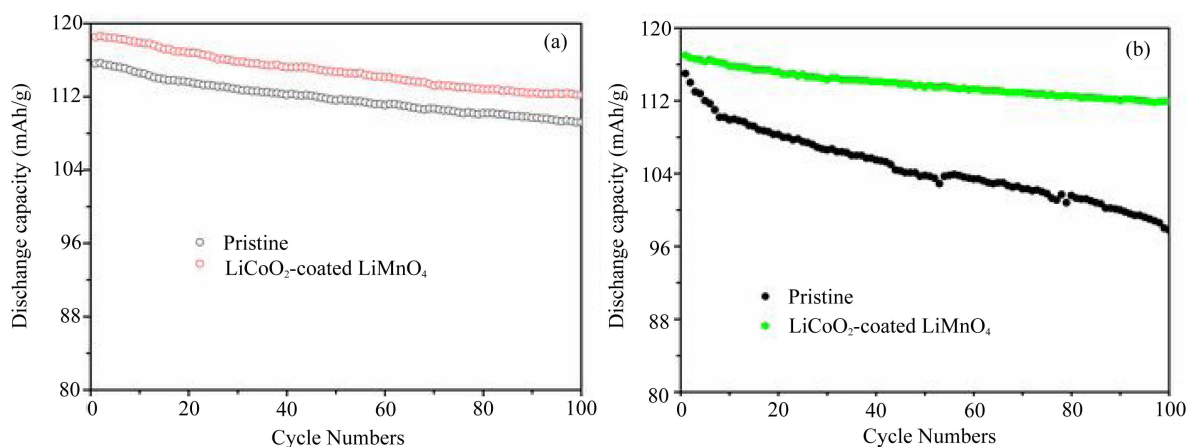


Figure 8. Cycling behaviors at (a) Room temperature ($25^{\circ}\text{C} \pm 2^{\circ}\text{C}$); (b) Elevated temperature ($55^{\circ}\text{C} \pm 2^{\circ}\text{C}$).

Table 1. The amount of Mn ions deposited on Li anode after 100 cycles at $55^{\circ}\text{C} \pm 2^{\circ}\text{C}$.

Samples	The quantity of Mn ions on Li anode ($\mu\text{g}/\text{cm}^2$)
Pristine LiMn_2O_4	22.54
LiCoO_2 -coated LiMn_2O_4	10.17

surface of pristine LiMn_2O_4 . The LiCoO_2 -coated LiMn_2O_4 sample exhibits much better cycling stability at elevated temperature (55°C) compared with the pristine sample. These results demonstrated that this is an effective way to improve the high-temperature cyclic performance of spinel LiMn_2O_4 .

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