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A novel method to fabricate lithium-ion polymer batteries based on $\text{LiMn}_2\text{O}_4/\text{NG}$ electrodes

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Abstract A novel method to fabricate lithium-ion polymer batteries (LiPBs) has been developed. The LiPBs was fabricated without microporous polyolefin separators, taking spinel lithium manganese oxide (LiMn_2O_4) and natural graphite (NG) as the electrodes. The thicknesses of the cathodes and the anodes are 190 and 110 μm , respectively. The NG anode was coated with a microporous composite polymer film (20 μm thick) which composed of polymer and ultrafine particles. The coating process was effective and simple to be used in practical application, and ensured the composite polymer film to act as a good separator in the LiPB. The LiPBs assembled with the coated NG anodes and pristine LiMn_2O_4 cathodes presented better electrochemical performances than liquid lithium-ion battery counterparts, proving that the microporous composite polymer film can improve the performance of the coated NG anode. In this paper, the spinel $\text{LiMn}_2\text{O}_4/(\text{coated})\text{NG}$ -based LiPBs exhibited high rate capability, compliant temperature reliability, and significantly, excellent cycling performance under the elevated temperature (55 °C).

Keywords Lithium-ion polymer battery · LiMn_2O_4 cathode · Composite polymer film · Coating · Natural graphite anode

Introduction

Spinel lithium manganese oxide (LiMn_2O_4), a new type of promising active cathode material for lithium-ion secondary batteries, boasts such merits as abundant and economical raw materials, low toxicity, and reliable safety. It is considered to be the ideal cathode material for lithium-ion secondary batteries powering electric vehicles (EVs) and

stationary energy storage equipment. However, $\text{LiMn}_2\text{O}_4/\text{NG}$ -based batteries suffer rapid capacity fading during cycles and storage, especially at elevated temperatures, which greatly constrains the commercial applications [1]. Many research groups have found that the performance deterioration of $\text{LiMn}_2\text{O}_4/\text{NG}$ -based batteries is related to the cathodes and given theoretical explanations [2–6]. Attempts have been done to restrain the capacity fading of spinel LiMn_2O_4 cathode materials [7–12], including element doping and surface modification of spinel LiMn_2O_4 powder. These attempts bring out a lot of performance improvement of the spinel although the essential problem has not been solved totally. At the same time, the attempts are not suitable for practical application because the modifying processes are extra cost and too complicated to control the characteristics of the cathode material, which makes them at the laboratory level at present.

The manganese dissolution of the spinel had been regarded as the dominant factor in the capacity fading of $\text{LiMn}_2\text{O}_4/\text{NG}$ -based batteries before some research groups [13, 14] found that the amount of manganese dissolution could not explain the overall capacity loss during cycles. It implies that the capacity fading of $\text{LiMn}_2\text{O}_4/\text{NG}$ -based batteries must result from something else besides the LiMn_2O_4 cathode. The NG anode was proved to play a big role in the capacity fading by Tsunekawa et al. [15]. The study revealed that the capacity fading of graphite was due to the deposition of Mn^{2+} . Other researchers [16, 17] also observed the reaction between Mn^{2+} and graphite that led to performance deterioration of the batteries.

In this paper, the performance of $\text{LiMn}_2\text{O}_4/\text{NG}$ -based batteries is supposed to be improved if the manganese dissolution is reduced and/or the reaction between Mn^{2+} and natural graphite is inhibited. We developed a novel method to fabricate LiPBs and the performance of $\text{LiMn}_2\text{O}_4/\text{NG}$ -based LiPBs was improved. We coated the electrodes with microporous composite polymer films by a simple process. One outcome is that the manganese dissolution is reduced because manganese ion diffusion is limited in flexuose micropores of the film. Another one is that the reaction between graphite and Mn^{2+} is inhibited

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because the NG anode is protected, especially the reactive sites on the surface. Furthermore, the microporous composite polymer films can act as the separators in lithium-ion polymer batteries (LiPBs), making the assembly without expensive polyolefin separators to cut down the producing cost of the batteries. The films consist of two commercial products, high molecular polymer and ultrafine particles. The ultrafine particles were dispersed uniformly in the polymer, which could enhance the characteristics of composite polymer films [18]. The electrodes were assembled into LiPBs and the electrochemical performances of the LiPBs were studied.

Materials and methods

Poly(vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP) copolymer and fumed silica (SiO_2) were chosen as the composites of the composite polymer films [19]. PVDF-HFP (Kynar 2801, EIF Atochem) was dissolved in butanone at 50 °C. Fumed SiO_2 (Cabosil TS-530, ~12 nm) was dispersed in butanol and dimethyl carbonate (DEC) by ultrasonic. The SiO_2 mixture was then dripped into the PVDF-HFP solution with intense stirring and 50 °C water bathing. A homogeneous composite polymer slurry was obtained at last. The weight ratio between PVDF-HFP and butanone and DEC is 1:5:3.9 [20]. Composite polymer slurries with different SiO_2 /PVDF-HFP weight ratios were prepared, and butanol was used to control the concentration of the composite polymer slurry.

Spinel LiMn_2O_4 cathodes and NG anodes were prepared by coating the slurry of active material (LiMn_2O_4 or natural graphite), PVDF binder and acetylene black (90:6:4 by weight) on aluminum and copper foils, respectively. The thicknesses of the cathodes and the anodes are 190 and 110 μm , respectively. The pristine electrodes were immersed in the composite polymer slurry for 30 s and took out to dry in the air, and then dried in a vacuum oven (100 °C) for 24 h to remove the residual solvents. A microporous composite polymer film was formed on the surface of the coated electrode. The thickness of the composite polymer film was kept between 20 and 25 μm by controlling the concentration of the composite polymer slurry.

The absorption capability of liquid electrolyte of the composite polymer film was measured by calculating the increased weight ratio of the coated electrode after it was immersed in a liquid electrolyte of 1 M LiPF_6 EC/EMC/DMC (1:1:1 by volume) for 2 h. The absorption capability was calculated as $(W_1 - W_0)/W_0$, with W_0 and W_1 being the weights of the coated electrode before and after it was immersed in the electrolyte. Three samples ($1 \times 1 \text{ cm}^2$) were studied for every composition of the composite polymer films and the mean value of the absorption capability was given as the final result.

Surface and cross-sectional morphology of the electrodes were observed by a scanning electron microscope (SEM, JEOL JSM-5600LV). The electrodes were sandwiched between two parallel stainless steel electrodes for electrochemical impedance spectrum measurements (EIS,

EG&G Potentiostat/galvanostat model 283) after they were immersed in the electrolyte for 2 h in a MBRAUN argon chamber. Module R(QR)(QR) was used to simulate the test cell with a ZSimpWin software, where R is a resistance and Q is a constant phase element.

Three types of LiPBs were assembled without polyolefin separators in aluminum plastic packages: (1) coated LiMn_2O_4 cathode and pristine NG anode (abbreviated as type a), (2) pristine LiMn_2O_4 cathode and coated NG anode (abbreviated as type b), (3) coated LiMn_2O_4 cathode and coated NG anode (abbreviated as type c), and (4) liquid lithium-ion battery counterparts were assembled in aluminum plastic packages with pristine LiMn_2O_4 cathodes, pristine NG anodes, and Celgard[®]2400 separators (abbreviated as type d). After preconditioning, the batteries were tested for resistance (Agilent Milliohmmeter 4338B) and electrochemical performances (Land, Wuhan China).

The LiPBs of type b were disassembled to extract the coated anodes after 100 cycles with 0.5 C current under 25 °C. The composite polymer films were peeled off from the coated anodes carefully. The net anodes and the composite polymer films were immersed in 1 M hydrochloric acid solutions separately for 48 h and the filtrates were used to measure the manganese contents by inductively Coupled Plasma-Atom Emission Spectrum (ICP-AES, Optima 4300DV, PerkinElmer). Three LiPBs were used in the test and the average values of manganese contents were calculated as the final results.

Results and discussion

Optimal composition of the composite polymer slurry

The absorption capability of liquid electrolyte of the composite polymer films has the maximum value when the SiO_2 /PVDF-HFP weight ratio is 1:10, as shown in Fig. 1. Generally, SiO_2 nanometer particles are dispersed uniformly to increase the porosity of the composite polymer films. When the density of SiO_2 is small, the coated film has small porosity and shows low absorption capability. The absorption capability increases with the SiO_2 density until the density is 9 wt%. When the density of SiO_2 is bigger than 9 wt%, the porosity of the film decreases because of the congregating of nanometer particles which inhibits the uniform dispersion of SiO_2 in the polymer, and the absorption capability decreases afterwards. The composite polymer film is considered to display the maximal absorption capability when the weight ratio between PVDF-HFP and SiO_2 is optimal. So the optimal composition of the composite polymer slurry is determined to be PVDF-HFP to butanone to DEC to SiO_2 to butanol = 1: 5: 3.9: 0.1: 4 by weight.

Characteristics of the coated electrodes

The SEM photos of pristine and coated electrodes are shown in Fig. 2. Figure 2a shows the surfaces of the pristine

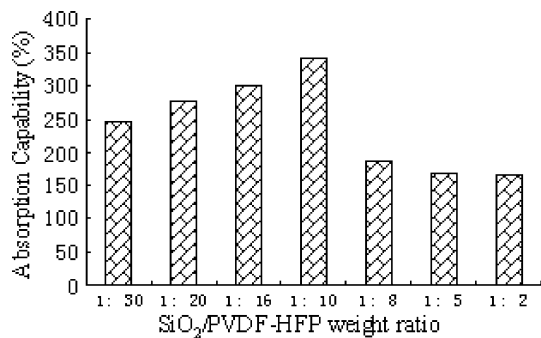


Fig. 1 Absorption capability of composite polymer films with different SiO₂/PVDF-HFP weight ratios

LiMn₂O₄ cathode and the pristine NG anode. The pristine electrodes are totally coated by the composite polymer film, and a typical example of the coated electrodes is shown in Fig. 2b. Figure 2c is an enlarged photo of Fig. 2b, in which a lot of micropores are visible on the surface of the film. The cross-sectional morphology of the coated electrode is shown in Fig. 2d, which demonstrates the porous structure and the thickness of the composite polymer film is around 20 μm. The micropores are filled with the liquid electrolyte in the LiPBs, forming lithium-ion conductive channels in the composite polymer film.

Figure 3 shows the EIS plots of the electrodes. The plots are nearly a straight line and the intercepts on the Z' axis can be used to compare the impedances of the electrodes. It shows that the impedance is in the sequence of coated LiMn₂O₄ > pristine LiMn₂O₄ > coated NG > pristine NG. The reason is that it is more difficult for lithium ions transferring in LiMn₂O₄ than in NG, and the coated film increases the transferring resistance, too. The simulated

Fig. 2 SEM photos of the electrodes (a) pristine electrodes; (b) coated electrode; (c) enlarged photo of (b); (d) cross-section of (b)

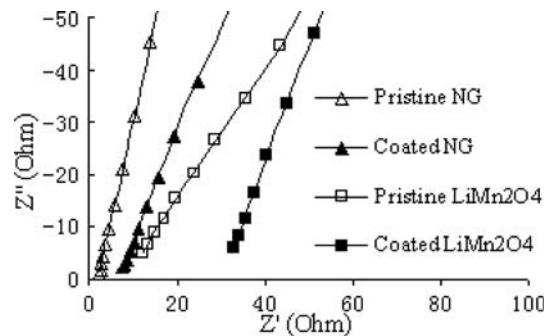
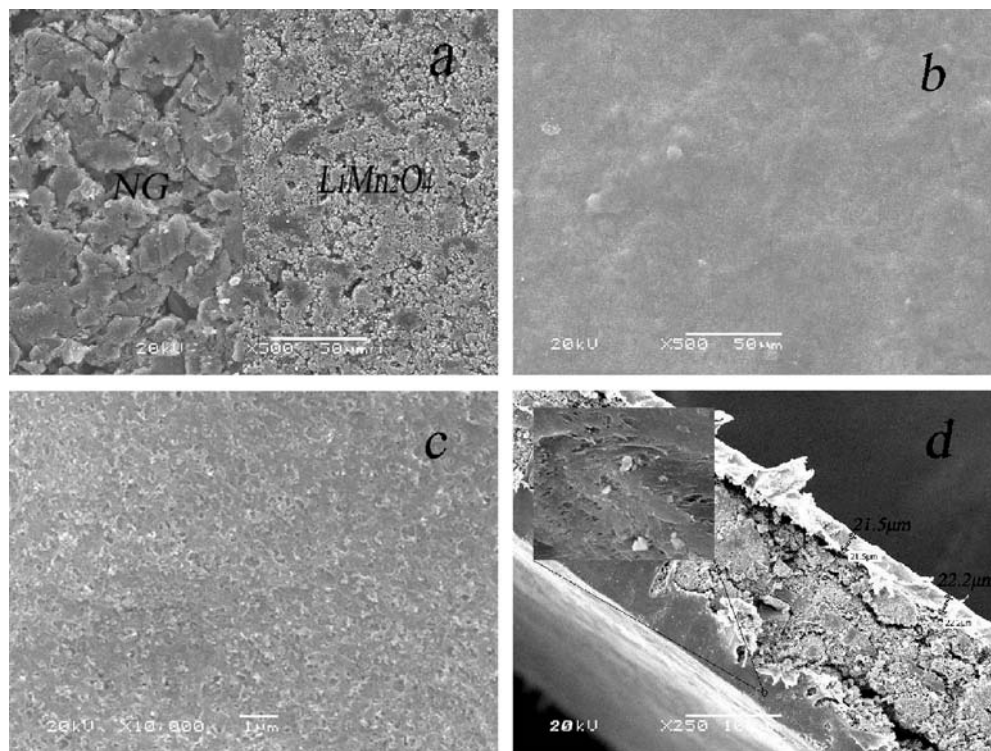


Fig. 3 Electrochemical impedance spectra of the electrodes

resistance values of coated LiMn₂O₄, pristine LiMn₂O₄, coated NG, and pristine NG electrodes are 26.9, 9.19, 6.58, and 1.98 Ω, respectively, giving an ionic conductivity close to 10⁻³ S/cm.

Resistances of different LiPBs

Table 1 shows the resistances of the four types of batteries. It can be concluded that the batteries with coated spinel LiMn₂O₄ cathodes (type a and c) have bigger resistances and there is no evident change of resistance when the NG anode was coated (type b), compared with the pristine LiMn₂O₄/NG-based battery (type d). The results mean that the composite polymer film influences the resistance of the cathode more than that of the anode. The different resistances of the four batteries can be easily understood when we take into account the fact that the resistance of a battery can be divided into the impedance of electrolyte and

Table 1 Resistances of different LiPBs

Type	a	b	c	d
LiMn ₂ O ₄ cathode	Coated	Pristine	Coated	Pristine
NG anode	Pristine	Coated	Coated	Pristine
Resistance(mΩ)	126	45	122	46

those of electrodes, the greatest of which decides the resistance of the battery. As for the LiPBs, the coated spinel LiMn₂O₄ cathode shows the greatest impedance and the pristine spinel LiMn₂O₄ cathode has greater impedance than the coated NG anode and the pristine NG anode as shown in Fig. 3, and the electrolyte's impedance is the least. So, the resistance of a LiPB is decided by the cathode, which can explain the difference of resistance between four types of batteries.

Cycling performance of LiPBs

Cycling performance of the LiPBs with 0.5 C current under 25 °C is shown in Fig. 4. The LiPBs prepared with coated cathodes present a low discharge capacity (about 82 mAh/g based on the weight of LiMn₂O₄), which can be explained by the great resistances of type a and type c. The LiPB of type b, prepared with the coated anode and pristine cathode, shows the same discharge capacity (about 108 mAh/g based on the weight of LiMn₂O₄) as the liquid counterpart type d and better cycling performance, which indicates that the composite polymer film improves the electrochemical characteristics of the NG anode. The reason is that the composite polymer film protects the NG anode from reacting with Mn²⁺. The reaction between Mn²⁺ dissolved from the spinel and graphite can increase the impedance and lead to performance deterioration [16]. In type b batteries, the reaction is inhibited because the composite polymer film protects the reactive sites on the graphite, resulting in the improvement of the NG anode. Figure 4 also shows that type a presents a lower capacity fading rate than type d, which implies that the manganese dissolution may be reduced because of the slow diffusion of Mn²⁺ in the micropores of the composite polymer film.

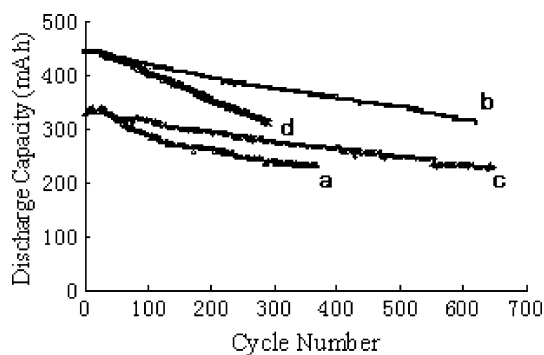


Fig. 4 Cycling performance of different LiPBs (0.5 C) (a coated LiMn₂O₄/pristine NG; b pristine LiMn₂O₄/coated NG; c coated LiMn₂O₄/coated NG; and d pristine LiMn₂O₄/pristine NG)

The cycling performance of different batteries demonstrates that the composite polymer film can improve the performance of coated electrodes, especially the performance of the coated NG anode, as we have supposed. For the duration of the study, LiMn₂O₄ cathode is not chosen for treatment based on its great impedance and low discharge capacity. Instead, the study focuses on type b batteries with the coated NG anodes, to demonstrate the improvement of the LiPBs by the surface coating treatment.

Rate capability of type b

The fully-charged LiPBs of type b were discharged under different rate currents at 25 °C. The discharge capacity ratios to the 0.2 C discharge capacities were calculated to be 99.5, 96.5, and 87.0% at 0.5, 1, and 2 C, respectively. And the LiPBs discharged 94.1, 93.6, 89.7, and 73.7% of the whole discharge capacities over 3.6 V at 0.2, 0.5, 1, and 2 C, respectively, displaying a high discharge voltage plateau. The rate discharge curves are drawn in Fig. 5, which shows that the LiPBs prepared with the coated NG anodes and pristine LiMn₂O₄ cathodes have high rate capability.

Temperature reliability of type b

High qualitative LiPBs can be deployed in various demanding situations such as extreme heat and coldness. Discharge tests were carried out in a 55 °C oven and a freezer set at -18 °C. The LiPBs of type b were fully charged under 25 °C, and then discharged to 3.0 V after they were stored in the oven or freezer for 4 h. The current was 0.2 C in the tests. The discharge capacities are 97.4% at 55 °C and 94.4% at -18 °C to that at 25 °C, which shows very compliant temperature reliability of the type b batteries.

Cycling performance of type b under an elevated temperature (55 °C)

Capacity fading of LiMn₂O₄/NG-based LiPBs is severe at elevated temperatures and the capacity retention under 55 °C improves when NG anodes are coated with the composite polymer films in Fig. 6. The test included 50 cycles with

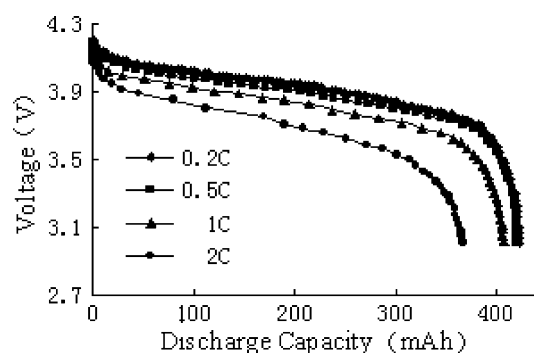


Fig. 5 Rate capability of the LiMn₂O₄/(coated)NG-based batteries

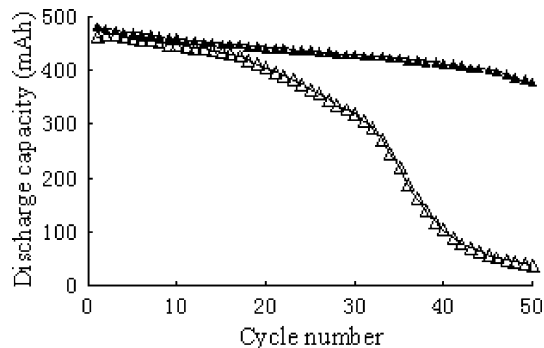


Fig. 6 Cycling performance of lithium-ion batteries under 55 °C (\blacktriangle LiPBs with pristine cathode and coated anode, type b; \triangle liquid lithium-ion batteries with pristine electrodes, type d)

0.5 C current under 55 °C. The capacity fading rate of type d is much bigger than that of type b, especially after 18 cycles. The manganese content in the electrolyte is low during the forepart of the cycles (before the 18th cycle) and influences the performance of NG anode a little. When the manganese content is increasing, the reduction of Mn^{2+} destroys the graphite and the performance of NG anode deteriorates greatly in type d. At the same time for type b battery, the composite polymer film protects graphite from reacting with Mn^{2+} and ensures good performance of the NG anode. So the $LiMn_2O_4$ /(coated)NG-based LiPBs exhibit excellent cycling performance at the elevated temperature.

It is observed that the aluminum plastic package of type d was filled with gas while there was no gas in the package of type b after 55 °C cycles. This demonstrates another merit of the composite polymer film, that is, inhibiting gas revolution in the batteries. It is coincident with that the composite polymer film protects the NG anode; otherwise gas revolution would happen because of the rebuilding of the solid electrolyte interface on the graphite.

Manganese content on the NG anode

Table 2 shows the results of the ICP-AES measurements. The coated NG anode of type b has only 60.3% manganese on the graphite (net NG anode) of that on the pristine NG anode of type d, and the composite polymer film adsorbs about 28% of the total manganese on the coated NG anode. It can be concluded that the composite polymer film can effectively decrease the manganese content on the coated NG anode. The reasons include: (1) the composite polymer film has adsorbability to Mn^{2+} , (2) the slow diffusion of

Table 2 Manganese content on the NG anode

Sample	Density of Mn^{2+} solution ($mg\ l^{-1}$)	Manganese content of sample ($\mu g\ cm^{-2}$)
Net NG anode of type b	10.64	1.36
Composite polymer film of type b	4.067	0.52
Pristine NG anode of type d	17.65	2.25

Mn^{2+} in the micropores of the film does not help the ions approach the anode, and (3) the reduction reaction of Mn^{2+} on the NG anode is reduced because the composite polymer film covers the reactive sites on the graphite surface. These improvements ensure good characteristics of graphite and as well as reduces side-reaction, leading to the superior performances of type b.

Conclusions

The critical issue of performance deterioration of $LiMn_2O_4$ /NG-based batteries in practical application should be solved with simplicity and high efficiency. A novel method was developed to fabric $LiMn_2O_4$ /NG-based LiPBs in this paper. A microporous composite polymer film, mainly composed of PVDF-HFP and fumed silica, was coated on the surface of NG anode by a simple process, serving as the separator of the LiPB. The $LiMn_2O_4$ /(coated)NG-based LiPBs boast high rate capability, compliant temperature reliability, excellent cycling performance, and good capacity retention under elevated temperatures. The improvement results that the graphite is protected by the composite polymer film from reacting with Mn^{2+} dissolved from the spinel $LiMn_2O_4$ cathode leads to the excellent performance of the NG anode.

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