

Magnesium Borate Fiber Coating Separators with High Lithium-Ion Transference Number for Lithium-Ion Batteries

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In this work, magnesium borate fiber (MBO) is used as a functional ceramic to coat onto a polypropylene (PP) separator (MBO@PP). This MBO coating layer increases the lithium-ion transference number (t_{Li+}) from 0.24 to 0.57 in the LiPF₆-based electrolyte due to the MBO acting as Lewis acid sites interacts with Lewis base PF⁻₆. The increase in the t_{Li+} reduces the

1. Introduction

Lithium-ion batteries (LIBs) are widely used as energy storage devices in our daily lives due to their high energy density, long cycle life, and low cost. Many researches and developments have been done to further improve their electrochemical performance such as energy density, high current charge and discharge rate as while as safety for application in large scale energy storage and electric vehicles power sources.^[1-3] As an indispensable component of LIBs, separators should also have their contributions in these respects. Since the conventional porous polyolefin separator severely shrinks at elevated temperature and could cause short circuit of the electrodes which would lead to the thermal runaway and explosion of the battery, thus lots of work has been done in recent years to improve the thermal stability of the commercial polyolefin separator. For example, our group coated nano-ceramic powders such as Al₂O₃ onto commercial polyolefin separator to improve thermal stability by enlarging the temperature range between shutdown and melting down as well as the dimensional stability at increased temperature.^[4,5] Zhu et al. deposited a thin layer of TiO_2 onto polypropylene (PP) separator by Atomic Layer Deposition (ALD) technology to overcome the thermal shrinkage and poor wettability of PP separator.^[6,7] Lee et al. studied the effect of SiO₂ coating with different particle sizes on polyolefin separator.^[8,9] However, most of the devel-

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concentration polarization and promotes the migration of lithium ions. Besides, the prepared MBO@PP separator has better wettability with liquid electrolyte, the electrolyte uptake as well as thermal stability. The LiFePO₄ half-coin with MBO@PP separator not only had better cycle stability, but also had a higher capacity retention rate at high current.

oped ceramic coated separators (CCS) are prepared by modifying commercial polyolefin separator with electrochemical inert solids ($Al_2O_3/TiO_2/SiO_2$), mainly aiming to improve the physical properties as thermal stability of the separator. However, they are not effective enough in the current state of the art in pursuit of better electrochemical performance as higher energy density, higher power density and so on. Therefore, besides ensuring the safety of the separator, it is an attractive way to endow the separator with certain electrochemical functions by simply introducing some functional ceramic materials.

Lithium ion transference number $(t_{i,\perp})$, representing the ratio of conductivity contribution of lithium ion is an important parameter of LIBs due to only Li⁺ ions participate in the electrochemical reaction, namely Li⁺ ions insertion/extrusion process. Unfortunately, the t_{Li+} of most lithium salt in carbonate based electrolyte with polyolefin separator is generally lower than 0.5, only about 0.2-0.4,^[10-12] meaning that the most migration ions in the electrolyte is anionic ions as PF_6^- , which is easily to cause concentration polarization, voltage drop,^[10,13] undesirable reaction and lithium dendrite generation and finally lead to the deterioration of cell performance.^[14] Therefore, it is necessary to increase $t_{ii\perp}$ to further improve the electrochemical performance of advanced LIBs. The most representative strategy is the single-ion polymer electrolyte, which directly immobilizes the anionic group on the polymer backbones thus gain a complete Li ions conductance with t_{11+} of close to 1.^[15-17] However, the low ionic conductivity (lower than 10^{-5} S·cm⁻¹ at room temperature) of such polymer electrolytes greatly hinders its application. So, to balance the requirements of conductivity and lithium ion migration, a simple method based on Lewis acid-base interaction is also developed to increase $t_{11,1}$.^[18] For example, Wang et al. deposited ZrO₂ with Lewis acid sites onto the separator to absorb Lewis base species in the electrolyte, PF_6^- and increase t_{Li+} by electrostatic interaction.^[12,19] The ZSM-5 molecular sieve with amounts of Lewis acid sites based on Si-O and Al-O backbones was also used as the coating layer on the separator to absorb PF_6^- thus the t_{Li+} increases from 0.28 to 0.44.^[11] In addition, it has been reported that electron-deficient functional group such as boron atoms in the borate ester



polymers can also adsorb anions to increase the t_{1i+} . Inspired by the above works combined with our previous work, we envisage the application of borate inorganic ceramics with both B-O electron-deficient group and high thermal shrinkage resistance of ceramic materials on the polyolefin separator. On one hand, borate-based ceramics can improve the thermal stability of the polyolefin separator same as the mechanism of Al₂O₃/SiO₂ ceramics coating layer to ensure its dimensional stability at elevated temperature. On the other hand, it also contains electron-deficient boron-oxygen function groups, which can capture anions through Lewis acid-base interaction to hinder the conductance of anions and increase t_{li+} in the cell. Here, we have chosen the common magnesium borate material, and in order to further enhance the interactions between borate-based ceramics and the anions, we selected magnesium borate Mg₂B₂O₅ fiber with one-dimensional structure and constructed a staggered three-dimensional grid onto the surface of separator to further enlarge the contact area and interaction sites of magnesium borate and the liquid electrolyte. Our results show this simple strategy could improve the performance of both thermal stability and electrochemical performance of the lithium ion battery for practical application.

2. Results and Discussion

The magnesium borate fibers were prepared according to the relevant literature,^[23] and the SEM and XRD characterization of the obtained products was shown in Figure 1a and 1b. The synthesized MBO exhibited an one dimensional wire morphology with a diameter of 400–600 nm and a length of 5–18 μ m, and the XRD patterns of MBO demonstrate a unique diffraction peak, which is consistent with JCPDS (#01-086-0531). In the surface element characterization, as shown in Figure 1c, we can clearly find the Mg, O, B elements in the magnesium borate fibers. Combing the information from structural and morphological characterization, it can be concluded that MBO fibers have been successfully synthesized.

The MBO@PP separator was prepared by filtering MBO fibers thin layer onto PP separators (Figure 2a), and the surface and cross sectional morphology of the membrane is shown in Figure 2b and 2c–d. It can be clearly identified that the synthesized MBO fibers were interlaced on the surface of pristine PP separator forming a three-dimensional network with porous structure. Figure 2c and 2d shows the cross-sectional structure of MBO@PP membrane. It was found that MBO fibers were uniformly deposited on the PP separator, and the thickness of the MBO fibers deposited layer was about 6 μ m with 0.346 mg·cm⁻² mass loading amount, which meets the expected staggered three-dimensional structure to enhance the interaction between the MBO and liquid electrolyte.

The thermal stability of the separator plays an important role in the safety of the lithium ion battery. At high temperatures, the polyolefin will shrink due to poor dimensional stability, which may cause a short circuit thus induce serious safety issue. The intuitive results of thermal stability of pristine PP and MBO@PP separators are shown by photographs. Since the melting point of PP is about 160 °C, we measured the size change of the separator at 130 °C and 160 °C for 30 minutes. As shown in the Figure 3a, PP separator shrank seriously at 160 °C,





Figure 1. a) Electron microscopic morphology of magnesium borate fibers; b) XRD pattern of magnesium borate fibers; c) EDS elemental map of the surface of magnesium borate fibers.

Figure 2. a) and b) are the surface electron micrographs of the PP separator and the MBO@PP separator, respectively; c) and d) are the cross-sectional electron micrograph of the MBO@PP separator.



Figure 3. a) Thermal shrinkage test of PP and MBO@PP separators under different temperature; b) Contact angle of the electrolyte on the PP and MBO@PP separators.

however, due to the presence of the MBO ceramic layer with high thermal resistance, the MBO@PP separator have inhibited the shrinkage to a certain extent and thermal stability of the separator was improved. As presented in Figure 3b, the contact angle of MBO@PP separator with EC/DEC electrolyte is reduced from 45° to 0° compared with that of PP separator. The MBO coating layer with three-dimensional network structure has better wettability with liquid electrolyte, which is beneficial to faster ion transportation and lower interface impedance between electrolyte and electrode. By calculating the mass change of the separator immersing in the electrolyte, the electrolyte uptake of PP and MBO@PP separators are 115% and 160%, respectively. Firstly, the one dimension fiber formed three-dimensional network with high porosity facilitates the infiltration of the liquid electrolyte and increases the electrolyte uptake. Secondly, this network structure composed of interlaced MBO fibers could also effectively enlarge the contact area between MBO and anions in the liquid electrolyte.

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Due to the enhancement of hydrophilicity of the ceramic materials and three-dimensional network structure formed by the MBO fibers, the electrolyte uptake of MBO@PP separator is significantly higher than that of PP separator. The ionic conductivity of MBO@PP separator calculated by the AC impedance (Figure 4a) is 0.98 mS \cdot cm⁻¹ at 30 °C, which is slightly higher than that of 0.96 mS·cm⁻¹ of the PP separator. The electrochemical stability of the MBO@PP separator was characterized by testing the cyclic voltammogram of the Li/separator/ SS cells.^[24,25] As shown in the Figure 4b, there is no other peak except for the deposition and peeling peak of lithium between 1 to 5 V versus Li/Li⁺. It is indicated that the addition of MBO did not introduce other electrochemical side reactions and did not affect the electrochemical stability of the PP separator. In addition, it should be noticed that the over potential of lithium metal deposition and stripping on stainless steel decreases after the PP separator was coated with MBO, which could be ascribed



Figure 4. a) lonic conductivity of PP and MBO@PP separators; b) cyclic voltammetry curves of PP and MBO@PP separators with stainless steel as the working electrode, lithium as reference and counter electrodes at a scan rate of 1 mV·s-1; Chronoamperometry curves of PP (c) and MBO@PP (d) separators soaked by electrolyte in Li-symmetric cells, insert: AC impedance curves of the cells before and after polarization.

to the polarization was reduced. The properties of MBO@PP separator was summarized in Table 1.

Magnesium borate coating layer has not only improved the thermal stability of PP separator, but also increased the $t_{\text{Li}+}$ of the electrolyte. As shown in Figure 4c and 4d, the $t_{\text{Li}+}$ of MBO@PP have increased from 0.24 to 0.57 compared with that of PP separator. It can be concluded that the boron-oxygen units in MBO acting as Lewis acid sites interacts with Lewis base PF_6^- , which restricts the migration of PF_6^- and in turn promotes the migration of Li^+ , so the $t_{\text{Li}+}$ of MBO@PP increased.^[20,21,26] Furthermore, the one dimensional fiber structure we introduced to form the coating layer enlarges the contact sites with the anions in the liquid and also could construct an one dimensional Li⁺ conduction pathway. The increase of migration number is beneficial to reduce concentration polarization, especially in the case of high current density, and improve cell performance.^[10]

To further investigate the interaction of MBO with different lithium salt anions, we also have tested the $t_{\text{Li}+}$ of MBO@PP in different lithium salt electrolyte, i.e. 1 M LiClO₄ dissolved in EC/DEC (v/v = 1), 1 M LiTFSI dissolved in EC/DEC (v/v = 1). As shown in Figure 5, in LiClO₄ system, compared with PP separator, the $t_{\text{Li}+}$ of MBO@PP increased from 0.15 to 0.58, which indicated that the MBO can also capture $\text{ClO}_4^{-,[27]}$ However, in the LiTFSI system, it is regret that the MBO@PP separator has not improved the $t_{\text{Li}+}$, and it is likely that MBO has a weaker interaction with the TFSI⁻ anion. From the above changes in the value of $t_{\text{Li}+}$ in the electrolyte of different lithium salts, we can find that the interaction of boron-oxygen groups in MBO

Table 1. Basic properties of PP and MBO@PP separator.						
Separator	Thickness [µm]	Electrolyte uptake [%]	Contact angle [°]	lonic conductivity [mS/cm]	$t_{\rm Li+}$	
PP MBO@PP	25 31	115 160	45° 0°	0.96 0.98	0.24 0.57	



Figure 5. a) and b) Chronoamperometry profiles of PP and MBO@PP separators soaked by LiClO₄ electrolyte in Li-symmetric cells; c) and d) Chronoamperometry profiles of PP and MBO@PP separators soaked by LiTFSI electrolyte in Li-symmetric cells.



with ClO₄⁻, PF₆⁻ is stronger than TFSI⁻, the relevant reason may be that the Lewis basicity of TFSI⁻ is weaker than that of the former two. According to the soft and hard acid-base principle, the boron-oxygen group as a hard Lewis acid site interacts with hard anions of ClO₄⁻ or PF₆⁻ to be stronger than the soft anion TFSI⁻.^[27,28]

In order to fully understand the effect of MBO modified layer on the electrochemical performance of electrodes, we assembled MBO@PP separator in the stable commercial cathode material LiFePO₄ half-coin and tested the rate performance. According to the results of the rate performance test of the LiFePO₄ half-coins (Figure 6a), with the increases of the discharge current density, the discharge capacity of LiFePO₄ cells assembled with MBO@PP and PP separators is decreased, specifically, when the charge-discharge rate is less than 2 C, there is no difference in the discharge capacity of MBO@PP and PP separators, 150 mAh \cdot g⁻¹ (0.5 C), 144 mAh \cdot g⁻¹ (1 C) and 133 mAh \cdot g⁻¹ (2 C). When the rate continues to increase to 5 C, the discharge capacity of the LiFePO₄ cells equipped with MBO@PP and PP separators shows apparent difference, especially when the rate is 10 C, the discharge capacity of MBO@PP separator is maintained at 95 mAh \cdot g⁻¹ (10 C), which is greater than 72 mAh \cdot g⁻¹ (10 C) of the PP separator. This is because MBO@PP separator has higher Li⁺ ionic conductivity than that of PP separator, which calculated from the apparent ionic conductivity multiplied by t_{li+} . It should be pointed out that although the apparent ionic conductivity from EIS test of PP



Figure 6. a) Discharge C-rate capabilities of LiFePO₄ half-coins assembled with PP and MBO@PP separators; b) and c) are related discharge profiles of cells.

and MBO@PP is almost the same, but the obtained higher t_{li+} of MBO@PP increases the conduction of Li⁺ to promote the electrochemical reaction of LIBs, companied by reducing concentration polarization, and easier transmission of lithium ions at high current density, so it has higher discharge capacity.^[12,13] Similar situation can also be found in the relevant capacity-voltage curves (Figure 6b and 6c), before the current is less than 2 C, the related discharge platforms of MBO@PP and PP separators are not different, so there is no difference in discharge capacity; when the current density continues to increase to 5 C or 10 C, the discharge platform of LiFePO₄ halfcell with PP separators is reduced to 2.87 V (5 C), 2.67 V (10 C), while LiFePO₄ half-cell with MBO@PP separator can maintain the discharge platform to 3.22 V (5 C), 3.05 V (10 C). We can conclude that the LiFePO₄ half-cell equipped with MBO@PP separator has a smaller polarization, especially at high current density, so it has a higher discharge platform and a higher discharge capacity. A more detailed characterization was achieved by cyclic voltammetry at different scanning rate, as shown in the supplementary Figure S1, when scanning rate increases, the potential difference becomes more obvious, but MBO@PP separator has smaller peak gap than PP separator at the same scanning rate, and the faster the scanning rate, the larger the difference is, indicating that the addition of MBO modified layer enhances the reversibility of LiFePO₄, promotes better cycle stability, and MBO@PP separator has a clear advantage at faster scanning rate. This result is consistent with the capacity-voltage curves, repeating that the MBO modification layer reduces the concentration polarization and the loss of discharge capacity of LiFePO₄ at high current density.

The cycle performance of LiFePO₄ half-coins assembled with PP and MBO@PP separators is shown in Figure 7a, the discharge



Figure 7. a) Cycle performance and columbic efficiency of LiFePO₄/Li halfcoins at 1 C rate assembled with PP and MBO@PP separator; b) corresponding AC impedance spectra of LiFePO₄ half-coins at 2th and 100th cycles.



capacity of them is 144 mAh·g⁻¹ at 1 C rate and the coulomb efficiency is close to 100%. There is basically no difference, but based on the corresponding AC impedance spectra in the Figure 7b, we have found that their impedance increased before and after the cycle, while the values of MBO@PP separator before and after cycling are lower than those of PP separator system, which indicates that MBO modified layer reduces the interface impedance between separator and LiFe-PO₄ positive electrode, and is beneficial to stability under long cycling. To further prove, in the supplementary Figure S2, the LiFePO₄ half-coin with MBO@PP separator has better capacity retention rate under 5 C current charge and discharge for 1000th cycle.

3. Conclusions

In summary, the magnesium borate fiber is used as the functional ceramic coating onto commercial PP separator; the prepared MBO@PP separator has better wettability with liquid electrolyte, higher electrolyte uptake as well as thermal stability. Besides, MBO coating layer increase the t_{Li+} from 0.24 to 0.57 in the LiPF₆ based electrolyte due to the MBO acting as Lewis acid sites interacts with Lewis base PF⁻₆, moreover, we have found that the interaction of boron-oxygen groups in MBO with ClO⁻₄, PF⁻₆ is stronger than TFSI⁻. With the increase of t_{Li+} , the migration of Li⁺ is promoted, especially at high current density, the rate performance of LiFePO₄ half-coins has also been improved.

Experimental Section

The reagents NaCl, KCl, MgCl₂·6H₂O, Na₂B₄O₇·10H₂O were purchased from Sinopharm Chemical Reagent Co., Ltd. Magnesium borate Mg₂B₂O₅ (abbreviated as MBO) fibers were prepared by the NaCl-KCl molten salt method.^[23] Firstly, NaCl, KCl, MgCl₂·6H₂O and $Na_2B_4O_7 \cdot 10H_2O$ were weighed and mixed according to the molar ratio of n(B)/n(Mg) = 3, n(NaCl) / n(KCl) = 1. An appropriate amount of ethanol as the dispersant solvent was added, followed by ballmilled process at 400 rpm for 2 h and dried at 80 °C for 12 h. Then, the obtained powders was reacted at 800 °C for 6 h in a muffle furnace, the product was dispersed in water by ultrasonic oscillation, filtered and washed three times, finally dried at 80 °C for 24 h. 8 mg magnesium borate fibers and 2 mg polyvinylidene fluoride (PVDF) were dispersed in 50 mL N-methylpyrrolidone (NMP) solvent. After ultrasonic dispersion for 30 minutes, they were filtered on PP (Celgard 2500) porous membrane, followed by dried at 60 °C for 24 h to remove the solvent, and finally punched into a separator (abbreviated as MBO@PP) with a diameter of 18.5 mm.

Characterization

The structure information of the synthesized MBO fibers was measured by X-ray powder diffractometer (XRD, Rigaku MiniFlex 600). The morphologies of the MBO fibers, MBO@PP and pristine PP separators were characterized by field scanning electron microscopy (FE-SEM, S-4800, Hitachi). The infiltration of the separators and the electrolyte was analyzed by a contact angle instrument (Powereach JC2000 C1, Shanghai Zhongchen Digital Technique Equipment Co., Ltd.). The electrolyte uptake of the separators was

obtained by calculating the quality difference before and after the separator absorbs the liquid electrolyte. The formula is as follows:

Uptake
$$[\%] = (W - W_0) / W_0 \times 100$$
 (1)

where W_0 and W are the mass before and after the separator absorbing the liquid electrolyte. The ionic conductivity was measured by electrochemical impedance spectroscopy (EIS) on an electrochemical workstation (Solartron, SI-1260, England), where the separator soaking in liquid electrolyte was sandwiched between two stainless steel (SS) electrodes in the frequency range of 0.1 Hz-1 MHz. The ionic conductivity was calculated as follows: $\sigma = l/(R_{\rm b} \times$ A), where A is the area of the stainless steel electrode (2 cm^2) , I is the separator thickness. The electrochemical stability window of the separators was estimated by a cyclic voltammetry (CV) program of CHI-660E electrochemical workstation(Chenhua660E, CH Instruments Ins), in which the stainless steel was used as the working electrode and the lithium metal foil was used as the counter the reference electrode at a scan rate of 1 mV \cdot s⁻¹under a voltage range of -0.5-5 V. The t_{li+} was determined by the steady-state current method,^[29] which is to analyze the polarization current and polarization resistance of the Li/separator/Li symmetric cell. The t_{Li+} was calculated from the following formula:

$$t_{Li^{+}} = \frac{I_{s}(\Delta V - I_{0}R_{0})}{I_{0}(\Delta V - I_{s}R_{s})}$$

$$\tag{2}$$

Where I_0 and I_s are the initial and steady state current; $\triangle V$ is the applied polarization potential (10 mV); R_0 and R_s are the interface impedance before and after polarization.

In order to evaluate the electrochemical performance of MBO@PP separators, they were tested in lithium iron phosphate (LiFePO₄) coin half-cell where lithium metal was used as the anode. LiFePO4 cathode electrode was prepared by doctor-blade casting of a NMPbased slurry composed of 80 wt.% LiFePO₄ (Taiwan Likai Co., Ltd.), 10 wt.% carbon black and 10 wt.% PVDF onto aluminum foil, then dried in vacuum oven at 80°C for 24 h. Coin-type cells were assembled in an Ar-filled glove box (Mbraun, Germany), in which the electrolyte was 1 M LiPF₆ dissolved in 1:1 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (Guotai Huarong Co., Ltd.). The cell cycle test was charged-discharged on LAND battery testing system (Wuhan LAND Electronics Co., Ltd.) at a constant current of 0.5 C (1 C = 150 mAh \cdot g⁻¹) with a voltage range of 2.5–3.8 V (vs. Li/Li⁺). Rate capacity of cells was tested by charging to 3.8 V and discharging at different current rates of 0.5 C, 1 C, 2 C, 5 C and 10 C. AC impedance data was measured on electrochemical workstation (Solartron, SI-1260, England) over the frequency range of 0.1 Hz to 100 kHz with an amplitude of 5 mV. Cyclic voltammograms (CV) were recorded at CHI-660E electrochemical workstation with different scan rate.

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