

Composite MnCO₃/PVDF-HFP separator towards high-performance lithium-ion batteries

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Abstract. Separator is an essential component of battery between anode and cathode, but the commercial micro-porous polyolefin separator can hardly satisfy the continuously increasing battery energy densities due to its poor mechanical stability, low wettability, and limited electrolyte uptake. Poly(vinylidene fluoride -hexafluoropropylene-MnCO₃)(PVDF-HFP-MnCO₃) separator is synthesized and investigated for lithium-ion batteries. In addition to enhanced battery stability owing to the stable pore structure, the separator has a high electrolyte uptake, which gives them a remarkable rate performance. LiFePO₄/Li cell with PVDF-HFP-MnCO₃ separator delivers a capacity up to 145 mAh g⁻¹ at 0.5 C, and only 4.7% capacity degradation was observed after 100 charge/discharge cycles.

Introduction

Lithium-ion batteries (LIBs) have widely used in electronic devices and electrical vehicles[1-3]. A LIB essentially consists of an anode, cathode and separator. The function of separator between anode and cathode is to prevent the direct contact of electrodes while providing lithium-ion channels to enable ions pass through. Therefore, separator plays a key role in operational safety, cyclic performance, rate performance of batteries[4, 5]. However, the poor mechanical stability, low electrolyte uptake, and unsatisfactory wettability of the most commonly used micro-porous polyolefin separator[2] restrict the applications of lithium-ion battery in many specific areas [6, 7]. To improve the battery performances, a variety of polymers have been proposed as separators[6, 8, 9]. Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) has drawn extensive interest because of its superior mechanical properties, wettability, thermal stability, and low crystallinity[2, 8, 9]. However, the separator performances are still need improved to satisfy continuously increasing battery energy densities. Introducing inorganic particles, including aluminum oxide[10], silicon dioxide[11] and titanium dioxide[12, 13], into polymer membranes is an efficient method to gain improved battery properties.

In this work, MnCO₃ was incorporated into PVDF-HFP to obtain lithium-ion batteries. The addition of MnCO₃ to the separator leads to a uniform, high porosity separator and improved electrolyte uptake, which expedites lithium-ion transfer and delivers remarkable rate performances and stability.

Experimental Section

Preparation of composite separator. Commercial PVDF-HFP powders were purchased from Solvay Co. Ltd. ($M_w = 100,000$, 25 wt% HFP). A homogenous $MnCO_3$ (Aladdin) suspension was obtained by ball milling 0.1 $MnCO_3$ powders in 40 mL acetone (Ke Long, China) for 2 h at 700 r/min. 1.0 g PVDF-HFP powders and 2 mL obtained $MnCO_3$ suspension were added into 14 mL acetone to stir 10 mins. Then, the mixed suspension was stirred in a water bath until the solution became translucent. The colloidal of PVDF-HFP- $MnCO_3$ was cast on a steel substrate by casting machine and dried at the room temperature. Detached from the steel substrate, PVDF-HFP- $MnCO_3$ separator was obtained. The PVDF-HFP separator was prepared in a similar procedure without adding $MnCO_3$.

Separator and electrochemical characterization. The surface morphology of the polymer separators were observed by using a field-emission scanning electron microscope (FE-SEM, Quanta, USA). Coincells (2032) of cathode/PVDF-HFP- $MnCO_3$ membrane/lithium anode were assembled in a glove box (water containing < 1 ppm). The rate capability was calculated based on the theoretical capacities of LFP (172 mA h/g). The cyclic performance and rate capacity of batteries were analyzed with a battery testing system (Neware, China). The AC impedance and cyclic voltammetry (CV) measurement of cells were analyzed with a CHI760E electrochemical workstation (Shanghai Chenhua, China).

Results and Discussion

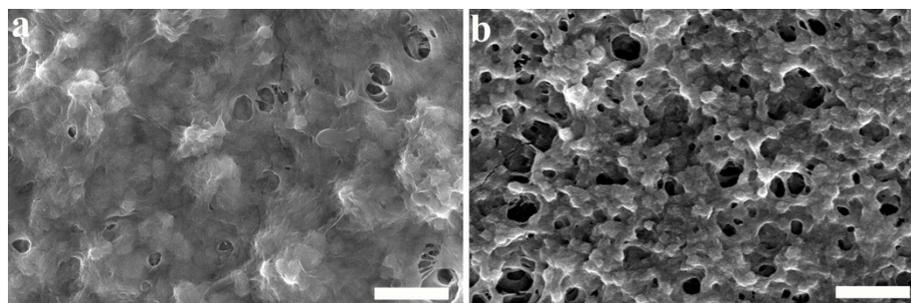


Fig. 1 SEM of (a) PVDF-HFP and (b) PVDF-HFP- $MnCO_3$ separators. The scale bar is 2 μm .

$MnCO_3$ /PVDF-HFP separator was obtained by simple casting and the mass fractions of $MnCO_3$ was 1%. As shown in the scanning electron microscopic (SEM) images of Figs. 1a and 1b, compared with pure PVDF-HFP, the introduction of $MnCO_3$ increases the porosity of the separators. The PVDF-HFP and PVDF-HFP- $MnCO_3$ separators exhibit the pore size of 420 nm, 386 nm, respectively. The introduction of $MnCO_3$ increases the porosity of PVDF-HFP- $MnCO_3$ up to 72.4%, about 20% higher than pure PVDF-HFP. As shown in Table 1, this significantly enhances the electrolyte uptake, which gives a high conductivity [14, 15]. The electrolyte we used here is 1 M $LiPF_6/EC-DMC-EMC-DEC$ (30:15:35:20).

The electrochemical performances of LFP/Li half cells with PVDF-HFP- $MnCO_3$ separators were compared that with pure PVDF-HFP and commercial Celgard 2400 separators. Typical discharge profiles of cells assembled with different separators are shown in Fig. 2a. The LFP/Li half cell with PVDF-HFP- $MnCO_3$ separator delivers a capacity of 145 mA h g^{-1} at 0.5 C, which is 16.5% higher than that with pure PVDF-HFP and 9.6% higher than that with commercial

Celgard 2400 separator. Furthermore, the LFP/Li half cells with $\text{MnCO}_3/\text{PVDF-HFP}$ shows good stability and only 4.7% capacity degradation was observed after 100 charge/discharge cycles. The rate performance of the LFP/Li half cell with PVDF-HFP-MnCO_3 separator is compared with those of pure PVDF-HFP and commercial Celgard separators. Fig. 2b shows the discharge profiles at different rates. The discharge capacity of the LFP/Li half cells with a PVDF-HFP-MnCO_3 separator was 90mAh g^{-1} at 5 C, which is well beyond those with other separators.

Table 1 The porosity and electrolyte uptake of different separators

	Porosity [%]	Electrolyte uptake [100%]
Celgard 2400	32.5	66.4
PVDF-HFP	60.5	100.0
PVDF-HFP- MnCO_3	72.4	178.6

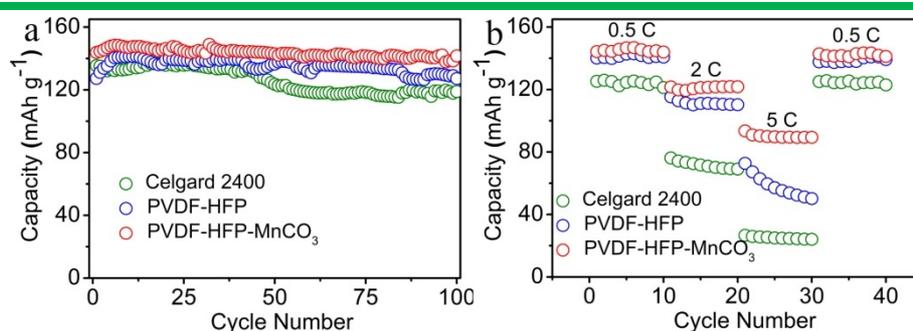


Fig. 2 (a) Cyclic performances of LFP/Li half cells with commercial Celgard 2400, PVDF-HFP, and PVDF-HFP-MnCO_3 separators at 0.5 C. (b) Rate performances at various C rates of LFP/Li half cells with Celgard 2400, PVDF-HFP, and PVDF-HFP-MnCO_3 separators

To further explore battery performances, the cyclic voltammogram (CV) curves of LFP cathode assembled in half cells with different separators at a scan rate of 0.2 mV s^{-1} are showed in Fig. 3a. The positions of the peaks reveal the electrode kinetics and reversibility, the intensity of the peaks is proportional to the lithium-ion diffusion coefficient[16]. As shown in Figures 3a, PVDF-HFP-MnCO_3 has lower over-potentials of 0.42 V, and higher intensity of the anodic and cathodic current peaks, indicating not only better battery kinetics and reversibility, but also a higher lithium-ion diffusion coefficient in comparison with other separators. The lithium-ion diffusion kinetics was studied by electrochemical impedance spectroscopy (EIS). A typical EIS profile is composed of a semicircle in the medium-frequency area and a slanted line in the low-frequency region. The semicircle represents the charge transfer process at the electrode/electrolyte interfaces, the slanted line represents the Warburg impedance and lithium-ion diffusion in the electrode[16]. Fig. 3b shows that the introduction of MnCO_3 significantly reduces the charge-transfer resistance. The improved cell performance by the incorporation of MnCO_3 particles into the separator can be attributed not only to an increase in the separator porosity (Table 1 and Fig. 1), but also to the enhancement of electrolyte uptake[17].

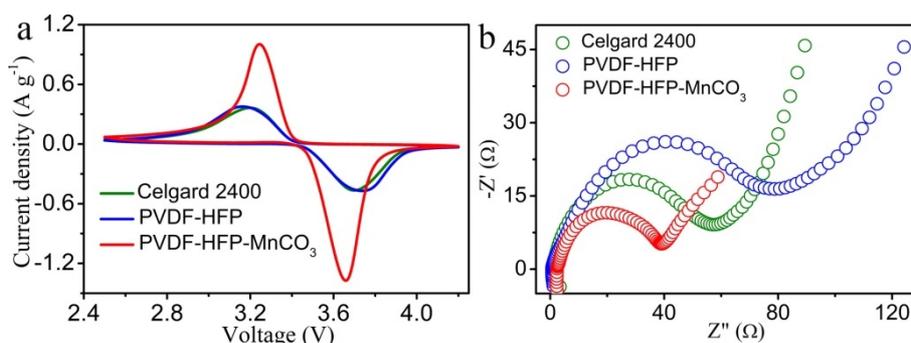


Fig. 3 (a) Cyclic voltammograms and (b) Nyquist plots of LFP/Li half cells with commercial Celgard 2400, PVDF-HFP, and PVDF-HFP-MnCO₃ separators. The scan rate for CV is 0.5 mV s⁻¹ in a potential window from 2.5 V to 4.2 V vs Li⁺/Li.

Conclusions

High-performance PVDF-HFP-MnCO₃ separator for lithium-ion batteries were prepared. The uniform incorporation of MnCO₃ in a PVDF-HFP separator enhances the porosity and electrolyte uptake, which expedites lithium-ion diffusion in the separator. LFP/Li half cells with PVDF-HFP-MnCO₃ separator exhibit much better electrochemical performances in comparison to cells with commercial Celgard and pure PVDF-HFP separators. This work offers an avenue to realize high-performance lithium-ion batteries for various applications.

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