

# Composite $\text{MnCO}_3$ /PVDF-HFP separator towards high-performance lithium-ion batteries

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**Keywords:** Lithium-ion batteries; polymeric separator;  $\text{MnCO}_3$ ; electrolyte uptake

**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- $\text{MnCO}_3$ )(PVDF-HFP- $\text{MnCO}_3$ ) 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.  $\text{LiFePO}_4/\text{Li}$  cell with PVDF-HFP- $\text{MnCO}_3$  separator delivers a capacity up to 145 mAh  $\text{g}^{-1}$  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.

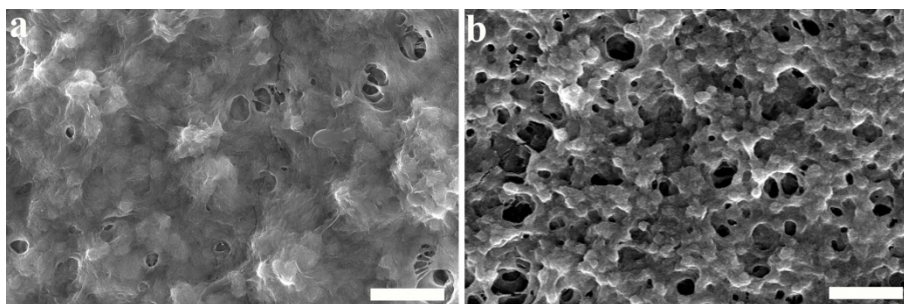
In this work,  $\text{MnCO}_3$  was incorporated into PVDF-HFP to obtain lithium-ion batteries. The addition of  $\text{MnCO}_3$  to the separator leads to a uniform, high porosity separator and improved electrolyte uptake, which expedites lithium-ion transfer and delivers remarkable rate performances 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 translucence. 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). Coin cells (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  $\mu m$ .

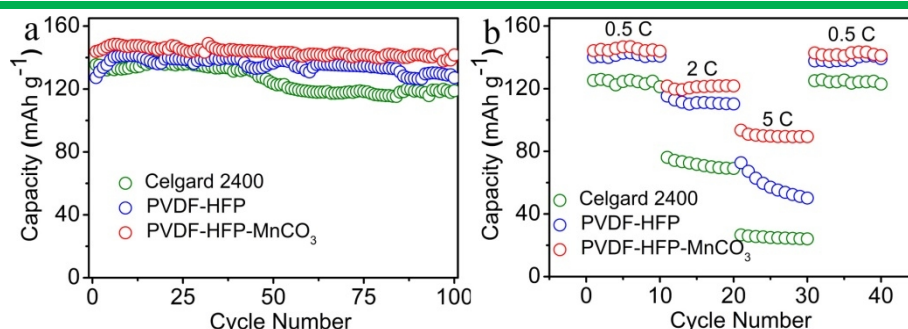
$MnCO_3$ /PVDF-HFP separator was obtained by simple casting and the mass fractions of  $MnCO_3$  was 1%. As shown in the scanning electron microscopic (SEM) images of Figs. 1a and 1b, compared with pure PVDF-HFP, the introduction of  $MnCO_3$  increases the porosity of the separators. The PVDF-HFP and 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 mAh  $g^{-1}$  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  $\text{PVDF-HFP-MnCO}_3$  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  $\text{PVDF-HFP-MnCO}_3$  separator was  $90 \text{ mAh g}^{-1}$  at 5 C, which is well beyond those with other separators.

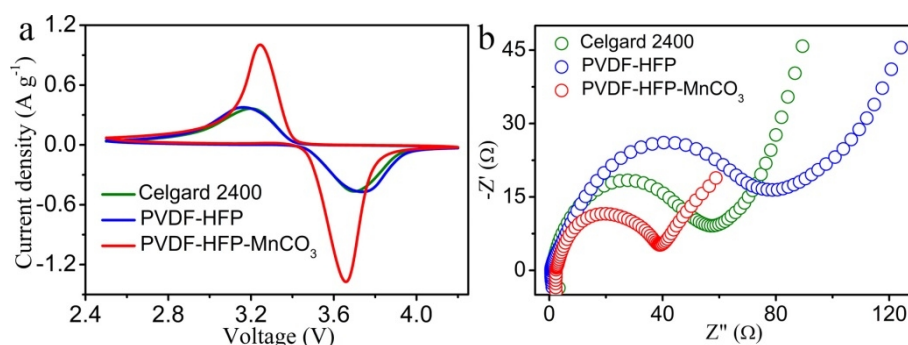
**Table 1** The porosity and electrolyte uptake of different separators

	Porosity [%]	Electrolyte uptake [100%]
Celgard 2400	32.5	66.4
PVDF-HFP	60.5	100.0
PVDF-HFP- $\text{MnCO}_3$	72.4	178.6



**Fig. 2** (a) Cyclic performances of LFP/Li half cells with commercial Celgard 2400, PVDF-HFP, and  $\text{PVDF-HFP-MnCO}_3$  separators at 0.5 C. (b) Rate performances at various C rates of LFP/Li half cells with Celgard 2400, PVDF-HFP, and  $\text{PVDF-HFP-MnCO}_3$  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  $0.2 \text{ mV s}^{-1}$  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,  $\text{PVDF-HFP-MnCO}_3$  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  $\text{MnCO}_3$  significantly reduces the charge-transfer resistance. The improved cell performance by the incorporation of  $\text{MnCO}_3$  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-MnCO<sub>3</sub> separators. The scan rate for CV is 0.5 mV s<sup>-1</sup> in a potential window from 2.5 V to 4.2 V vs Li<sup>+</sup>/Li.

## Conclusions

High-performance PVDF-HFP-MnCO<sub>3</sub> separator for lithium-ion batteries were prepared. The uniform incorporation of MnCO<sub>3</sub> 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-MnCO<sub>3</sub> 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.

## Acknowledgments

The work was financially supported by the Science & Technology Support Funds of Sichuan Province (Grant No. 2016GZ0151), the Fundamental Research Funds for the Chinese Central Universities (Grant No. ZYGX2015Z003), the National Natural Science Foundation of China (Grant No. 21403031 and 51501030) and the Robert A. Welch Foundation (Grant No. F-1066).

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