

Short communication

# PVdF-HFP/metal oxide nanocomposites: The matrices for high-conducting, low-leakage porous polymer electrolytes

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## Abstract

Highly conducting porous polymer electrolytes comprised of poly(vinylidene-fluoride-co-hexafluoropropylene) (PVdF-HFP), metal oxide (TiO<sub>2</sub>, MgO, ZnO)/or mesoporous zeolite (MCM-41, SBA-15), ethylene carbonate (EC), propylene carbonate (PC), and LiClO<sub>4</sub> were fabricated with a simple direct evaporation method. It was found that when metal oxide or mesoporous zeolite was mixed with PVdF-HFP, the impedance spectroscopy showed that the room temperature conductivity increased from  $1.2 \times 10^{-3} \text{ S cm}^{-1}$  (for pure PVdF-HFP) to  $2.1 \times 10^{-3} \text{ S cm}^{-1}$ . SEM micrographs showed that the pore size of the composite membrane was similar to that of pure PVdF-HFP membrane but the porosity decreased, nevertheless the solution uptake increased. The increasing in solution uptake is not related directly to the surface area or dielectric constant of the oxides. It may be due to the affinity of the metal oxide toward the electrolyte solution. Furthermore, the solution leakage of PVdF-HFP/MgO and PVdF-HFP/SBA-15 composite electrolytes also decreased compared to pure PVdF-HFP electrolyte. These polymer composite electrolytes were stable up to 5.5 V (versus Li/Li<sup>+</sup>) and the lithium ion cells assembled with these polymer electrolyte show a good performance at a discharge rate below *C*/2.

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## 1. Introduction

Polymer electrolytes (SPEs) have received considerable attention, because of their potential applications in solid-state batteries, electrochromic devices and fundamental research of ion transport in disordered phases [1]. Amongst the polymer electrolytes, PVdF-HFP films have received special attention as one of the promising host polymers for polymer electrolytes because of its excellent mechanical strength and electrochemical stability. PVdF-HFP films have been used as polymer matrix of polymer electrolyte in the most commonly commercialized plastic lithium-ion batteries (PLiON<sup>TM</sup>) by Telcordia Technologies (formerly Bellcore) since Gozdz et al. found the preparation process of the porous film [2]. Several reports [3] had revealed the various appealing properties, such as high solubility and lower crystallinity and glass transition temperature, of PVdF-HFP as a host for polymer electrolyte in rechargeable lithium-ion batteries. It is recognized that PVdF-HFP constitutes a two-

phase separated gel composed of the swollen polymer chains and the solution retained in the cavities of the porous polymer [4]. PVdF-HFP electrolytes were prepared by solution casting and then reswollen in Li salt electrolyte solution [5]. High ionic conductivity can be obtained this way while maintaining good mechanical properties.

The ionic conductivity of PVdF-HFP based electrolytes increases with increasing amount of the liquid electrolyte incorporated into the polymer matrix and decreasing the interaction between ion pair of the lithium salt. Many researches have been focused on increasing the liquid electrolyte content by controlling the components and morphology of the polymer electrolytes. For example, Huang and Wunder [6] showed that the addition of SiO<sub>2</sub> was an effective way to generate micropores in the PVdF-HFP matrix. Magistris and coworkers [7] reported that the addition of inorganic ceramics (such as Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, etc.) into the polymer electrolyte had been shown to improve the mechanical property, the working temperature of the electrolytes and the stability of the electrode–electrolyte interface. Godz et al. [8] revealed that adding SiO<sub>2</sub> increases the wettability and ionic conductivity of PVdF-HFP. Kim et al. [9] found that the addition of nanoscale inorganic fillers, such as alumina

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(Al<sub>2</sub>O<sub>3</sub>), silica (SiO<sub>2</sub>), copper oxide (CuO), titania (TiO<sub>2</sub>) to the polymer electrolyte resulted in the improvements of transport properties, mechanical and electrochemical properties as well as the increase in the absorption level of electrolyte solution. In addition to these effects, metal oxides act as solid plasticizer hindering the reorganization of polymer chains and can interact with polar groups of the polymer by Lewis acid–base reaction [10]. Therefore, the properties such as ionic conductivity, lithium ions transference number and activation energy for ions transport are improved. It is also shown [11] that the effects of the metal oxides, particularly, TiO<sub>2</sub> nanoparticles, in the PEO-based polymer electrolyte were not attributable to increase the polymer segmental motion but probably to the dipole interaction of metal oxide with the polymer component. Moreover, the metal oxide can reduce the interfacial resistance between the polymer electrolyte and lithium metal electrode by the solid-solvent role of the filler. It seems likely that metal oxide nanoparticles improve the conductivity of polymer electrolytes via an interaction with the ions rather than with the polymer.

On the other hand, there were some contrasting reports [12], in which the fillers of similar types have a negligible reducing effect on conductivity. The ambiguousness in comparing the reported results is due to that the conductivity is sensitive to many factors such as salt species and its concentration, particle size, thermal history and preparative methods. In this paper, PVdF-HFP blended with various inorganic nanoparticles such as metal oxides and mesoporous zeolites were prepared at the same conditions with the similar components except the inorganic additives (PVdF-HFP/ZnO may contain some ethylene glycol which cannot be removed during the preparation). The effect of the inorganic nanoparticles on the carriers transport properties of the polymer electrolytes was investigated and the charge/discharging cycling of lithium ion cells assembled with these polymer composite electrolytes are evaluated. The inorganic additives used in this study have significantly differences in dielectric constant, basicity, and surface area. The purpose of this study is to find out the major effect, amongst so many effects reported in literatures (*vide ante*), of oxide on the electrochemical and/or electric properties of PVdF-HFP/oxide composite electrolytes.

## 2. Experimental section

### 2.1. Materials and the preparation of PVdF-HFP/oxide composite membranes

LiClO<sub>4</sub> was dried under reduced pressure prior to use. Ethylene carbonate (EC), propylene carbonate (PC), poly(vinylidene-fluoride-co-hexafluoropropylene) (PVdF-HFP, MW = 40,000; VDF/HFP = 78/22), and solvents were obtained from commercial resources and used without further treatment. TiO<sub>2</sub> [13], ZnO [14], MgO [15] nanoparticles, MCM-41 [16a,b] and SBA-15 [16c] were prepared as literature reports. The composite membranes were prepared by both direct evaporation method: 2 g of PVdF-HFP was mixed with 4.64 g EC in 6 ml acetone. To the solution, 0.01 g of metal oxide was well suspended in 3 ml acetone and then added under vigorous stirring at 60–70 °C

for 12 h. After oxide was completely mixed with PVdF-HFP, the solution was blade coated on a Teflon plate. When the acetone was evaporated, the resulting film was heated in a vacuum oven at 80 °C, to remove trace amount of solvent. The mechanically stable free standing membranes were peeled off from the Teflon plates and stored in a dry-box. In the glove box, the composite membrane was cut into a disk with a diameter of 1 cm and soaked in a 1.0 M LiClO<sub>4</sub>-EC/PC (1:1) solution at room temperature for 1 h to activate the porous polymer electrolyte. The procedures for measuring the properties of composite membranes and the resulting composite polymer electrolytes are the same as what we reported previously [17].

### 2.2. Physical and electrochemical studies of composite electrolytes

The porosity and the electrolyte solution uptake of the polymer membranes as well as the solution leakage and the electric/electrochemical properties of porous composite electrolyte were measured according to the literature report [17]. Lithium ion cell was assembled in a glove box by sandwiching the electrolyte film between the anode and the cathode. The anode and cathode were prepared by coating anode and cathode slurries onto copper and aluminum substrates, respectively. The anode and cathode slurries were obtained by mixing electroactive materials (LiCoO<sub>2</sub> for cathode and MCMB for anode) with super-P carbon black, and a binding material in a specific weight ratio. Scanning electron microscopy (SEM) images were obtained with a Hitachi S-800 at 15 kV. Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA-7 thermal analysis system using dry nitrogen (or oxygen) as a carrier gas at a flow rate of 100 ml s<sup>-1</sup>. The TGA experiments were conducted from 25 to 850 °C with a linear heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimetry (DSC) measurements were performed on a Mettler Toledo DSC 822<sup>e</sup> apparatus. Samples were heated from 50 to 220 °C at a heating rate of 10 °C s<sup>-1</sup> and then cooled to 50 °C. Three heating-cooling cycles were recorded.

## 3. Results and discussion

### 3.1. Morphology, thermal stability, porosity, and electrolyte uptake of PVdF-HFP/oxide composite membranes

Fig. 1 shows the typical SEM microscopic images of the pure PVdF-HFP and PVdF-HFP films with various metal oxides. The films casted from the mixture of PVdF-HFP and metal oxide were opaque and smooth in appearance and did not show any phase separation in the SEM image. The cross-section SEM pictures revealed that pure PVdF-HFP film has a sponge-like structure whereas rather compact structure (it seems that the film was made from compressing small spherical particles) was observed in PVdF-HFP/oxide films. Compact structure may suggest low porosity. In order to explore the porosity of the polymer membranes, *n*-butanol absorption was performed as described in the literature [18,19]. It was found that the porosity of PVdF-HFP/oxide films is smaller than that of pure PVdF-HFP (the

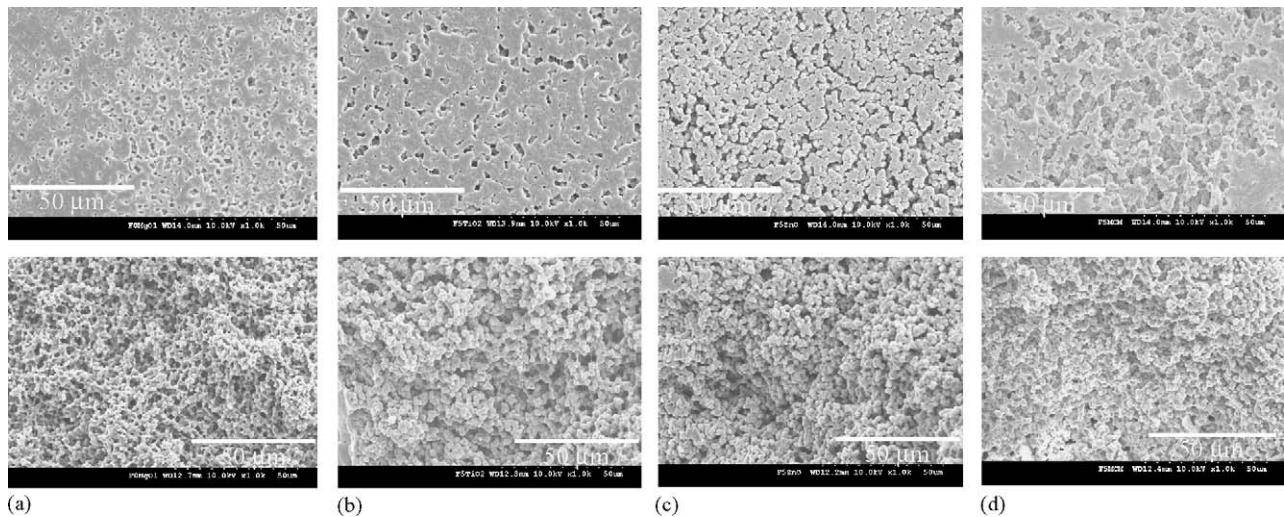


Fig. 1. The SEM images of (a) pure PVdF-HFP; (b) PVdF-HFP/5% TiO<sub>2</sub>; (c) PVdF-HFP/5% ZnO; (d) PVdF-HFP/5% MCM-41 (up: top view; down: cross-section view. Magnification: 1000×).

porosity of pure PVdF-HFP, PVdF-HFP/TiO<sub>2</sub>, PVdF-HFP/ZnO, PVdF-HFP/MgO, PVdF-HFP/MCM-41, and PVdF-HFP/SBA-15 is 0.52, 0.26, 0.27, 0.23, 0.42, and 0.52, respectively), consistent with the SEM data. Although the porosity of PVdF-HFP decreased after oxide was added, the solution uptake increased (the solution uptake for pure PVdF-HFP, PVdF-HFP/TiO<sub>2</sub>, PVdF-HFP/ZnO, PVdF-HFP/MgO, PVdF-HFP/MCM-41, and PVdF-HFP/SBA-15 is 55%, 110%, 62%, 61%, 93%, and 82%, respectively). This result suggests that blending oxide into PVdF-HFP can enhance the electrolyte absorption, due to the higher affinity of oxide toward EC/PC molecules (the solvents of the electrolyte). The high solution uptake of PVdF-HFP/MCM-41 and PVdF-HFP/SBA-15 is probably due to the high surface area of MCM-41, which can retain electrolyte solution. The physical properties of the metal oxides and mesoporous zeolites were listed in Table 1. Higher solution uptake suggested that composite films may have a higher conductivity. The conductivity data will be presented later in the article. The solution leakage of various PVdF-HFP/oxide composite electrolytes is displayed in Fig. 2. It was found that PVdF-HFP/metal oxide composite electrolytes and pure PVdF-HFP have similar solution leakage. However, PVdF-HFP/MCM-41 has the biggest solution leakage due to it has a largest solution uptake, whereas PVdF-HFP/SBA-15 has the smallest solution leakage. The high solution leakage of PVdF-HFP/MCM-41 is due to the high solution uptake of this composite matrix. The low solution leakage of PVdF-HFP/SBA-15 may be because of both PVdF-HFP chains and electrolyte

Table 1  
The physical properties of metal oxides and mesoporous zeolites

Sample	Surface area (m <sup>2</sup> )	Particle size (nm)	Dielectric constant
TiO <sub>2</sub>	52	~30	86–170
ZnO	41	20–30	8.4
MgO	42	30–50	9.8
SBA-15	780	100 × 250	1.4–2.5
MCM-41	1032	~100	1.4–2.5

were encapsulated in the pores of BSA-15, although we did not have any evidence.

The thermal stability of the as-prepared polymer membranes was tested with thermogravimetric analysis, Fig. 3a, which showed that the thermal stability of PVdF-HFP/oxide was better than that of pure PVdF-HFP. This is a typical phenomenon which showed that the thermal stability of the matrix increased when high thermal stability oxide particles were added. Typical DSC curves of pure PVdF-HFP and its oxide composite films are shown in Fig. 3b. The thermograms of all films exhibit an endothermic peak and an exothermic peak. The melting point and melting enthalpy of first heating-cooling cycle is similar to those of second and third cycles. Slightly increasing in melting point and decreasing in crystallization temperature was detected in PVdF-HFP/oxide composite, but the crystallinity did not change.

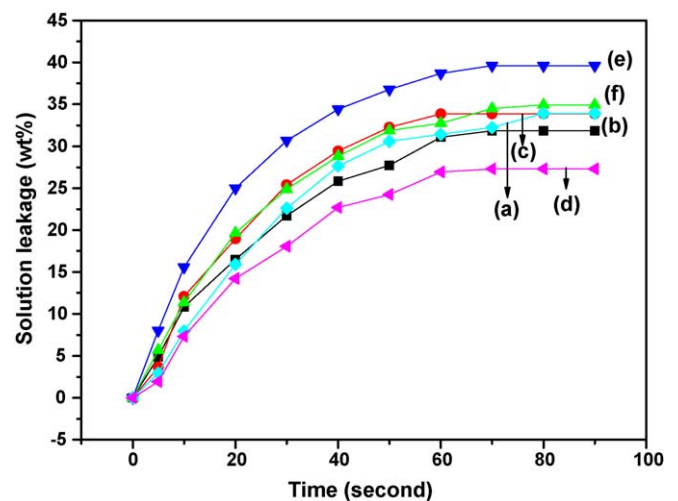


Fig. 2. Solution leakage of electrolyte on (a) PVdF-HFP; (b) PVdF-HFP/MgO; (c) PVdF-HFP/ZnO; (d) PVdF-HFP/SBA-15; (e) PVdF-HFP/MCM-41; (f) PVdF-HFP/TiO<sub>2</sub> matrix.



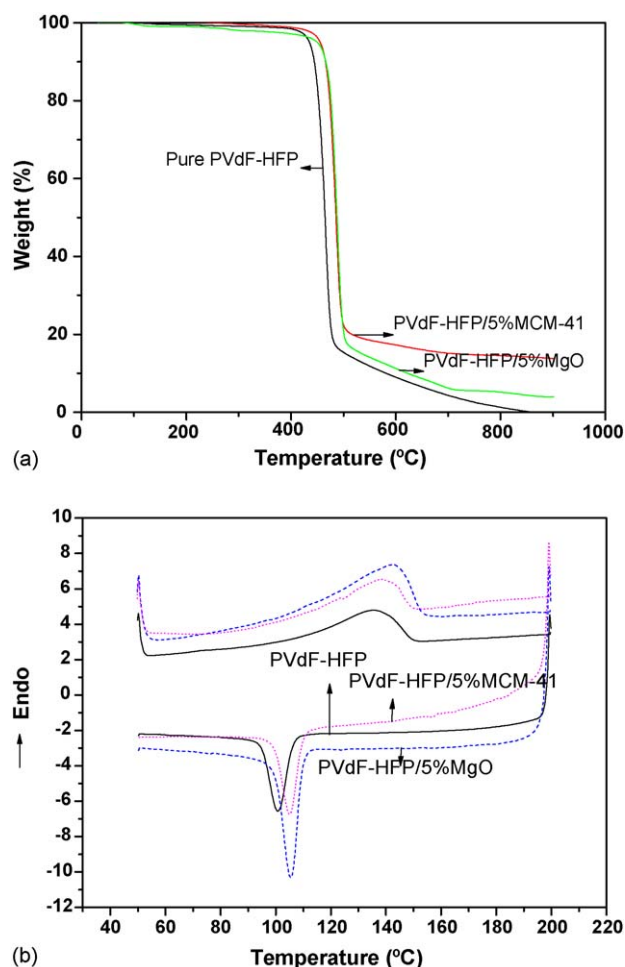


Fig. 3. (a) TGA curves of PVdF-HFP/oxide composites. (b) DSC patterns of PVdF-HFP/oxide composites.

### 3.2. Ionic conductivity of composite electrolytes

As described in the previous paragraph, the solution uptake of PVdF-HFP increased after blending oxide into it. We may expect that the conductivity of PVdF-HFP/oxide will be higher than pure PVdF-HFP. Variable temperature conductivity of PVdF-HFP and PVdF-HFP/oxide composite electrolytes is displayed in Fig. 4. The conductivity increased with increasing temperature, a typical behavior of lithium polymer electrolytes. Similar behavior has also been observed in PEO-based electrolytes. The room temperature conductivity of PVdF-HFP/oxide is higher than PVdF-HFP and greater than  $1 \times 10^{-3} \text{ S cm}^{-1}$  at temperatures as low as  $10^\circ\text{C}$  (the lowest temperature we can measure in our system), high enough for practical applications in lithium-ion batteries. As seen in Fig. 4, PVdF-HFP/5% MCM-41 has the highest conductivity amongst the electrolytes prepared in this article. The high conductivity was related to the high solution uptake of PVdF-HFP/MCM-41 described in the previous paragraph. Nevertheless, the solution uptake of pure PVdF-HFP, PVdF-HFP/TiO<sub>2</sub>, PVdF-HFP/ZnO, and PVdF-HFP/MgO is similar, why the conductivity of PVdF-HFP/ZnO has the highest conductivity among them? Enhancement of ion transport in PEO polymer electrolytes by addition of nanoscale inor-

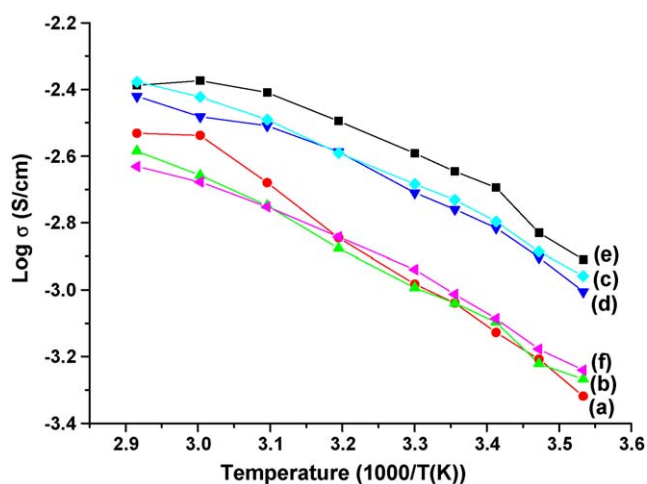


Fig. 4. Variable temperature conductivity of (a) PVdF-HFP; (b) PVdF-HFP/MgO; (c) PVdF-HFP/ZnO; (d) PVdF-HFP/SBA-15; (e) PVdF-HFP/MCM-41; (f) PVdF-HFP/TiO<sub>2</sub> matrix.

ganic oxides explored by <sup>7</sup>Li-NMR and electrochemical has been showed [20] that the increase in ionic conductivity is not attributed to a corresponding increase in polymer segmental motion, but more like a weakening of polymer-cation association induced by the nanoparticle. The similar effect can be adopted in PVdF-HFP/oxide system. Furthermore, Kearley et al. [21] studied the interaction between PEO oligomer, lithium salt and oxide additive in LiCF<sub>3</sub>SO<sub>3</sub>/CH<sub>3</sub>O(CH<sub>2</sub>)<sub>2</sub>Li<sub>2</sub>O/TiO<sub>2</sub> system with an inelastic neutron scattering (INS) and found that the addition of nanosized metal oxide fillers to polymer electrolytes probably has little effect on the conformation of the chains. Instead, the filler/salt interaction plays an important role in the increased conductivity of polymer/oxide composite electrolytes. If the filler/salt interaction is the major factor in determining the ionic conductivity of the composite electrolytes, we may expect the conductivity was related to the dielectric constant of the oxide filler at the similar electrolyte uptake. However, we found that the conductivity of PVdF-HFP/oxide composite electrolytes was independent of the dielectric constant (see Table 1). The high conductivity of PVdF-HFP/ZnO is probably due to the presence of ethylene glycol which was used to disperse the ZnO nanoparticle. It seems that the ionic conductivity of PVdF-HFP/oxide composite electrolyte depends on their solution uptake and the function of the oxide is to change the porosity and solution uptake of PVdF-HFP by interaction with both electrolyte solution and polymer matrix.

### 3.3. Electrochemical properties of composite polymer electrolyte

For determining the electrochemical stability window of the composite polymer electrolytes, a linear sweep voltammetry experiment was performed in the potential range of 0.0–6.0 V (versus Li/Li<sup>+</sup>) with a scan rate of  $5 \text{ mV s}^{-1}$ . Fig. 5 shows the current–voltage response of a Pt coated stainless steel electrode/polymer electrolyte/Pt cell. The onset current flow is associated with the decomposition voltage of the electrolyte. It was

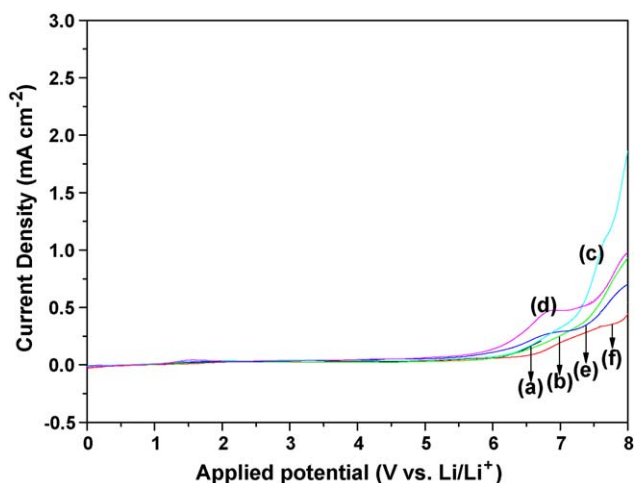


Fig. 5. Linear sweep voltograms of electrolyte on (a) PVdF-HFP; (b) PVdF-HFP/MgO; (c) PVdF-HFP/ZnO; (d) PVdF-HFP/SBA-15; (e) PVdF-HFP/MCM-41; (f) PVdF-HFP/TiO<sub>2</sub> matrix.

found that the current flow is very small when the voltage is below 5.5 V (versus Li/Li<sup>+</sup>). The fact that the oxidation occurs at potentials higher than 5.5 V for all PVdF-HFP/oxide makes these materials very suitable for lithium-ion battery applications.

To evaluate the electrochemical performance of a lithium ion polymer cell using PVdF-HFP/oxide electrolytes, MCMB/PVdF-HFP–MCM-41/LiCoO<sub>2</sub> cells were constructed. The assembled cells were subjected to preconditioning with a cut-off voltage of 4.2 V for the upper limit and 3.0 V for the lower limit at a charge rate of 45  $\mu\text{A cm}^{-2}$  for three cycles. The charge/discharge curves of the lithium ion polymer cell at various discharging rate were shown in Fig. 6. This cell delivered a discharge capacity of 23, 104, and 102 mAh for the first charge/discharge cycle at 1C (1.0 mA), C/2 (0.5 mA) and C/5 (0.2 mA) rate, respectively. The columbic efficiency, which is defined as the ratio of discharge capacity to charge capacity, is 63%, 88% and 91%, respectively, for the first cycle. For

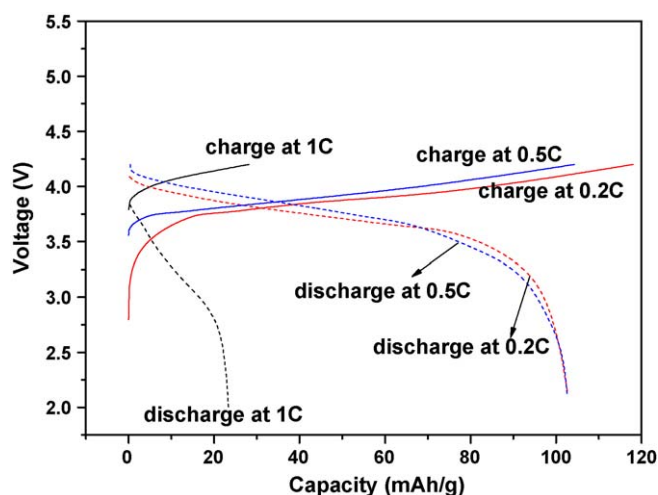


Fig. 6. The charge/discharge curves of a model batter using PVdF-HFP/5% MCM-41 as an electrolyte. The test was carried out at discharge rate of 1.0C, 0.5C, and 0.2C within the voltage range of 2.0–4.2 V.

further constant current cycle at C/2 rate, the capacity decreased slightly as cycling, the capacity is 65 mAh at seventh cycle, i.e. 63% of the initial capacity. The decline in capacity is primarily due to the lost of interfacial contact between electrodes and polymer electrolyte upon cycling, which gradually increased the internal resist of the cell. The voltage drops in passing from the charge to discharge increases with the discharge rate, reflecting a large polarization that reduces the discharge capacity. A promising capacity of 104 mAh is obtained at C/2 rate, the discharge capacity falls, however, at 1C rate (23 mAh). This is not sufficient to give high-rate performance in a lithium-ion polymer cell, and has to be improved. Further study in improving the performance of PVdF-HFP/oxide composite electrolytes via tuning the ratio of PVdF-HFP to oxide is in progress.

#### 4. Conclusion

PVdF-HFP/oxide polymer membranes were fabricated by mixing PVdF-HFP and oxide nanoparticles. The porosity of the PVdF-HFP/oxide membranes decreased, however the solution uptake increased, as a consequence, the ionic conductivity increased. Lithium ion cell using PVdF-HFP/oxide composite electrolyte revealed a better performance at discharge rate of C/2.

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