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Structure and performance of porous polymer electrolytes based on P(VDF-HFP) for lithium ion batteries

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Abstract

In order to develop polymer electrolyte for lithium ion batteries, highly porous P(VDF-HFP) membranes were prepared by using phase inversion method, then they were immerged in 1 mol kg^{-1} solution of $LiClO_4$-EC/PC(1:1) to form porous polymer electrolytes. Conductivity of the polymer electrolytes was found to be as high as 10^{-3} S cm^{-1}. Structures of the porous membranes were observed with SEM. Porous membranes with different structure, porosity and pore diameter were prepared by changing the processing conditions. There are two kinds of typical structure, one is honeycomb-like (type I), and the other is network-like (type II). Membrane structures were found to be important to the performance of the porous polymer electrolytes. Small pore diameter with narrow distribution is needed to prevent solution leakage and high porosity is needed to achieve high conductivity. The type II membranes can meet the requirements. The model lithium ion batteries made of the resulting porous polymer electrolytes have good cycleablity.

Keywords: Polymer electrolyte; Poly(vinylidene fluoride); Porous membrane; Lithium ion battery

1. Introduction

Lithium ion batteries are widely used in portable electronic devices at present and they are competent choices for electrical vehicles because of their advantages such as high energy density, high single cell voltage and no memory effect. Conventional lithium ion batteries use liquid electrolyte, which makes batteries unsafe because of electrolyte leakage, and they are heavy because metal package is needed. Now these problems have been solved by the application of polymer electrolyte, which greatly improves safety and makes batteries lighter by using plastic package, what is more, it makes the shape design of batteries more flexible. So the research and development of polymer electrolyte has been paid more attention to.

The research of polymer electrolyte in the early days was emphasized on dry polymer electrolyte based on polyethers, which began with Wright's research about the complex of PEO and sodium salts [1]. The conductivity of that kind of polymer electrolytes is very low, so a lot of research work has been done to improve the conductivity, and it has been improved by several magnitude [2,3], but it is still not enough for practical use. After 1990s, the emphasis of research has turned to polymer gel electrolytes with conductivity as high as 10^{-3} S cm^{-1}, which is enough for practical use. Polymers used in gel electrolyte [4–8] include PVDF, PAN, PMMA, PEO, etc. Among them, PVDF and its copolymers are very important because of their high strength and good stability [9–12].

Considering the requirements of industrial production, Gozdz et al. developed a kind of porous polymer electrolyte based on PVDF and its copolymer [13]. The method is to prepare porous membrane first, then it is used as separator to assemble a battery, which is activated by adding liquid electrolyte to it in a dry room at last. The porous membrane is swelled and becomes polymer electrolyte similar to gel electrolyte. This process is quite similar to that of producing lithium ion batteries with liquid electrolyte, thus, the application of polymer electrolyte becomes more feasible. Later, there were further studies on such a kind of polymer electrolyte [14,15], and phase inversion method had been used to prepare porous membrane [16–18]. But detailed study about the influences of membrane structure on the performance of porous polymer electrolyte has not been reported.

In this paper, porous membranes of P(VDF-HFP) copolymer were prepared by phase inversion method and were

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used to form porous polymer electrolytes. More attention was paid to the influences of membrane structure on performance of the porous polymer electrolyte.

2. Experimental

2.1. Materials

P(VDF-HFP) copolymer containing 10% HFP unit was obtained from Solvay and was directly used. NMP and acetone obtained from Beijing Yili Fine Chemicals Co. Ltd. were distilled before being used. Hydrated lithium perchlorate ($LiClO_4 \cdot 3H_2O$) obtained from Beijing Baili Chemical Developing Center was dried under vacuum at 120°C for 24 h to remove water before being used. Ethylene carbonate (EC) was obtained from Baker Chemical Co. and was directly used. Propylene carbonate (PC) obtained from Shanghai Reagent Factory I was distilled under vacuum before being used. The $LiCoO_2$ powder and the 1 M $LiPF_6$ solution in EC/DEC was obtained from Merck Co. and was directly used.

2.2. Preparation of the porous membranes

Porous membranes were prepared by phase inversion method. A certain amount of copolymer was dissolved into the mixture of NMP and acetone. The solution was cast on a newly cleaned glass plate and desired thickness was made using a doctor blade. After the evaporation of acetone, the glass plate was put into steam atmosphere and phase inversion occurred. The resulting membrane was washed with deionized water and dried under vacuum.

Nine porous membranes with different structures were prepared by changing the composition of casting solution and the temperature of preparation. Their serial number and preparation conditions were listed in Table 1.

2.3. Structure characterization of the porous membranes

The membrane specimens were broken by freeze fracture technique at first, their sections were coated with gold by ion sputter, then their section morphology was observed with JMS-6301F field emission SEM. To avoid damaging porous membrane, 5 kV acceleration voltage was used. The freeze fracture processing was omitted when the surface morphology of these membranes was observed with SEM. Pore diameters of these membranes and their distribution can be estimated based on SEM micrographs.

Porosity was measured by the following method: immerge the membrane into *n*-butanol for 1 h, weigh the mass of membrane before and after absorption of *n*-butanol, then calculate the porosity of membrane based on the following equation:

$$p = \frac{m_a/\rho_a}{m_a/\rho_a + m_p/\rho_p} \quad (1)$$

where m_p is the mass of the dry membrane, m_a the mass of butanol absorbed in the wet membrane, ρ_a the density of butanol, and ρ_p the density of polymer.

2.4. Preparation of the porous polymer electrolytes

The membrane was dried under vacuum at 80°C for 2 h, and then was put into a dry glove box instantly. After the mass of membrane was weighed, it was immerged into 1 mol kg^{-1} solution of $LiClO_4$-EC/PC(1:1) for 1 h to make porous polymer electrolyte. Excrescent solution at the surface of the polymer electrolyte was absorbed with filter paper. The serial number of the polymer electrolytes was named corresponding to that of the membranes used (Table 2).

The polymer electrolytes used for model lithium ion batteries were prepared using 1 M $LiPF_6$-EC/DEC solution.

2.5. Measurement of conductivity of the porous polymer electrolytes

The resulting porous polymer electrolyte was put between two stainless steel electrodes in a dry glove box and sealed in a battery container. Then the container was taken out from the glove box and put into an oil bath with thermostat. The resistance of the polymer electrolyte was measured using ZL5 intelligent LCR meter, which was made by Shanghai

Table 1
Conditions of the porous membrane preparation

S. no.	Composition (w/w/w) P(VDF-HFP)/NMP/acetone	Temperature (°C)
M1	1/4/0	70
M2	1/4/0	80
M3	1/4/0	90
M4	1/3/1	70
M5	1/3/1	80
M6	1/3/1	90
M7	3/7/5	70
M8	3/7/5	80
M9	3/7/5	90

Table 2
Corresponding relationship between the polymer electrolytes and their membranes

Membranes	Polymer electrolytes
M1	E1
M2	E2
M3	E3
M4	E4
M5	E5
M6	E6
M7	E7
M8	E8
M9	E9

Research Institute of Instruments. The frequency range is 10 Hz–100 kHz. The bulk resistance of the polymer electrolyte was found from the impedance spectrum, and the conductivity was calculated based on the following equation:

$$\sigma = \frac{h}{\pi/4d^2 R_b} \quad (2)$$

where σ is the conductivity, R_b the bulk resistance, d the diameter, and h the thickness of the specimen.

2.6. Characterization of solution leakage of the porous polymer electrolytes

The porous P(VDF-HFP) electrolyte sample was cut into a specimen of 2 cm in diameter. After the mass was weighed, the specimen was put onto three layers of filter paper and covered with other three layers of filter paper. Then a weight of 100 g was put on the top of the assembly. After a certain time, the specimen was taken out and its mass was weighed. All these operations were done in a dry glove box.

Absorption ratio of electrolyte solution, R_A, was defined as the ratio of the mass of the absorbed electrolyte solution to the mass of the porous membrane. Leakage ratio of electrolyte solution, R_L, was defined as the change of R_A before and after the solution leakage test.

$$R_A = \frac{m_l}{m_p} \quad (3)$$

$$R_L = \frac{R_{Af} - R_{Ai}}{R_{Ai}} \quad (4)$$

where m_l is the mass of absorbed electrolyte solution, m_p the mass of porous membrane, R_{Ai} the initial absorption ratio of electrolyte solution before the test, and R_{Af} the final absorption ratio of electrolyte solution after a certain time of the test.

2.7. Cycle test of lithium ion batteries

The cathode was prepared by mixing the powder of $LiCoO_2$, conductive carbon black and PTFE together to form a film, and it was dried under vacuum for 48 h, then immerged into 1 M $LiPF_6$-EC/DEC electrolyte solution. The anode used was lithium metal. In a dry glove box, the porous polymer electrolyte was put between the cathode and the anode to form a model cell, which was sealed in a battery container. Cycle test was conducted using Land Battery Test System made by Wuhan Land Electronic Co. Ltd. The test was carried out at a constant current density of 0.50 mA cm^{-2} and within the voltage range of 3.0–4.3 V.

3. Results and discussions

3.1. Morphology of the porous membranes

Typical SEM micrographs of section and surface of the porous polymer membranes were shown in Fig. 1. It was found that the membranes have symmetrical morphology, and structure difference can be seen among samples prepared under different conditions. Two kinds of typical structure were found, one is honeycomb-like (type I), and the other is network-like (type II).

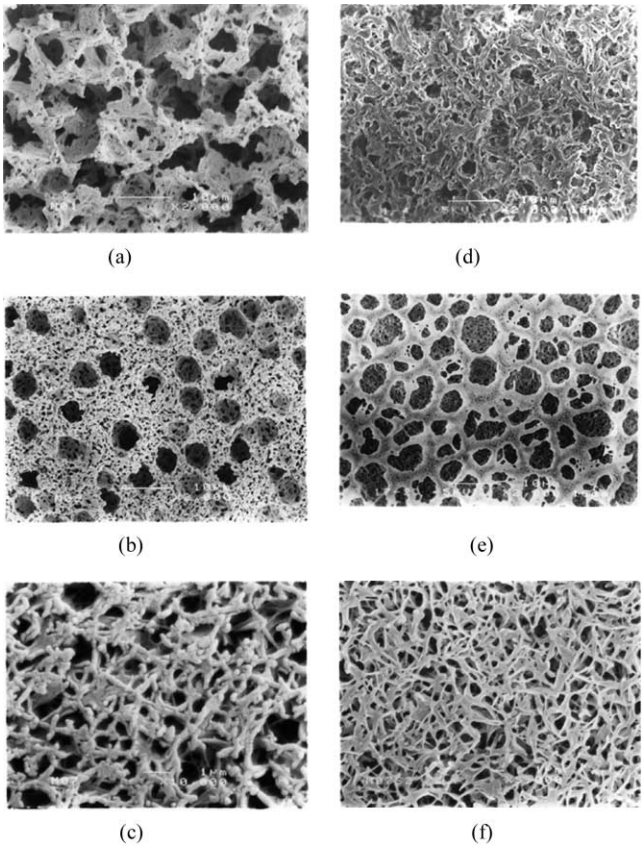

Fig. 1. Typical SEM micrographs of bulk and surface of porous P(VDF-HFP) membranes. Parts (a), (b) and (c) are the bulk morphology of M1, M9 and M7, respectively; parts (d), (e) and (f) are the surface morphology of M1, M9 and M7, respectively.

The found data of porosity and pore diameter of the samples are listed in Table 3. Here, d_n is the number average pore diameter, its value is close to diameters of small pores; d_S is the area average pore diameter, its value is close to diameters of big pores. The dispersion coefficient of pore

Table 3
Structure parameters of the P(VDF-HFP) porous membranes

S. no.	Type of membrane	Porosity	Pore diameter		
			d_S (μm)	d_n (μm)	μ
M1	I	0.83	11	1.3	8.5
M2	I	0.84	10	1.1	9.1
M3	I	0.82	9.0	1.1	8.2
M4	II	0.80	0.55	0.24	2.3
M5	I	0.79	4.9	0.94	5.2
M6	I	0.83	5.8	1.1	5.3
M7	II	0.78	0.63	0.30	2.1
M8	II	0.78	0.61	0.26	2.3
M9	I	0.74	3.7	0.82	4.5

diameter, m, is defined as d_S/d_n to characterize the distribution of pore diameters of the membranes.

For the type I membranes, pore diameters show bimodal distribution. The difference between the size of big pores and small pores is remarkable, so their μ value is large ($\mu > 4$). Their d_n value is close to each other, which means that their small pores have similar sizes. For the type II membranes, their pore diameter is almost uniform, so their m values are much smaller than those of the type I membranes ($\mu \approx 2$).

3.2. Solution leakage of the porous polymer electrolytes

3.2.1. Characterization of solution leakage

In order to find a parameter to characterize the solution leakage of the porous polymer electrolyte, some polymer electrolyte samples were chosen to test the weight change with test time according to the method described in Section 2.6, and the weight was measured every 10 min. The normalized data of a typical sample were shown in Fig. 2.

The data found can be fit into an exponential decay curve, that is

$$y = y_0 + A_1 \, e^{-t/t_1} \quad (5)$$

where y is the relative weight ratio of the sample at the moment of t; y_0 the final relative weight ratio of the sample; A_1 the final weight loss ratio, t_1 the time constant of weight loss. For the sample of Fig. 2, the resulting data of the parameters are 0.85, 0.15 and 13.7 min, respectively.

It has been found that for all these samples, time constant of weight loss is <15 min and their weight is almost constant after 30 min. So the leakage ratio of electrolyte solution at 30 min (R_{L30}) can be used to characterize the solution leakage of the samples.

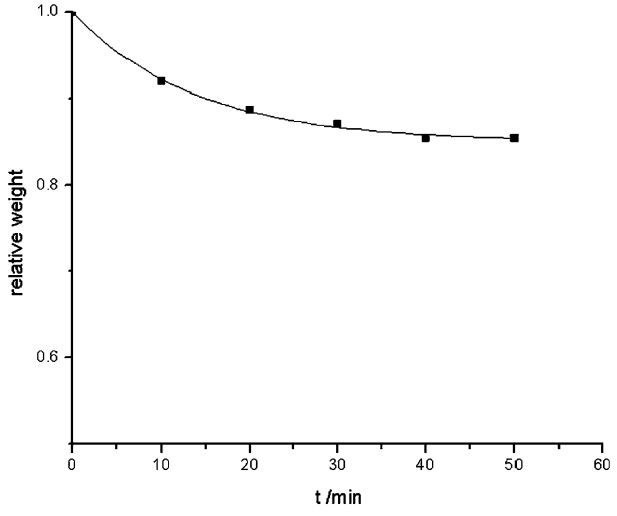

Fig. 2. Typical weight loss curve of the porous polymer electrolytes in the solution leakage test. Relative weight is the ratio of the weight at that time to the initial weight of the membrane.

Table 4
Solution leakage of the porous polymer electrolytes

S. no.	Type of membrane	R_{Ai}	R_{Af}	R_{L30}
E1	I	5.19	4.05	0.220
E2	I	5.76	3.88	0.327
E3	I	5.61	3.94	0.298
E4	II	4.95	4.95	0
E5	I	4.75	4.17	0.121
E6	I	4.59	3.91	0.149
E7	II	3.38	3.38	0
E8	II	3.78	3.67	0.027
E9	I	3.02	2.87	0.050

Data obtained in solution leakage test of these nine samples of porous polymer electrolyte are listed in Table 4. Obviously, R_{Ai} is corresponding to porosity, but not exactly related to it, because the solution absorbed in the polymer electrolyte is different from the liquid used in the porosity test.

3.2.2. Relationships between membrane structures and solution leakage of the polymer electrolytes

There are two processes in the solution leakage of the porous polymer electrolytes; one is that electrolyte solution in the surface layer exudes through surface pores, and the other is that electrolyte solution transfers from the interior to the surface layer. So solution leakage of the porous polymer electrolytes is influenced by their structures of interior and surface layer. For these nine samples, structure and pore diameter of their surface is consistent with that of their interior. Therefore, solution leakage of these samples is mainly controlled by their bulk structure, and the structure parameters in following discussions refer to bulk ones.

It seems that solution leakage should decrease with porosity, but it is not true in our experiment. For example, membrane M4 has very high porosity, but sample E4 has very low leakage ratio of electrolyte solution, even it cannot be observed in the test. That is to say, porosity is not the main factor that controls solution leakage in our experiment.

Therefore, the main factor that controls solution leakage should be pore diameter. By comparing data in Table 3 with Table 4, it can be found that solution leakage is remarkably influenced by d_S. Fig. 3 shows that R_{L30} increases with d_S. That is to say, big pores are easy to result in solution leakage.

For the type I porous polymer electrolyte, the diameter of big pores is large and proportion of big pores is high, so its solution leakage is very serious. When d_S is about 10 μm, such as E1, E2 and E3, R_{L30} is higher than 20%, even as high as 30%, because solution is very easy to leak through such big pores. When d_S decreases to about 5 μm, such as E5 and E6, R_{L30} decreases to 10–15%. E9 has a smaller value of d_S (3.7 μm), thus, R_{L30} is so low as to be 5%.

The type II porous polymer electrolyte has small pore diameters (<1 μm) with narrow distribution, so its R_{L30} is very low. For E4 and E7, no solution leakage can be observed in the test, though E4 has very high porosity.

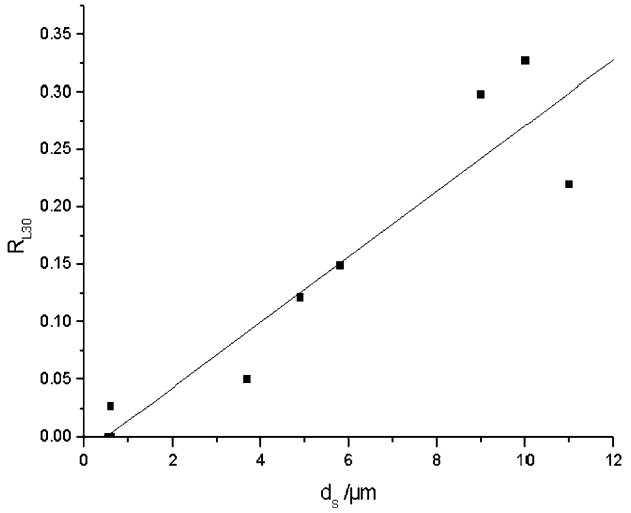

Fig. 3. Relationship between solution leakage of the polymer electrolytes and pore diameters of the membranes.

Obviously, pore diameter and its distribution are the decisive factors of solution leakage.

A good porous polymer electrolyte should have low solution leakage, and it is hoped that no solution leakage would occur when it is used. It can be found in experiment that the key to decrease solution leakage is to decrease pore diameter of the membrane. The ideal case is that pore diameter is smaller than 1 μm and distribution of pore diameter is narrow, thus solution leakage is small enough to be neglected. The type II membrane can meet the requirements, so it is suitable for porous polymer electrolytes.

3.3. Conductivity of the porous polymer electrolytes

3.3.1. Ac impedance spectrum

A typical ac impedance spectrum of the porous polymer electrolyte using blocking electrode of stainless steel is a straight line in low frequency range and bends to the real axis in high frequency range. The bulk resistance can be found in spectrum by extending the curve to the real axis.

The conductivity of these nine samples of porous polymer electrolyte is shown in Table 5.

Table 5
Conductivity of the porous polymer electrolytes

S. no.	Type of membrane	R_{Af}	d_S (μm)	Conductivity (mS cm^{-1})
E1	I	4.05	11	1.47
E2	I	3.88	10	1.51
E3	I	3.94	9.0	1.05
E4	II	4.95	0.55	1.64
E5	I	4.17	4.9	0.94
E6	I	3.91	5.8	0.66
E7	II	3.38	0.63	1.12
E8	II	3.67	0.61	0.63
E9	I	2.87	3.7	0.31

3.3.2. Relationships between membrane structures and conductivity of the polymer electrolytes

It was found in experiments that membrane structure has great influence on conductivity of the porous polymer electrolytes, so two structure parameters of porosity and pore diameter are considered as follows.

Since conductivity is measured after the solution leakage test in our experiments, and R_{Af} represents the actual amount of electrolyte solution preserved in the membrane, it is better to use R_{Af} in stead of porosity in the following discussion about conductivity. Obviously, R_{Af} is controlled not only by porosity, but also by leakage ratio of electrolyte solution. Of course, porosity is more important.

The influence of membrane structure on conductivity of the porous polymer electrolyte is markedly different for the two types of membranes since their structure characteristics are quite different. The following dissection is carried out separately for the membranes of types I and II.

For the type I membranes, the number average pore diameter d_n is almost the same, but the area average pore diameter d_S is quite different, so d_S can represent the difference of pore sizes among different samples. From the experiment data, it may be seen that the conductivity generally increases with R_{Af} and d_S, but the influence of R_{Af} is much stronger.

This can be explained by conductive mechanism of the porous polymer electrolyte. Obviously, there are two phases existed in the porous polymer electrolyte, one is the gel phase formed by swollen polymer and the other is the liquid phase formed by liquid electrolyte. The gel phase may play an important role in ion transport, but it is not dominant in the above-mentioned membranes. The swell of the polymer is restricted by the crystallinity of the polymer and the mild preparation conditions, so its volume ratio is quite lower than that of liquid phase because of high porosity. Besides, conductivity of swollen polymer is much lower than that of liquid electrolyte. It is, therefore, considered that the conductivity of the porous polymer electrolyte is dominated by the liquid phase formed in pores. That is to say, ions are mainly conducted in the paths formed by interconnection of pores, so size and number of these conductive paths determine their conductivity. Higher absorption ratio of electrolyte solution means more volume ratio of liquid phase in the porous polymer electrolyte, which leads to more and wider conductive paths, and results in higher conductivity, so the influence of R_{Af} on σ is quite strong. Larger pore size is convenient for interconnection of pores to form wider conductive paths, which results in higher conductivity, but this influence is relatively weak.

For the type II membranes, pore diameter and its dispersion coefficient is so similar that there is little difference among their structure. Based on the data in Table 5, it can be seen that the conductivity of type II porous polymer electrolyte is mainly controlled by absorption ratio of electrolyte solution. The conductivity of sample E4 is much higher than

that of E7 and E8 since its R_{Af} is much higher than that of E7 and E8.

It is notable that for both membranes of type I and type II, R_{Af} is a main factor that controls their conductivity. If solution leakage is negligible, R_{Af} is determined by porosity, so porous polymer electrolyte should have porosity high enough to ensure high conductivity.

Good porous polymer electrolyte should have high conductivity with negligible solution leakage. It was found that high porosity is needed for high conductivity and small pore diameter with narrow distribution is needed for low solution leakage. Our experiments show that porosity should be >80% and pore diameter should be <1 μm.

Among two types of membranes, the type I membranes have bimodal distribution of pore diameter, so diameter of big pores is very large when porosity is high; but for a type II membrane, its pore diameter can remain small when its porosity is high. That is to say, type II membrane is more suitable for the application of porous polymer electrolyte. For example, among the type II membranes, M4 and M7 have high porosity and small pore diameter, so their corresponding samples E4 and E7 has high conductivity (>1 mS cm^{-1}) as well as negligible electrolyte leakage. In addition, mechanical strength of the type II membranes is higher than that of the type I membranes.

3.4. Cycleability of lithium ion batteries

In order to verify electrochemical performance of the porous polymer electrolytes, model cells are assembled to test their cycle performance of charge and discharge. A typical charge and discharge curve of the first cycle is shown in Fig. 4. Relative values of discharge capacities as a function of cycle number of a typical sample are shown in Fig. 5. It can be seen in Fig. 5 that the discharge capacity decreases in the first three cycles and remains at the same level in the following cycles, which proves good cycleability of the lithium ion battery with the porous polymer electrolyte.

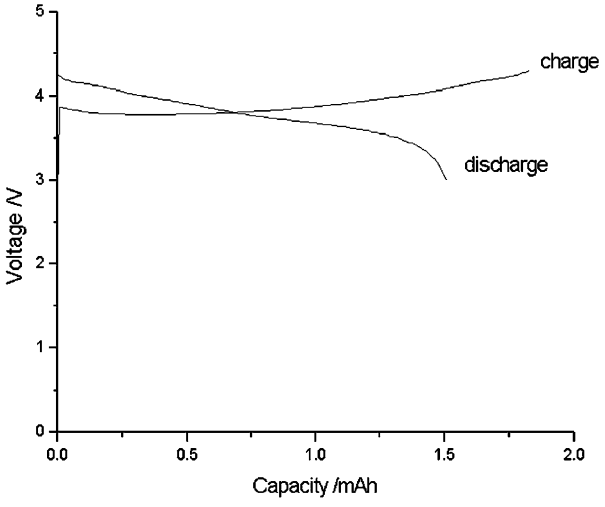

Fig. 4. Charge and discharge curve of the first cycle of a model lithium ion battery using the porous polymer electrolyte. The test was carried out at a constant current density of 0.16 mA cm^{-2} and within the voltage range of 3.0–4.3 V.

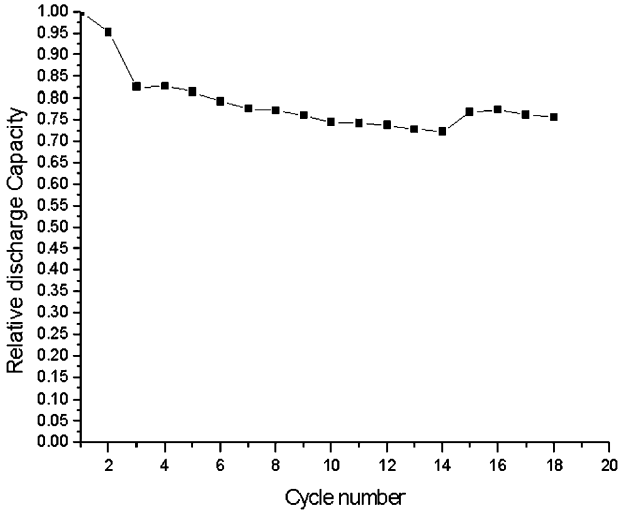

Fig. 5. Relative value of discharge capacity as a function of cycle number of a model lithium ion battery using the porous polymer electrolyte. The test was carried out at a constant current density of 0.50 mA cm^{-2} and within the voltage range of 3.0–4.3 V.

4. Conclusions

Highly porous P(VDF-HFP) membrane can be prepared by the phase inversion method. The structure of membranes can be easily controlled by the composition of casting solution and processing conditions. This kind of process has advantages of low cost and nonpollution.

The resulting membranes have good electrochemical stability and suit the application of porous polymer electrolyte. The conductivity of the porous polymer electrolytes prepared from such membranes can reach 10^{-3} S cm^{-1}.

Structure of the porous membranes has decisive effect on conductivity and solution leakage of the porous polymer electrolytes. Ideal membranes for porous polymer electrolyte should have high porosity and small pore diameters with narrow distribution. The experiments show that porosity should be >80% and pore diameter should be <1 μm.

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