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PVDF-HFP/PMMA-coated PE separator for lithium ion battery

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Abstract Microporous poly(vinylidenefluoride-co-hexa-fluoropropylene) (PVDF-HFP)/poly(methyl methacryate) (PMMA)-coated polyethylene (PE) separators were prepared by a simple dip-coating process with various compositions of PVDF-HFP/PMMA mixture under 40% relative humidity condition. The results indicate that the porosity, liquid electrolyte uptake, and ionic conductivity of the coated separators are largely affected by a ratio of PVDF-HFP/PMMA mixture and the highest porosity, electrolyte uptake, and ionic conductivity can be achieved at a composition of PVDF-HFP/PMMA (5/5). The results of the cell performance tests also reveal that the PE separator coated with PVDF-HFP/PMMA in a ratio of 5:5 provides better rate capability and cycle stability than other PE separators coated with different ratios.

Keywords Polymer-coated membrane · Polymer electrolyte · Phase inversion · Poly(vinylidene-co-hexafluoropropylene) · Poly(methyl methacrylate) · Lithium secondary battery

Introduction

Lithium-ion batteries have widely been used in portable consumer electronics because of their lack of memory effect, slow self-discharge, and high energy density. In addition, the demand for the battery is growing due to the growing energy storage needs for portable electric devices and hybrid vehicles, and aerospace applications [1].

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A lithium-ion battery is composed of the four primary functional components, the anode, cathode, electrolyte, and separator. Among them, one of the key components is a separator located between oppositely charged electrodes. Its primary role is to provide physical barrier between the electrodes to prevent electrical short circuits while it is permeable to ionic flow. Up to now, microporous polyethylene membranes have been widely used as separators in most commercialized lithium ion batteries due to their comprehensive performance and cost. However, the PE separator has some disadvantages; a poor compatibility with a liquid electrolyte that could weaken the battery performance and a low thermal stability that might cause battery explosion [2, 3].

To supplement these shortcomings of the PE separator, various gel polymer electrolytes (GPEs) prepared by immobilizing Li salts and non-aqueous solvents in a polymer matrix have attracted much attention due to high ionic conductivity that is comparable to liquid electrolytes [4]. Usually poly(ethylene oxide) (PEO) [5], poly(vinyl choride) (PVC) [6], poly(acrylonitrile), poly(methyl methacrylate) (PMMA) [7], poly(vinylidene fluoride) (PVDF) [8, 9], and poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [10–12] had been studied as a polymer matrix for GPEs. Among them, PVDF-HFP has been most widely used because of its excellent mechanical and chemical stability that require for the long-term performance of Li battery [12]. Also, PMMA-based gel polymer electrolyte is also very attractive since it has a high affinity with liquid electrolyte that arises from the similar chemical structure (carbonyl group) between PMMA and the plasticizers (ethylene carbonate (EC), PC) [4]. In addition, blend-based systems such as PEO/PMMA [13], PVDF/PMMA [14], PMMA/PVC [15, 16] combine the advantages of each polymer for GPEs. However, GPEs have not been commercialized yet due to the insufficient

mechanical property and the deficiency of shutdown behavior. In order to overcome these problems, the new strategy combing a GPE with a mechanical support such as a PE separator has recently been reported [17].

In a previous study, we studied that porous polymer-coated PE separators were fabricated using a dip-coating process and confirmed that micro-porous structures of the coating layer were generated at high humidity levels during the evaporation of solvent [18].

Here, we study that porous PVDF-HFP/PMMA-coated PE separators were prepared with various composition of PVDF-HFP/PMMA by a simple dip-coating process at a high humidity condition. The effects of various compositions of PVDF-HFP/PMMA in the polymer-coated separators on the morphology, porosity, and ionic conductivity of the prepared separators were investigated and discussed in this study. The cell performance tests using coin cells assembled with the prepared separators were also performed and the effects of the prepared separators on the cell performances were discussed.

Experimental

PVDF-HFP (kynar2801) and poly(methyl methacrylate) (Mw=996000), was purchased from Aldrich and used as received. An electrolyte solution consisting of 1.0 M $LiClO_4$ in 1:1 (v/v) EC/diethyl carbonate mixture was donated from TechnoSemichem Company (Korea). Other solvents were reagent grade and used as received.

To prepare the coating solution, 5 wt.% PVDF-HFP/PMMA mixture was dissolved in acetone at room temperature for 12 h (the weight ratios of PVDF-HFP/PMMA were 10/0, 8/2, 6/4, 5/5, 4/6, 2/8, and 0/10, respectively). Microporous PE separators (SKLiBS, 12 μm thickness, SK Energy) were then dip-coated in the coating solution and dried under 40% relative humidity by using a humidity control system. The coated separators with a 22 μm thickness were selected and subjected for characterization.

The observation of the morphology of the PVDF-HFP/PMMA-coated PE separators was carried out by using a scanning electron microscope (SEM; JSM-6390, Jeol). The samples were dried and sputter-coated with a thin gold film prior to the SEM observation.

The porosity and the pore diameter of the polymer-coated separator were determined using mercury porosimeter (Auto pore IV 9520, Micromeritics). Mercury porosimetry provides a wide range of information such as the pore size distribution, the total pore volume, the porosity, the skeletal/apparent density, the average pore diameter, and the specific surface area of a sample. In mercury porosimetry, pore shape was assumed to be cylindrical pore geometry. Mercury porosimetry is based on the capillary law governing liquid penetration into the small pores.

Because mercury, not wetting liquid, does not enter the pores spontaneously into the pores, pressure is applied to intrude mercury into the pores. The pressure is used to calculate pore diameter by the Washburn equation (Eq. 1):

$$D = -\left(\frac{1}{p}\right)4\gamma\cos\varphi \qquad (1)$$

where D is pore diameter, P the applied pressure, γ the surface tension, and φ the contact angle. The average pore diameter could be determined from the average value of each diameters calculated by the Washburn equation.

The electrolyte uptake of the PVDF-HFP/PMMA-coated separator was measured by soaking the separators in a $LiClO_4$-based liquid electrolyte solution at different time periods and calculated by Eq. 2:

$$EU = \frac{W_2 - W_1}{W_1} \qquad (2)$$

where, W_1 and W_2 are the masses of the dry and wet PVDF-HFP/PMMA-coated PE separators, respectively.

The ionic conductivity of the separators soaked with an electrolyte solution at room temperature was determined by an AC impedance technique over the frequency ranging from 0.01 to 100 kHz using a Solatron SI 1260 frequency response analyzer combined with an SI 1287 electrochemical interface at a constant potential of 10 mV. The samples with an area of A and a thickness of L were sandwiched between two stainless steel blocking electrodes to measure their electrolyte resistance (R_b, Ω). The conductivity (σ, S/cm) was then calculated from Eq. 3.

$$\sigma = L/(R_b \times A) \qquad (3)$$

To investigate the linear sweep voltammetry, the PVDF-HFP/PMMA-coated PE separators were soaked in a liquid electrolyte solution in an Ar-filled glove box. Then, the soaked separators were sandwiched between lithium metal and a stainless steel, and assembled into a tightly sealed test cell. The linear sweep voltammetry of the assembled test cells was measured in the range from 3 to 5.5 V at 5 mV/s

A lithium-ion cell was assembled by sandwiching the prepared separator between a meso-phase carbon micro bead (MCMB) anode and a $LiCoO_2$ cathode after immersing them in the liquid electrolyte. The cathode was composed of 94 wt.% of $LiCoO_2$ as a positive active material, 3 wt.% of PVDF as a binder, and 3 wt.% of super-P carbon as a conductive agent. The anode was composed of 93.5 wt.% of MCMB as a negative material, 6 wt.% of PVDF as a binder and 0.5 wt.% of super-P carbon as a conductive agent. The cell was enclosed in a 2032-type coin cell. All the assembly procedures of the cells were carried out in a dry box filled with argon gas. The rate capability measurements and the discharge cycling tests of the lithium-ion polymer cells were conducted using a Toyo

battery test equipment (TOSCAT-3000U). Charging process was terminated at an end current of approximately 0.02 C rate (0.06 mA). Discharge current was fixed to a constant–current value with an end voltage of 3.0 V. The rest time was fixed to about 20 min between charge and discharge mode. All the measurements were performed at room temperature.

Results and discussion

To confirm porous structure, porosity, and pore size on the coated layer in the prepared separators with various composition of PVDF-HFP/PMMA, the prepared separators were observed by SEM and mercury porosimeter. Figure 1a–f shows the SEM images of the surfaces of the prepared separators with various composition of PVDF-HFP/PMMA (10/0, 6/4, 5/5, 4/6, 8/2, and 0/10). These images revealed that the morphology of the PVDF-HFP/PMMA-coated PE separators was determined by the ratio of PVDF-HFP to PMMA. As shown in Fig. 1, various pores were observed in the coated polymer layer of the separators coated with up to 80 wt.% PMMA (Fig. 1a–e). In Fig. 1a, the surface morphology of PVDF-HFP-coated layer showed honey comb-like pattern known to be formed by a dip-coating process of PVDF-HFP under atmospheric humidity [19]. The honey comb-like structure is considered to be formed as a result of the template effect of water droplets produced during solvent evaporation [19–21]. As PMMA content increased (PVDF-HFP contents decreased), honey comb-like structure was destroyed and then bigger-sized pores were generated on the coating layer (Fig. 1c,d).

However, above 80 wt.% PMMA, pore size diminished abruptly and no pores were finally observed in the coated polymer layer in case of the surface of PMMA-coated separator (Fig. 1f).

Figure 2 shows the porosity and average pore diameter of the PVDF-HFP/PMMA-coated PE separators as a function of composition in PVDF-HFP/PMMA. It was found that the porosity of the PVDF-HFP/PMMA-coated PE separators slightly increased as increasing up to 50 wt.% PMMA (PVDF-HFP/PMMA (5/5)), while the porosity of the PVDF-HFP/PMMA-coated PE separator sharply decreased above 60 wt.% PMMA. Also, the average pore diameter of PVDF-HFP/PMMA-coated PE separator showed the same behavior to the porosity. In view of the results in Figs. 1 and 2, the differences in the pore structure and porosity could be attributed to the fact that solubility of two polymers for humidified atmosphere (water vapor), which function as non-solvent, made a difference during a phase inversion which produced pores in the coated polymer layer on the PE separator. In other word, during the evaporation of solvent (acetone), PMMA is expected to have more interaction with moisture at atmosphere than PVDF-HFP and then few pores was created in PMMA-coated layer.

Figure 3 represents the variation of the electrolyte uptakes of the PVDF-HFP/PMMA-coated separators with various composition of PVDF-HFP/PMMA. The electrolyte uptake of the PVDF-HFP/PMMA-coated PE separators slightly increased as increasing up to 50 wt.% PMMA (PVDF-HFP/PMMA (5/5)), but sharply decreased above 60 wt.% PMMA (PVDF-HFP/PMMA (4/6)). It was observed that the membranes containing up to 60 wt.%
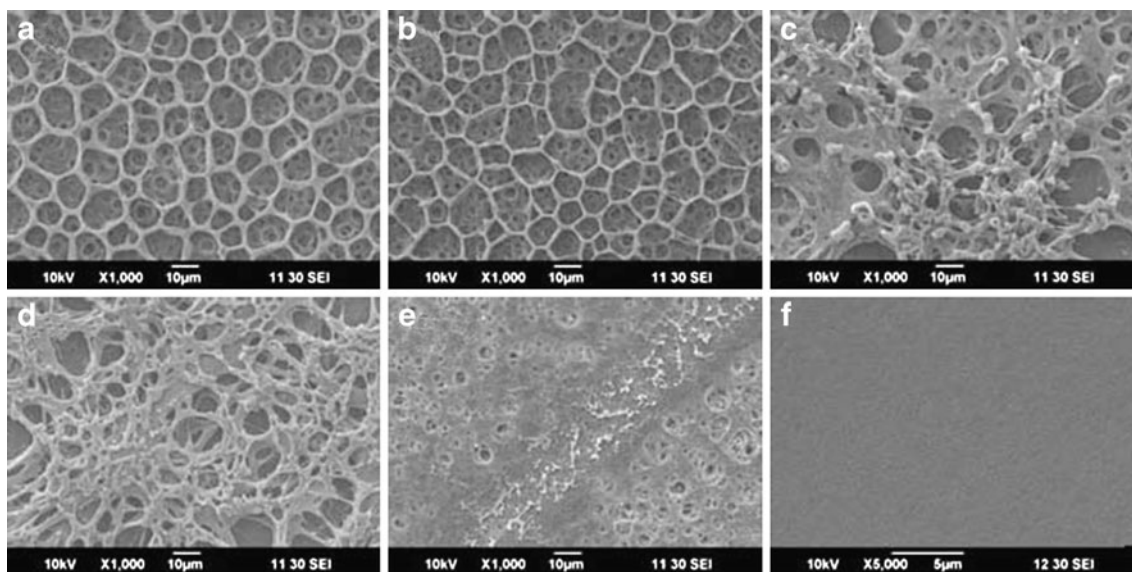

Fig. 1 SEM images of the surface of the PVDF-HFP/PMMA-coated PE separators prepared at various composition of PVDF-HFP/PMMA a 10/0, b 6/4, c 5/5, d 4/6, e 8/2, and f 0/10
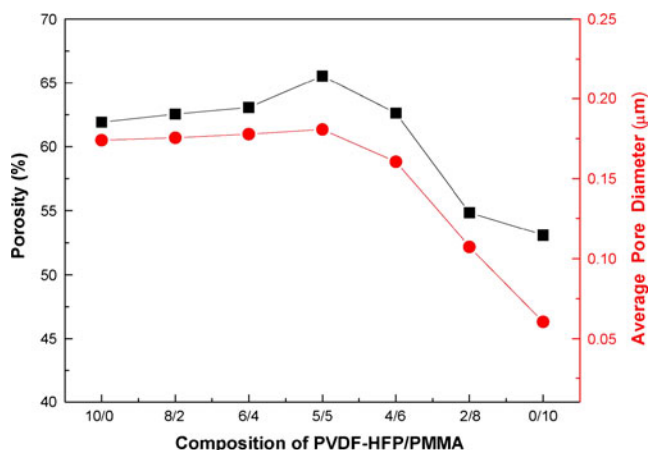
Fig. 2 The porosity and average pore size of the PVDF-HFP/PMMA-coated PE separators as a function of composition of PVDF-HFP/PMMA

Fig. 4 The ionic conductivities of the PVDF-HFP/PMMA-coated PE separators as a function of composition of PVDF-HFP/PMMA

PMMA (PVDF-HFP/PMMA (4/6)) showed higher electrolyte uptake than bare PE separator. The highest electrolyte uptake was measured to be 403 wt.% at composition of PVDF-HFP/PMMA (5/5) which had the highest porosity and average diameter. These results are directly related to porous structure of the prepared separators.

Figure 4 shows that the ionic conductivity of the PVDF-HFP/PMMA-coated separators increased as PMMA increased up to 50 wt%. However, the ionic conductivity of the prepared membrane with above 50 wt.% PMMA was decreased. Especially, the PVDF-HFP/PMMA (5/5)-coated PE separator showed the highest ionic conductivity (1.69 mS/cm). The liquid electrolyte uptake has been considered as a key factor to determine the ionic conductivity of lithium battery separator in many previous research works [13–17].

However, the results shown in Fig. 4 imply that the other factors such as the porosity and inherent properties of the coated polymer could affect the overall ionic conductivity of
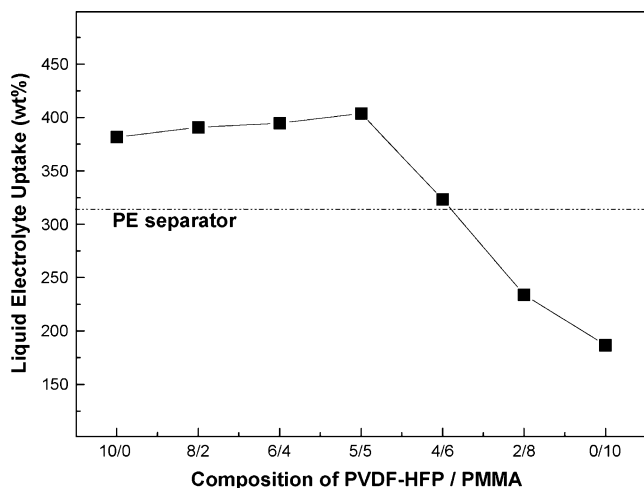
the prepared separator. The increased ionic conductivities up to 50 wt.% PMMA could be attributed to the effect of the increased amorphous domain formed in the coated layer in the presence of higher content of PMMA since no significant increase in both the porosity and ionic uptake was observed up to 50 wt.% PMMA as shown in Figs. 2 and 3. On the other hand, the decreased ionic conductivities above 50 wt.% PMMA were observed and these could be attributed to the decrease in the porosity of the separators and the resulting decreases ionic uptake above 50 wt.% PMMA although the increased PMMA generated more amorphous domain. It was also observed that the 4/6 and 2/8 samples with lower liquid electrolyte uptakes showed relatively higher ionic conductivities compared to 10/0, 8/2, and 6/4 samples with higher liquid electrolyte uptake. These results imply that the PMMA content dominates the overall ionic conductivities of the coated separators compared to the porosity and the resulting liquid electrolyte uptake. In addition, PE separator showed the lowest ion conductivity compared to the coated separators even with lower liquid electrolyte uptake due to the absence of the pored coating layer and PMMA.

Electrochemical stability of the polymer-coated separator at the range of operating voltage in lithium ion battery is important for practical application. There should be no electrochemical reaction of the polymer-coated separator in the prepared cell during charge–discharge. The electrochemical stability of the test cells containing PVDF-HFP/PMMA-coated separators was evaluated by using a linear sweep voltammetry between 3 and 5.5 V. As shown in Fig. 5, it is noticed that the oxidation peaks of the cells containing all the PVDF-HFP/PMMA-coated separators, were stable up to 5.0 V. Therefore, we consider that the polymer coated separators can be a good candidate for an electrolyte of lithium ion batteries operated at high voltage.

In order to evaluate the effects of the PVDF-HFP/PMMA-coated separators on the electrochemical performance of the

Fig. 3 The electrolyte uptakes of the PVDF-HFP/PMMA-coated PE separators as a function of composition of PVDF-HFP/PMMA

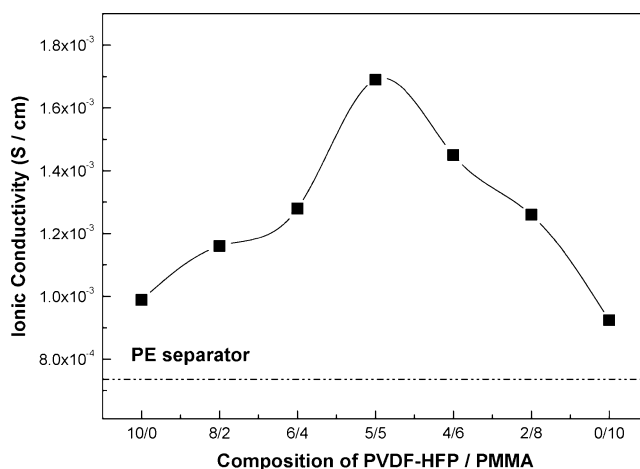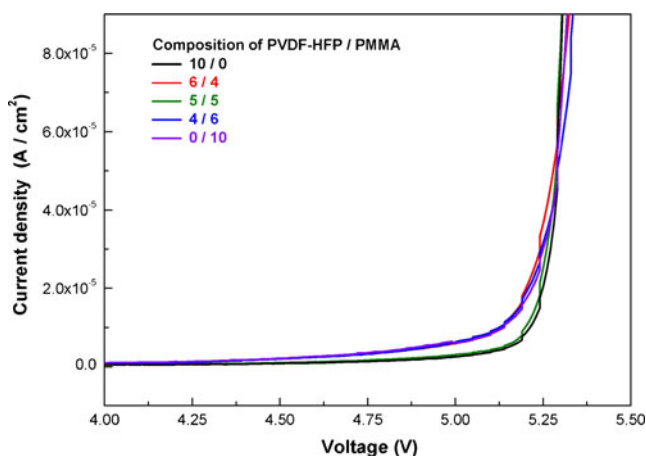**Fig. 5** The linear sweep voltammetry of the test cell with the prepared separators

Fig. 6 The relative discharge capacities of lithium ion cells assembled with the PVDF-HFP/PMMA-coated PE separators at various composition of PVDF-HFP/PMMA as a function of the current rate

lithium-ion polymer cells, several coin type cells composed of the coated separator, electrolytes, a LiCoO$_2$ cathode, and a graphite anode were assembled and subjected to battery performance tests. For the preconditioning cycle, cutoff voltages of 4.2 V for the upper limit and 3 V for the lower limit at 0.1 C rate (0.3 mA) were employed for the first two cycles prior to the rate capability measurements. After a preconditioning cycle, the cells were charged at a current density of 1.5 mA(0.5 C rate) up to a target voltage of 4.2 V. This was followed by a constant voltage charge with a decline of the current until the final current reached 20% (0.02 C) of the charging current and then it was discharged down to a cutoff voltage of 3 V at the same current density (0.5 C rate).

Figure 6 shows the relative discharge capacities of the lithium-ion cells assembled with the PVDF-HFP/PMMA-coated separators at various composition of PVDF-HFP/PMMA as a function of the current rate. In this figure, the relative discharge capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge capacity delivered at 0.2 C rate (0.6 mA). Figure 6 shows that no significant difference in the capacity rate performance between bare PE separator and the PVDF-HFP/PMMA-coated separators was observed up to 0.5 C. However, as C rate increased from 1 to 2 C, the relative discharge capacities of the cells assembled with the coated PE separators began to decrease more than that of the cell with a bare PE separator. This result can be attributed to the fact that the coin cell (2032 type) assembled with a thinner bare PE separator (12 μm) has a larger inner space to contain more liquid electrolytes than the cells with thicker PVDF-HFP/PMMA-coated separators (22 μm). It was also found that the PVDF-HFP/PMMA (5/5)-coated separator showed the higher rate capability at above 1 C rate than that the other compositions of PVDF-HFP/PMMA-coated PE separators since PVDF-HFP/PMMA (5/5)-coated PE separator has a higher ionic conductivity than the others as shown in Fig. 4. The poor
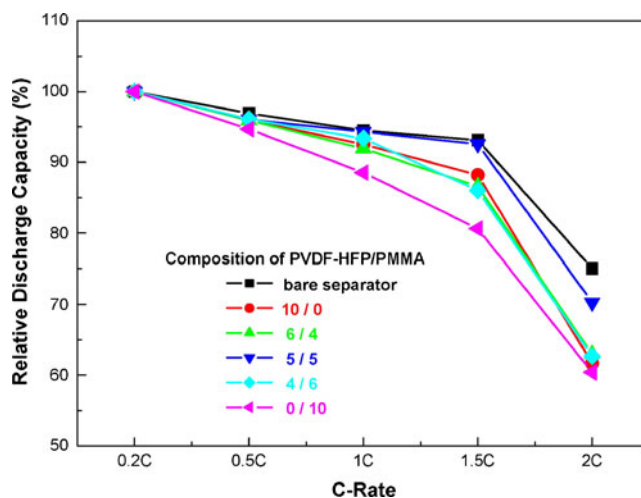
rate capability of the cell containing PMMA-coated separator is mainly considered due to the dense non-porous structure of the coated polymer layer on the bare PE separator that prevents the migration of lithium ions.

Figure 7 shows the discharge capacity profiles of the cells assembled with the PVDF-HFP/PMMA-coated separators at various composition of PVDF-HFP/PMMA, measured at 0.5 C rate as a function of the cycle number. The initial discharge capacities of the cell using the PVDF-HFP/PMMA-coated separators were measured to be approximately 3 mAh. In this cycle test, the relative discharge capacity is defined as the percent ratio of the discharge capacity to the initial discharge capacity. As shown in Fig. 7, the cell using the PVDF-HFP/PMMA (5/5)-coated PE separator showed higher relative discharge capacities than
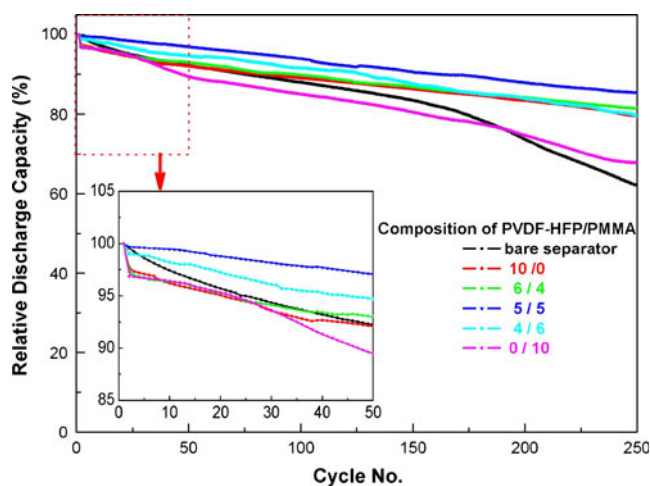

Fig. 7 The relative discharge capacities as a function of the cycle number in the cells assembled with the PVDF-HFP/PMMA-coated PE separators at various composition of PVDF-HFP/PMMA (charge 0.5 C/discharge 0.5 C)

those using the other PVDF-HFP/PMMA-coated PE separators and bare PE separator. After 250 cycles, the cells containing the PVDF-HFP/PMMA (10/0, 6/4, 5/5, and 4/6)-coated PE separators maintained 79.2%, 80%, 86%, and 78.5% of their initial discharge capacities, respectively, but the cell using the PMMA-coated separator and the bare PE separator maintained only 67.5% and 62.2% of their initial discharge capacities, respectively. These results indicate that the separators with the porous coated layer can improve the durability of the cells since they can hold more liquid electrolytes for a long cycle period. Furthermore, the PVDF-HFP/PMMA (5/5)-coated separator shows the highest long-term cycle performance among the prepared separators due to its higher porosity, pore size, electrolyte uptake, and ionic conductivity.

Conclusions

In this study, porous PVDF-HFP/PMMA-coated PE separators were successfully prepared at various composition of PVDF-HFP/PMMA by a simple dip-coating process under relative humidity 40% condition. The pore size and porosity decreased from over 50 wt.% in the PMMA content. Especially, the PVDF-HFP/PMMA (5/5)-coated PE separator showed the highest ionic conductivity (1.69 mS/cm). The PVDF-HFP/PMMA-coated PE separators showed sufficient electrochemical stabilities of up to 5.0 V by linear sweep voltammetry test. In battery performance test, the coin cell with PVDF-HFP/PMMA (5/5) has excellent discharge capacity and good discharge cycle performance, as compared to that with the others.

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