Inorganic thin layer coated porous separator with high thermal stability for safety reinforced Li-ion battery

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ARTICLE INFO

ABSTRACT

A novel approach for improving the thermal and dimensional stability of a polymer based separator is investigated. The surface of the micropores in the polyolefin based separator is fully covered by a thin layer of SiO_2 deposited by the chemical vapor deposition method. Through this new process, the thermal and dimensional stability of the microporous separators is greatly enhanced, thus allowing the commercialization of polymer based separators for large sized battery systems. The morphology of the modified separators as a function of the thickness of the inorganic layer is considered to be a key factor for the optimization of their thermal and dimensional stability without sacrificing their ionic conductivity for the sake of the cell performance. At the optimum thickness of the thin and conformal layer of SiO_2, we obtain a polymer separator which is highly stable at high temperature, even above the melting point of the polymer membrane, with satisfactory cell performance, such as its ion conductivity, C-rate and cycle life.

1. Introduction

With the diversification of the performance of mobile devices and electric or hybrid-electric vehicles (EVs or HEVs), lithium (Li) secondary batteries have been studied to obtain higher energy and power densities. However, the safety problems of Li-ion batteries have recently received considerable attention, owing to the increased potential for fire and/or explosion under unwanted conditions, such as hard internal shorts. Among the various components in Li-ion batteries, the separators play a critical role. First, they act as a spacer between the positive and negative electrodes to prevent internal shorts. Second, they should have high Li-ion conductivity to maximize the available capacity of the active materials in the two different electrodes. The former role is related to the chemical, electrochemical, mechanical and thermal properties of the separators required to guarantee their safety. The latter is related to the pore structures and wettability of the separator by the electrolyte required to show a high energy and power density and long cycle life in Li-ion batteries [1–6].

Since Li-ion batteries were first commercialized by Sony in 1991, porous polyolefin films consisting of polyethylene and/or polypropylene have been used as the separators in Li-ion batteries due to their appropriate properties, such as their electrochemical stability, thickness, and mechanical strength. Generally, thin and porous polyolefin separators have a high porosity. They can provide good effective ionic conductivity, thus enabling high specific battery performances to be obtained [7–13]. They also have the necessary mechanical strength to withstand high tension/pressure during the cell manufacturing process. In addition, they have suitable tortuosity that can prevent the growth of lithium dendrites during the charge–discharge process on a negative electrode. Nevertheless, they have several drawbacks when it comes to applying them to future energy storage devices. Especially, their low thermal stability gives rise to high thermal shrinkage around their melting or softening temperature [5,6]. Thus, research into polyolefin based separators has focused on achieving higher mechanical integrity at high temperature by employing a predetermined amount of inorganic particles in the polyolefin based separator to achieve superior thermal stability [14,15]. Typically, inorganic particles with a polymeric binder were coated on the commercialized separator [15]. However, this process inevitably increases the thickness of the separator, although the inorganic nanoparticles are helpful to modify the low thermal stability and dimensional stabilities. A thicker separator reduces the amount of active materials that can be placed in the restricted cell space.

To address these problems, we report a novel method of producing a conformal coating of an inorganic thin layer into the pores of a polymer separator. As a model system, the chemical

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vapor deposition (CVD) method was employed to obtain a thin layer of SiO_2 from silicon tetrachloride ($SiCl_4$) and H_2O on the surface inside the pores. The CVD method is a deposition process in which the chemical precursors (in the gas, liquid or solid state) are transported in the vapor phase and decompose on the substrate to form a film of the desired materials under high temperature and vacuum conditions. Also, there is an attendant nanoscale-growth of the film. It is one of the film deposition methods used in the semiconductor industry for the fabrication of such devices as electronics components owing to its high throughout, high purity and low cost of operation. As an inorganic precursor, $SiCl_4$ was used. Shortly after their chemical reaction with H_2O, the SiO_2 thin films were directly deposited inside or on the surface of the pores of the polyolefin membrane [16–22].

In this study, we investigated the effects of the inorganic layer in a polyolefin based separator on not only its thermal stability, but also the cell performances. By employing the CVD method, the thermal and dimensional stability of the polyolefin separator was enhanced without any significant change in the thickness. In addition, we also observed several positive effects of the inorganic materials on the cell performances of the Li-ion battery. Because the deposition process can be conducted under normal pressure, the issues on the cost of separation production and the scale up might be overcome.

2. Experimental

2.1. Preparation of the SiO_2 coated polyethylene (PE) separator

The deposition of a thin layer of SiO_2 on and/or in the PE separator was conducted by the following method. The commercialized PE separator (SV-718, Tonen) was treated by oxygen plasma equipment (harrick plasma, power: 115 V, AC 60 hz) for 1 min. The PE separator was loaded into a chamber containing a saturated water vapor. The separator was then dosed with water vapor for a few minutes. This condition is sufficient to form a multilayer of adsorbed H_2O on the surface of the PE separator to induce the below chemical reaction with silicon tetrachloride ($SiCl_4$, Aldrich). The $SiCl_4$ vapor is then evaporated at 70 °C in the other chamber and allowed to react with the adsorbed water layer on a 2.5 × 7 cm sized PE separator. We defined this procedure as 1 cycle and the cycle is repeated for the layer-by-layer growth of the SiO_2 thin film to further increase the film thickness.

$$SiCl_4(liquid) + 2H_2O(liquid) \rightarrow SiO_2(solid) + 4HCl(gas) \qquad (1)$$
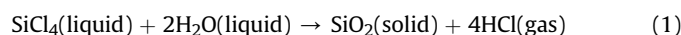
2.2. Cell fabrication

The anode had a composition of 94 wt% graphitized mesocarbon microbeads (MCMB2528) and 6 wt% Kynar 741 as a polymeric binder. The cathode was composed of 90 wt% $LiCoO_2$, 6 wt% Super-P, and 4 wt% PVdF. The electrolyte for the coin-cell (2032 type) was $LiPF_6$ (1 M) with ethylene carbonate (EC)/diethylene carbonate (DEC)/ethyl–methyl carbonate (EMC) (1:1:1. v/v/v, Techno SEMI-CHEM Co., Ltd., Korea). The lithium coin cell was assembled by sandwiching the composite separator between an MCMB anode and a $LiCoO_2$ cathode and then activated by filling the space in between them with the liquid electrolyte.

2.3. Characterization

To examine the surface properties of the PE separator, the contact angle of the samples was measured with a semi-automatic contact angle meter (FM40 Easydrop, Kruss GmbH). The
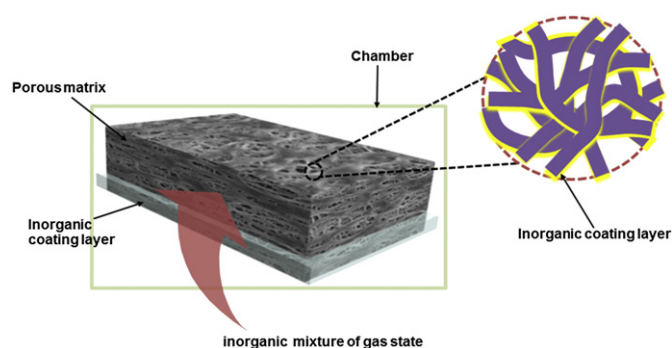

Fig. 1. A schematic diagram of the proposed separator prepared by the chemical vapor deposition method.

morphology of the deposited inorganic layer coated separator was characterized by scanning electron microscopy (SEM, JSM-7000). The thermal stability of the composite separator was observed after it was placed in an oven and heated at 150 °C for 20 min. Then, thermogravimetric analysis (TGA 6000, Seiko Instruments) was used to evaluate the thermal properties of the composite separators. They were heated from 30 to 400 °C at a heating rate of 10 °C min under an N_2 atmosphere. The tensile strength of the separators was determined using a universal tensile machine (Nexygen Plus model LR30K tester, Lloyd Instruments). The test specimens were 6 mm wide and approximately 19 μm thick in accordance with ASTM D882-88. The grip distance was 50 mm and the cross-head speed was 10 mm min^{-1}. The surface chemical bonding was analyzed using X-ray photoelectron spectroscopy (XPS, VG Microtech ESCA2000). The excitation source was Mg Kα radiation (photoelectron energy = 1253.3 eV) and all of the XPS measurements were made at a takeoff angle of 56°. The absolute binding energies of the different surface species were calibrated use the C1s line at 284.6 eV. The ionic conductivity (σ) of the separator was determined by AC impedance spectroscopy (CHI-660, CH Instruments) over the frequency range from 0.01 to 100 kHz. An AC perturbation of 5 mV was applied to the cell. The composite separator with an area of A and thickness of L was sandwiched between two parallel stainless-steel (SUS) discs (ϕ = 1.77 cm^2) to measure the electrolyte resistance (R_b). The conductivity was then calculated using the following equation:

$$\sigma = L/R_b A \qquad (2)$$

For the charge–discharge test, the cells were charged up to 4.2 V at 0.2 C rate and then discharged to 3.0 V at various C-rates. The charge process was cut off at 20% of the initial constant current.

3. Results and discussion

Fig. 1 shows a schematic diagram of the inorganic thin layer overcoated PE separators prepared by the chemical vapor deposition method. Generally, polyolefin based separators have a pore size of less than 1 μm. Hence, controlling the film thickness of the inorganic layer might be of importance to ensure that the composite separator can maintain its initial ion conductivity. In this study, because the SiO_2 thin film should be deposited homogeneously by the CVD method on the inner surface of the PE substrate, the surface should have hydrophilic characteristics in order to increase its compatibility with water molecules. Unfortunately, PE separators have a highly hydrophobic surface. Thus, to make the surface of the PE separator hydrophilic, the membrane was treated with an oxygen plasma. To confirm the change of the surface properties from hydrophobic to hydrophilic, water contact angle
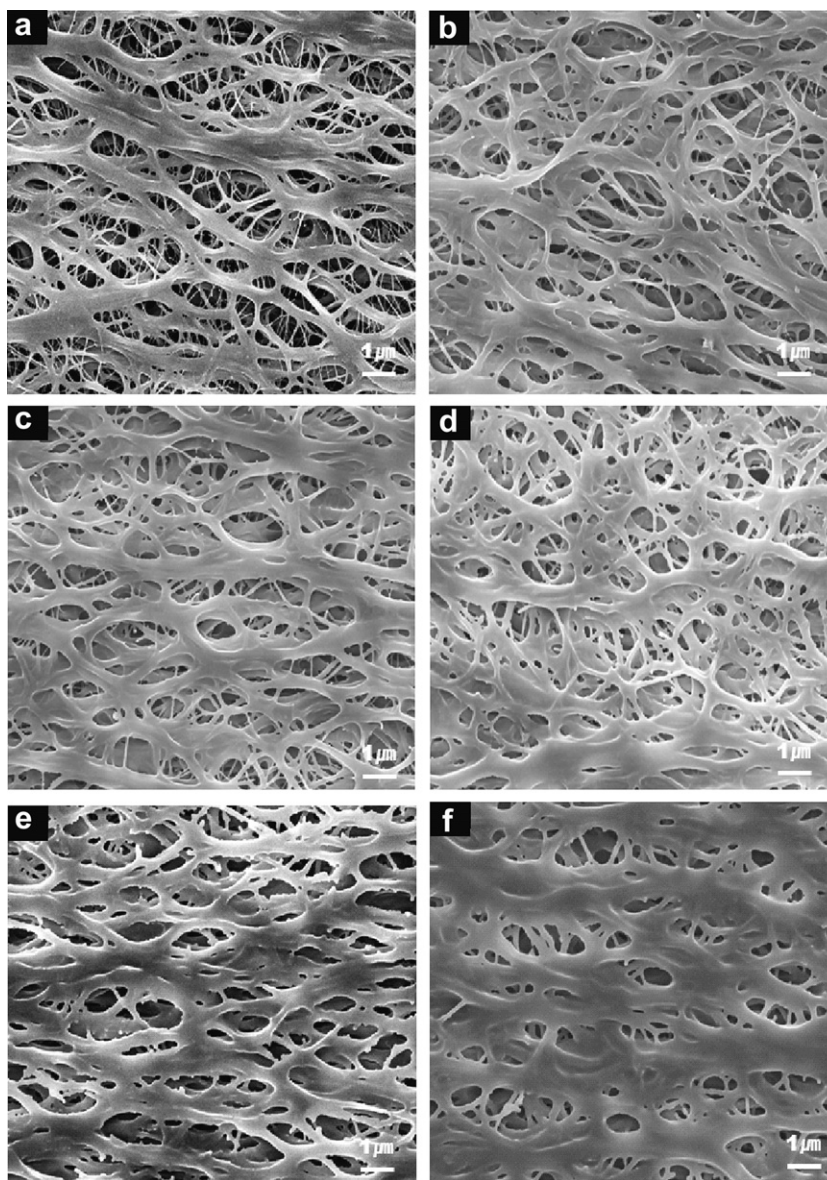
Fig. 2. SEM images of the surfaces of the composite separators with the SiO$_2$ thin film as a function of the number of cycles of chemical vapor deposition: (a) bare PE separator (b) 1 cycle (c) 3 cycles (d) 5 cycles (e) 7 cycles (f) 10 cycles.

measurements were performed. After the membrane was treated with an oxygen plasma, water contact angle was changed from 166.9° to 38.6°. From this data, it was confirmed that the surface of the treated PE separator is more hydrophilic than that of the pure PE separator.

The operating principle of the lithium ion rechargeable battery is based on its charge and discharge by the reversible intercalation/deintercalation of lithium ions in the positive/negative electrode, while the electrons generated by the difference in the electric potential of the active materials cause a current to flow through the external circuit. Although the separator is not directly involved in the cell performance, its structure, such as the pore size and uniform pore distribution, significantly affects the battery performance, including its energy/power densities, cycle life and safety [2–4]. The commercialized polyolefin separators have the appropriate pore size and pore distribution to play a role in ion conduction in lithium ion rechargeable batteries. Fig. 2 shows the scanning electron microscopic (SEM) images of the composite

separators, whose morphology is influenced by the amount of SiO$_2$ thin film, which is controlled by varying the number of deposition cycles. The SEM images show the changes in the pore structure of the PE separator as a function of the number of deposition cycles. As the number of deposition cycles is increased, the pore size of the PE separator decreases gradually. From the SEM images, it can be seen that the SiO$_2$ layer generated by the CVD method becomes a thin and very condensed film and is stacked well on the surface of the PE separator. Moreover, a uniform porous structure was also observed when the inorganic layer was prepared using from 1 to 10 cycles (Fig. 2a–f).

One of the essential requirements of the separator in a Li-ion battery is its ability to transport ions. Along with the change in the SiO$_2$ volume per deposition cycle, as shown in the SEM observation above, the increase in the thickness of the inorganic layer can affect the ionic conductivity of the composite separator. Fig. 3 shows the ionic-conductivity measured at room temperature. As shown in Fig. 3, the ion conductivity decreased gradually with
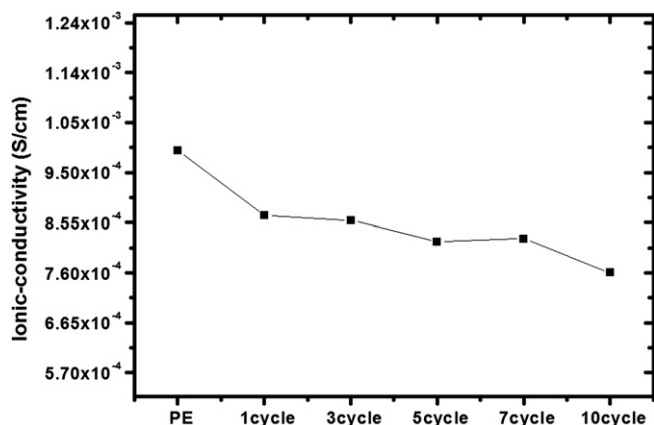
Fig. 3. The ionic conductivity of the composite separators with the SiO_2 thin film as a function of the number of cycles of chemical vapor deposition: (a) bare PE separator (b) 1 cycle (c) 3 cycles (d) 5 cycles (e) 7 cycles (f) 10 cycles.

Fig. 5. The tensile strength of the composite separators with the SiO_2 thin film as a function of the number of cycles of chemical vapor deposition: (a) bare PE separator (b) 1 cycle (c) 3 cycles (d) 5 cycles (e) 7 cycles (f) 10 cycles.

increasing number of deposition cycles. First, the decreased pore size is one possible reason for the decreased ionic conductivity. Second, the thin layer of SiO_2 on the PE separator might have a different degree of compatibility with the organic electrolyte compared to the pure PE separator. After dropping one droplet of the electrolyte on both the pure PE separator and the composite separator (5 cycles), we checked their compatibility with the electrolyte. Fig. 4 shows the wetting behavior after one drop of the electrolyte was dropped on the surface. Generally, a polyolefin separator is intrinsically poorly compatible with liquid electrolytes, because of its hydrophobic surface and low ability to hold organic solvents with a high dielectric constant. Fig. 4 shows that the composite separator is highly effective in absorbing polar liquid electrolyte, compared with the original PE separator. This superior wetting behavior may be attributed to the thin SiO_2 coating layer, where the liquid electrolyte can infiltrate preferentially through the well-connected interstitial fiber voids. From this data, we can eliminate the second possibility, because the SiO_2 layer enhances the compatibility with the electrolyte.

The separator of the Li-ion battery must be sufficiently mechanically strong to withstand the high tension during the battery assembly procedure and prevent internal short-circuits caused by the rough electrode surface, debris and growth of lithium dendrites. As the tensile strength is one of the mechanical properties, the commercialized polyolefin separator has appropriate mechanical integrity. To investigate the effect of the deposited SiO_2 layer on the tensile strength of the PE separator, we varied the number of deposition cycles and checked its tensile strength. Fig. 5 shows the relationship between the number of deposition
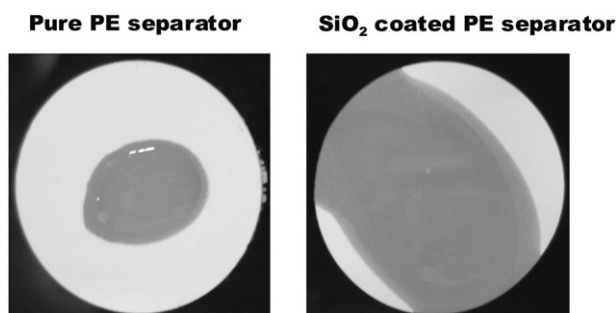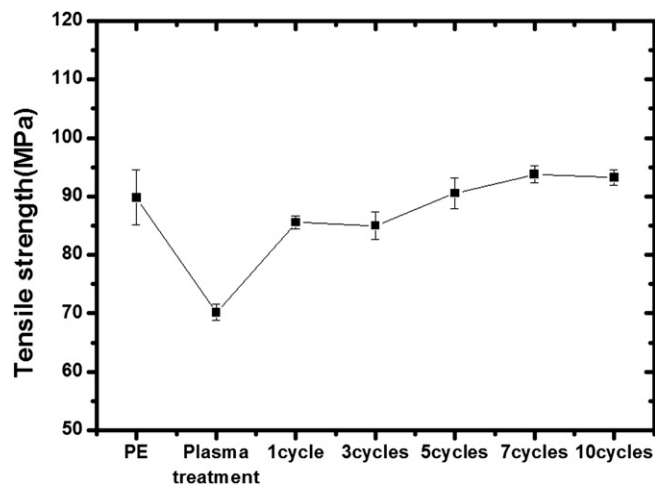

Fig. 4. Photographs of the PE separator and composite separators with the SiO_2 thin film after dropping the electrolyte.

cycles and the resulting mechanical tensile strength of the composite separators. As can be seen in Fig. 5, the initial deposition of a SiO_2 layer for 1 cycle has a somewhat negative effect. To find the reason for this, we also investigated the tensile strength of the PE separator treated only by the oxygen plasma, as shown in Fig. 5. Generally, it is known that polymeric films can be damaged by oxygen plasma treatment. Therefore, it can be confirmed that the initial decrease of the tensile strength is due to the degradation of the polymer by the treatment. However, in the case of the composite separator prepared using CVD method, the tensile strength is increased due to the inorganic layer. This enhanced tensile strength is thought to originate from the intermolecular adhesion force derived from the compact SiO_2 film. However, the tensile strength of the coated PE separator is really no better than that of the starting PE membrane.

With the growing need for portable electronic devices and hybrid vehicles with high energy storage capability, as well as the potential market for electrical vehicles in the future, scientists have to consider the safety issues of lithium rechargeable batteries in accordance with their high performance. From the view point of the safety issues in the Li-ion battery, polyolefin separators have intrinsic drawbacks: polymer based separators may lose their dimensional stability, which may cause internal short-circuiting or lead to thermal runaway when the temperature reaches their melting point or higher. To investigate the dimensional stability of the composite separators prepared by CVD modification, their thermal shrinkage behavior was observed after storing the separators at 150 °C (which is higher than the melting point of PE (~130 °C)) for 20 min. As shown in Fig. 6, more enhanced thermal stability and dimensional stability was obtained with increasing number of deposition cycles. The polyolefin separator suffered from a high degree of shrinkage during its exposure to high temperature conditions, while the composite separators maintained their dimensional stability even above their melting temperature after 5 cycles. This excellent thermal stability originates from the passivation layer of SiO_2 in the composite separators resulting from the CVD process. In a Li-ion battery, the PE separator is required to be capable of ion-flow shutdown at the temperature below that at which thermal runaway occurs. Because of high thermal stability of the composite separator originated from SiO_2 coating, they may not have shutdown temperature around 130 °C. In fact, temperature-related safety problems are mostly related to the dimensional stability of the separator, which is critical to large-size Li-ion
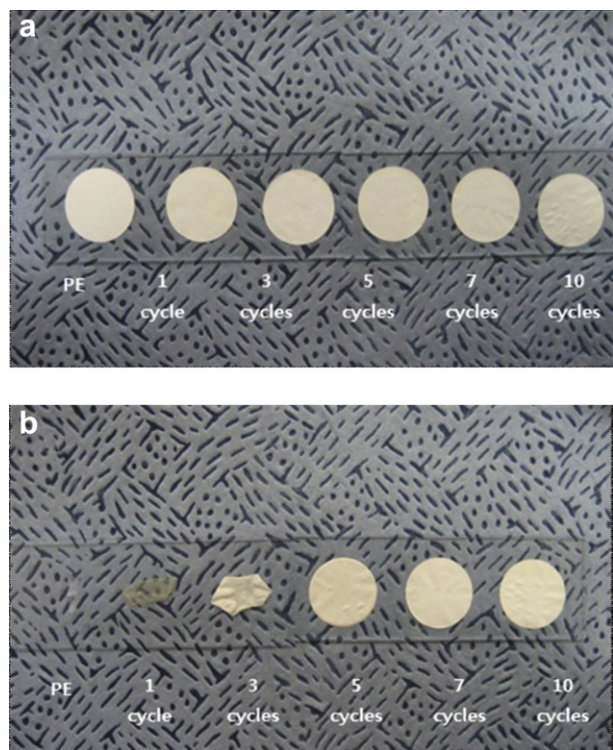
Fig. 6. Photographs of the composite separators with the SiO$_2$ thin film for various numbers of cycles of chemical vapor deposition: (a) before (b) after being stored at 150 °C for 20 min.

batteries. Therefore, the composite separators with excellent dimensional stability are highly desirable for the development of large-size Li-ion batteries, especially these for hybrid–electric vehicles. Furthermore, the TGA curves of the deposited inorganic layer based separator, as shown in Fig. 7, lend support to these results. The noticeable weight loss of the original PE separator started at around 150 °C and continued thereafter, while the weight loss of the composite separator was greatly retarded. This enhanced thermal stability is attributed to the coating of the SiO$_2$ thin layer, which can act as superior insulation and mass transport barrier against the volatile compounds generated during the decomposition of PE under thermal conditions.
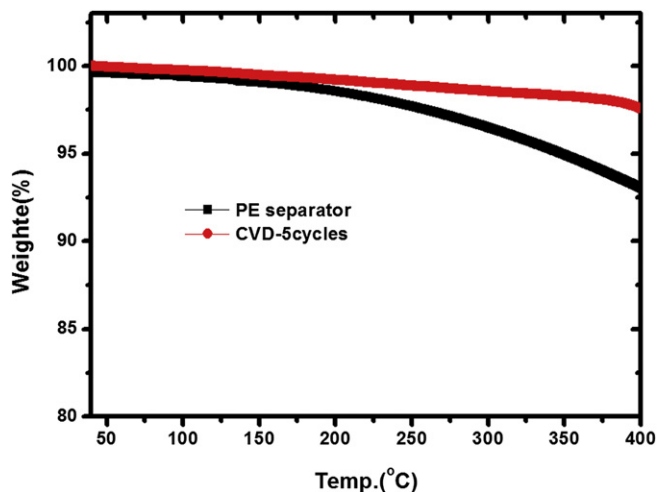

Fig. 7. Thermogravimetric curves of the composite separators with the SiO$_2$ thin film.
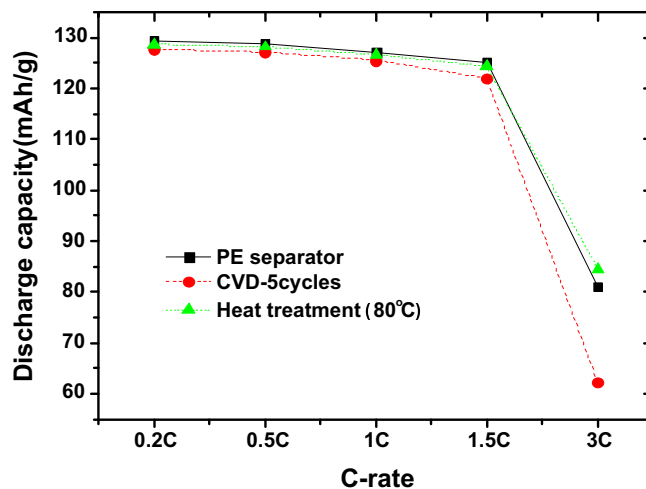

Fig. 8. Discharge capacities of the unit cell at various discharge rates after charging at 0.2 C in order to compare the rate performance of the cells with the PE separator and the composite separators with the SiO$_2$ thin film.

In general, CVD reactions often leave byproducts, which must be removed in various ways, because of their potential influence on the cell performance [23]. To investigate the effect of CVD processing on the cell performance, we prepared coin-type Li-ion batteries with the SiO$_2$ coated separator with and without heat treatment (80 °C for 24 h) under vacuum conditions before the assembly of the cell and then plotted the relative capacity of the cell against the discharge current to observe the cell performance. The rate characteristics of the cells were evaluated by charging the cell at a constant current of 0.2 C and then discharging them at various current densities, as shown in Fig. 8. A capacity drop is observed with increasing C-rate in all of the cells. This behavior was influenced by the electrical polarization caused by the increase in the serial resistance with increasing discharge C-rate. Moreover, the discharge capacity of the PE separator decreased when the inorganic layer was deposited by the chemical vapor deposition method, whereas the heat treated composite separator had very similar discharge capacity to that of the normal PE separator, as shown in Fig. 8. This result is indicative of the effect of the CVD processing on the cell performance and that of the heat treatment of the composite separator on the chemical and electrochemical stability. It might be due to the effective removal of the byproducts and residual water during the thermal annealing process.

To investigate the surface state of the composite separator, X-ray photoelectron spectroscopy (XPS) was used with a wide binding energy ranging from 0 to 1100 eV. XPS is a method used to investigate the surface environment of materials and has been widely used to study the oxidation states of solids [23,24]. In the XPS spectra shown in Figures S1, the strong C1s peak of the neat PE separator was observed at 284.6 eV before and after CVD processing or heat treatment without any peak shift, which is in accordance with the presence of the C–C segments of the polyolefin membrane. The XPS spectra of Si2p and O1s at 103.2 eV and 532.7 eV, respectively, measured from the surface of the composite separator were derived from the oxidation states of the SiO$_2$ layer. Another peak from Si2s is also observed, which might be due to the unreacted SiCl$_4$ or oxygen defects of the PE separator. As shown in Figure S1, furthermore, the height of the C1s peak decreased after the CVD process, indicating the good coverage of the SiO$_2$ thin film fabricated using the CVD process.
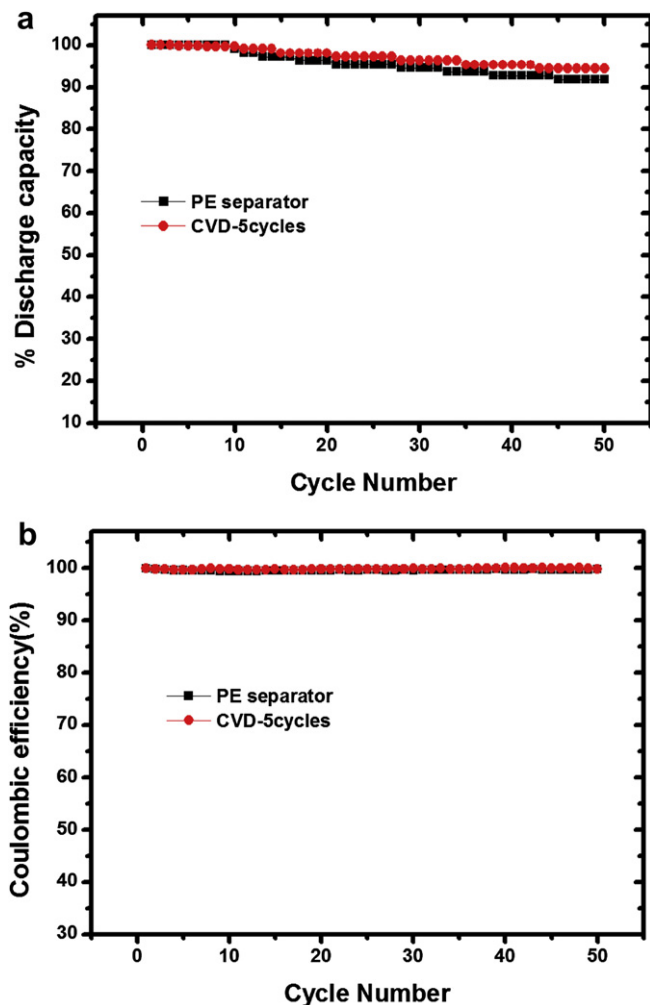
Fig. 9. (a) Charge–discharge capacity as function of number of cycles of unit cell at room temperature at 0.5 C (b) coulombic efficiency as function of number of cycles.

Finally, to investigate the effect of the coating of a SiO_2 thin film on the PE separator, the cycling performance (0.5 C charge-0.5 C discharge) was measured and shown in Fig. 9. As can be seen in Fig. 9, the PE separator with SiO_2 showed a comparable cycle life with a coulombic efficiency of nearly 100%. The charge and discharge capacities shown in Fig. 9a indicate that the discharge capacity of the composite separator at the 50th cycle is about 95% of the initial value, which results from its better wettability with the polar non-aqueous liquid electrolyte than that of the PE separator.

4. Conclusions

We proposed the use of the chemical vapor deposition method as a way to coat inorganic materials into the pores of PE separators in order to enhance their thermal and dimensional stability so as to produce safe, reinforced Li-ion batteries. Increased thermal and dimensional stability was achieved by the deposition of an inorganic layer in the porous membrane, which was carried out at room temperature. Several positive effects resulting from the deposition of the inorganic layer were evaluated as a function of its thickness, confirming the superior thermal and dimensional stability at high temperature and extended cycle life. This study introduces a new paradigm for the separators of Li-ion batteries that can decrease the possibility of their unwanted explosion.

Appendix A. Supporting information

Supplementary data related to this article can be found online at doi:10.1016/j.jpowsour.2012.03.038.

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