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Article

Development of Al_2O_3 Coated PVA (Polyvinyl Alcohol) Composite Nonwoven Separator For Improving Thermal and Electrochemical Properties

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SUMMARY

In modern world, lithium-ion batteries are widely used in electronic devices, such as smartphones, laptops, and electric cars. However, they are highly unstable during charging and their capacity drops significantly over time, despite them being highly efficient and easy to use. Therefore, it is imperative to develop more efficient batteries. Polyolefin-based lithium-ion battery separators are limited by their weak thermal stability. In order to overcome such limitations, we developed a ceramic-coated and nonwoven materials-based composite separator. We hypothesized that the method used to develop the separator will have improved thermal and electrochemical properties because of superior air permeability and electrolyte uptake. This separator was manufactured by utilizing the Dip-coating method, whereby ceramic layers composed of Al_2O_3 nanoparticles and Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) were coated to both sides of a Polyvinyl alcohol (PVA) support which was fabricated by electrospinning. The ventilation map and electrolyte uptake demonstrated that the composite nonwoven separator had superior electrolyte uptake properties when compared to conventional PE separators. This resulted in excellent electrochemical properties - especially a great increase in high-rate discharge characteristics. Finally, thermal shrinkage was improved compared to conventional PE separators indicating greater thermal stability. Overall, our PVA separator displayed superior thermal and electrochemical properties. By gaining knowledge on improving heat and thermochemical properties, we can gain critical insight on future lithium-ion battery designs that have to work in extreme conditions.

INTRODUCTION

The Lithium-ion battery is a type of rechargeable battery that has a graphite cathode and lithium anode. Lithium-ion batteries are currently used as a power source for many modern electronic devices such as drones, electric vehicles, smartphones, and smart watches. The safety of lithium-ion secondary batteries is ultimately determined by their propensity for internal short circuits, which occur when the cathode and anode directly contact with each other. Separators prevent physical contact between the cathode and the anode, and are therefore the most important component of the battery that guarantees safety (1). However, even though the separator plays a vital role in ensuring a battery's safety, it is primarily regarded as a pathway for lithium ions. As a result, most of the studies regarding separators are focused on the battery's performance improvements, which leave studies on safety extremely lacking (2).

The most common separator used in lithium-ion secondary batteries is made with polyolefin materials that provide chemical and electrochemical stability and remarkable mechanical properties (2-4). However, due to the material properties of polyolefin and the manufacturing process for lithium-ion secondary batteries, the components undergo extreme heat contraction at high temperatures, resulting in increased prevalence of internal short circuits (2-4). In order to overcome the limits of polyolefin materials, many recent studies have focused on nonwoven separators that have been produced by electrospinning, due to their great thermal stability (4-7). However, because the manufacturing of most of these nonwoven separators utilizes macromolecules that require organic solvents, they inevitably raise concerns regarding safety, health, and the environment. Moreover, the manufacturing process produces large pore structures that lead to defective charging from internal short circuits (2, 8). It is necessary to control the pore size in nonwoven separators during the manufacturing process, in order to adapt nonwoven separators successfully in lithium-ion secondary batteries. In this vein, many studies are aiming to coat polymer binder or polymer binder plus Al_2O_3 or ZrO_2 ceramics on nonwoven separators (4, 9-14).

In this study, a single composite ceramic nonwoven separator with improved thermal stability and electrochemical properties was developed. We hypothesized that composite PVA and PVA coated with Al_2O_3 nanoparticles and PVDF-HFP (6Al-PVA) separators would produce better electrochemical and thermal stability properties when compared with commercial polyethylene (PE) separators. A Polyvinyl alcohol (PVA) supporter was utilized due to its water-soluble properties, thus precluding the need for organic solvents and rendering the manufacturing process more environmentally friendly. PVA is also extremely chemically stable, has superior physical and chemical properties compares to those of current separator materials, and is widely used in the fabrics and film industry (12). To control the PVA supporter's pore size, layers of Al_2O_3 nanoparticles and

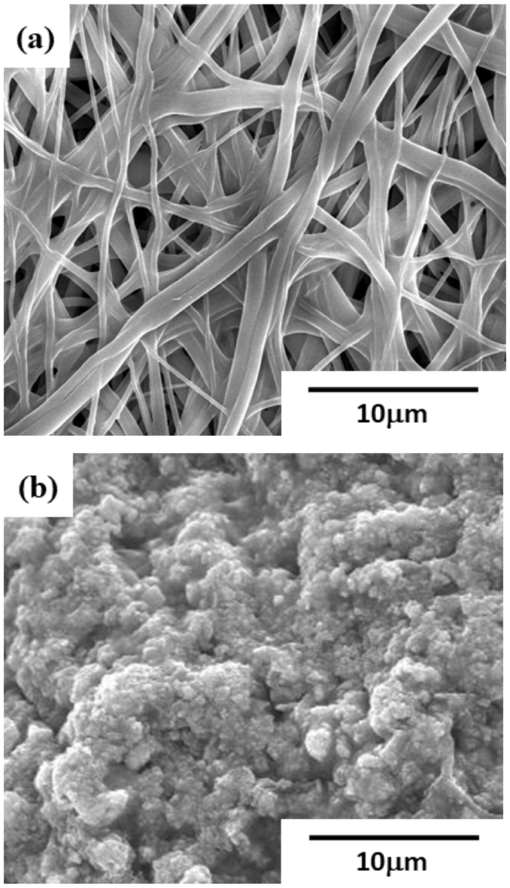

Figure 1. Electron microscopy images of different seperators. (a) PVA nonwoven separator and **(b)** 6Al-PVA composite separator. Values mentioned: 1-2 μm, 5-10 μm , less than 1 μm.

Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) binders were coated onto both sides of PVA supporter using the Dip-coating method. The electrochemical properties and thermal stability of the resulting separator was then compared against conventional PE separators. Results from this study will evaluate the feasibility of incorporating such separators into lithium-ion secondary batteries. We determined that a battery with PVA separator has improved thermal and electrochemical properties.

RESULTS

We observed the microscopic structure of the PVA nonwoven supporters and PVA coated with Al_2O_3 nanoparticles and PVDF-HFP (6Al-PVA) by electron microscopy (**Figure 1a**). A single strand of the PVA supporter as manufactured by electrospinning had a thickness of roughly 1-2 μm with pore sizes ranging from 5-10 μm (**Figure 1a**). For 6Al-PVA, a ceramic coating layer of Al_2O_3 and PVDF-HFP polymer binder was observed on the surface of the PVA nonwoven supporter (**Figure 1b**). As a result of the additional ceramic coating layers, the pore size of the PVA supporter was reduced to less than 1 μm.

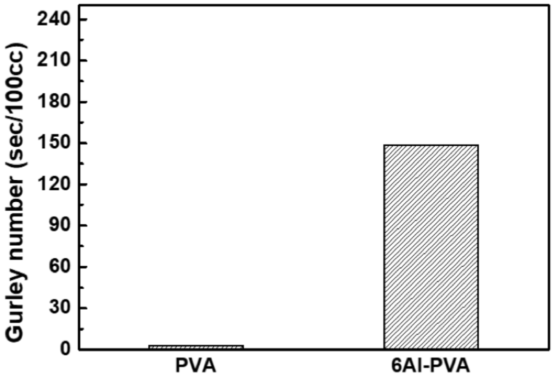

Figure 2. Air permeability test results of PVA nonwoven separator and 6Al-PVA composite separator. Valued mentioned: 2.7 s/sec, 148.7 s/sec.

We hypothesized that the addition of a ceramic coating would alter the physical properties of the separator. To test this hypothesis, we measured the air permeability. Higher air permeability, meaning that air experiences more difficulty when penerating an object, is associated with improved battery performance. The uncoated PVA supporter had an air permeability of 2.7 s/sec (**Figure 2**), which is considered extremely poor and can be explained by pore sizes between 5~10 μm. By contrast the 6Al-PVA nonwoven separator's air permeability was much improved at 148.7 s/sec (**Figure 2**). Given that the introduction of a ceramic coating layer could considerably affect electrolyte uptake, we measured electrolyte uptake. Electrolyte uptake of the 6Al-PVA separator was compared to a conventional PE separator. The 6Al-PVA separator had a greater than 47% increase in electrolyte uptake by comparison to the conventional PE separator (**Figure 3**). The increase in electrolyte uptake means the 6Al-PVA separator has a greater capacity for electrical conductance.

To evaluate the developed separator's electrochemical properties, we built a coin-type full cell. A full cell, just like a typical lithium-ion battery, uses an active material as the anode and materials such as graphite for the cathode. The charge/discharge profiles of coin-type full cells containing PVA nonwoven supporter and 6Al-PVA were measured. The coin-type full cell containing the PVA nonwoven supporter did not reach its final discharge and continued to charge (**Figure 4a**). This phenomenon is explained by minute internal short circuits that are caused by the pores of the PVA nonwoven supporter. This is also commonly observed in other types of nonwoven separators (3.8). In contrast, the 6Al-PVA full cell was able to successfully complete charging (**Figure 4b**). This is because the introduction of the ceramic coating layer allows control of the PVA nonwoven supporter's pore sizes, resulting in decreased pore sizes and the inhibition of internal short circuits. The superior air permeability and electrolyte uptake observed in the 6Al-PVA separator should influence the discharge rate, which was therefore tested directly. The discharge rate of the 6Al-PVA separator was compared against a conventional PE separator. The 6Al-PVA separator,

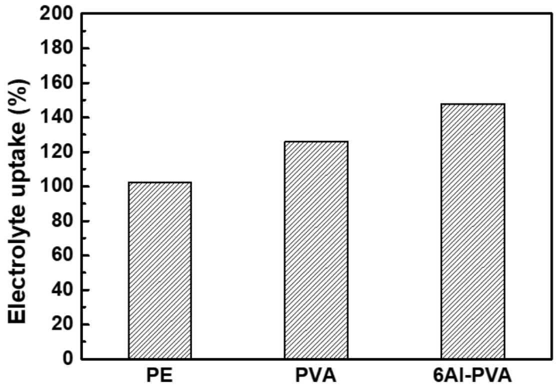

Figure 3. Electrolyte uptake test results of various separators. PVA nonwoven separator, 6Al-PVA composite separator, and conventional PE separator. Value mentioned: 47%.

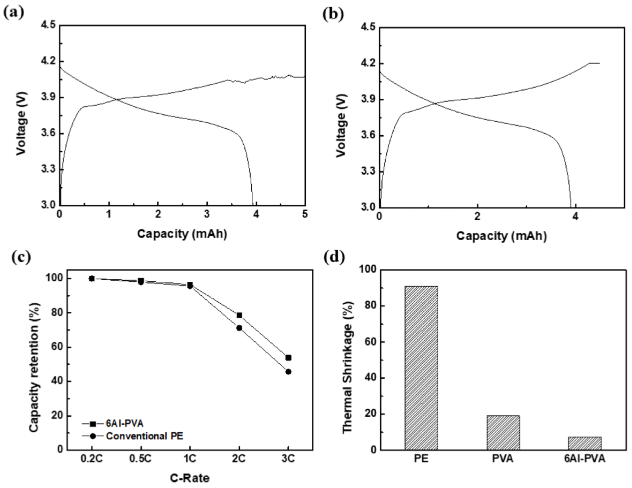

Figure 4. Electrochemical properties of separators. Charge-discharge of PVA nonwoven separator (**a**) and 6Al-PVA composite separator (**b**).The high-rate discharge test results of 6Al-PVA and conventional PE (**c**). Thermal shrinkage test results of conventional PE, PVA, and 6Al-PVA at 150°C (**d**). Values mentioned: 53.9%, 45.7%, 91%, 7.4%.

in 3C discharge had 53.9% of its initial capacity remaining, while the conventional PE separator, in 3C discharge had only 45.7% of its initial capacity remaining (**Figure 4c**). This is likely due to the superior electrolyte uptake of the 6Al-PVA separator.

Lastly, in order to test the thermal stability of the 6Al-PVA separator, we performed a thermal shrinkage test at 150°C. The conventional PE separator had 91% of thermal shrinkage at 150°C, while 6Al-PVA separator had 7.4% of thermal shrinkage at the same temperature (**Figure 4d**). This proves the 6Al-PVA separator's highly increased thermal stability, which can be explained by the PVA nonwoven separator's inherent thermal stability (120°C thermal shrinkage: 19%, 150°C thermal shrinkage: 34%) and the ceramic coating layer functioning as a thermal-resistant material.

DISCUSSION

In this study, we developed a composite ceramic nonwoven separator coated with Al_2O_3 and a polymer binder PVDF-HFP with improved thermal stability and electrochemical properties. We determined that the PVA nonwoven separator's inherent superior air permeability and electrolyte uptake remained consistent even after the coating with a ceramic layer. After the ceramic coating, the PVA nonwoven separator's minuscule pores were reduced to less than 1 μm, which diminished incomplete charging due to internal short circuits. We believe that higher air permeability for PVA nonwoven separator comes from the ceramic coating filling the pores.

As determined by the high-rate discharge experiment, we found that the 6Al-PVA separator exhibited a superior discharge rate in comparison to a conventional PE separator. This may be explained by the 6Al-PVA separator's excellent electrolyte uptake. The improved electrolyte uptake is likely due to the hydrophilic properties of the PVA supporter used in manufacturing the 6Al-PVA. Moreover, micropores on the ceramic coating layer may also retain additional electrolytes.

Lastly, we observed that the 6Al-PVA separator had markedly diminished thermal shrinkage, with only 7.4% of thermal shrinkage while the conventional PE separator had 91% thermal shrinkage. Thus, the 6Al-PVA separator has superior thermal stability without any loss in electrochemical properties.

Our study has potential limitations regarding reproducibility/batch-to-batch variability in separator construction because only one sample was used. Currently, we found that the moisture content in the experiment can affect the reproducibility of separator morphology strongly. Therefore, sample reproducibility could be improved by producing and testing the supporters in a controlled atmosphere.

In conclusion, the composite ceramic nonwoven separator (6Al-PVA), built by coating a ceramic layer on PVA nonwoven supporter, has superior high-rate discharge properties and thermal stability by comparison to a conventional PE separator. In the near future, we anticipate that such PVA-based, ceramic-coated nonwoven separators may replace conventional PE separators in the lithium-ion batteries of EVs and drones that require a high-rate of discharge.

MATERIALS AND METHODS

The PVA supporter (NTpia, thickness: 20 ± 1 μm) was manufactured by electrospinning, with polymer binder PVDF-12% w/v HFP (Kynar 2801, molecular weight = 470,000, named PVDF-HFP), and 40~50 μm Al_2O_3 nanoceramic particles being used. The coating solution was produced by spraying Al_2O_3 and PVDF-HFP binder in acetone (solids were controlled 5% w/v and Al_2O_3 / PVDF-HFP ratio was controlled 60% w/v Al_2O_3 : 40% w/v PVDF-HFP). The coating solution was coated on PVA nonwoven supporter through Dip-coating. The separator coated with the above solution is referred to as 6Al-PVA.

Structural analysis of the PVA supporter and coated separator was performed by electron microscopy (FE-SEM, JEOL JSM-7000F), and a Gurley-type densometer (Toyoseiki) was used to analyze air permeability. Gurley-type densometer was used to compress 100 cc of air and measure the time the air takes to go through the separator. The Gurley value represents the time required for a certain air to pass a certain area of separator under certain pressure. A thermal shrinkage test was conducted to test the separator's thermal stability properties. A specimen was prepared at a size of 5 cm x 5 cm and was kept at 120°C and 150°C for one hour. Then, the change in area was measured, and shrinkage percentage (%) = (Wf - Wi) / Wi × 100, was calculated (Wi = initial area of the separator, Wf = final area of the separator after putting 1 hour at designated temperatures). To calculate the electrolyte uptake, the separator was immersed in electrolyte solution for one hour, and weighed before and after the immersion was measured. To measure ionic conductivity, a Li metal/separator/Li metal symmetrical cell (2032 coin) was built and Re values were measured via an AC impedance analysis (Solatron 1280C). Ionic conductivity was calculated by using the following equation (σ (ionic conductivity) = d / (A * Re), where d=separator thickness, A=separator area, Re=electrolyte resistance).

To produce a coin-type full cell, $LiCoO_2$ was used to form a cathode, and graphite was used to form an anode. An electrolyte solution was produced by adding 1M $LiPF_6$ and Ethylene Carbonate (EC) / Ethyl Methyl Carbonate (EMC) (30% w/v : 70% w/v) with 3% w/v Vinylene Carbonate (VC). The coin-type full cell was galvanostatically charged and discharged in a voltage range from 3.0 to 4.2 to measure the reversible capacity. And the rate discharge tests were performed in the range of 3.0–4.2 V at currents of 0.2, 0.5, 1.0, 2.0, and 3.0 C. Capacity was calculated by a charge-discharge tester while constructing a coin type full-cell with designated capacities per unit area for anode and cathode. The capacities per unit area for the cathode and anode were 3.4 ± 0.1 mAh/cm^2 and 3.8 ± 0.1 mAh/cm^2, respectively.

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