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Preparation of a PVdF-HFP/polyethylene composite gel electrolyte with shutdown function for lithium-ion secondary battery

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Abstract

In order to improve the safety of lithium-ion secondary battery, a PVdF-HFP/polyethylene (PE) composite gel electrolyte with thermal shutdown function was prepared as an internal safety device. The composite gel electrolyte consists of a PVdF-HFP polymer, PE thermoplastic resin, and 1.0 mol/dm^3 $LiClO_4$/PC + EC (or $LiPF_6$/GBL + EC) plasticizer. When the PE content is over 23 wt.%, the electrical impedance of the composite gel electrolyte can increase rapidly by several orders, around the melting point of PE (mp: 90 or 104−115°C). By the SEM observation it was found that the PE particles uniformly dispersed in the PVdF-HFP gel electrolyte could be fused and formed into a continuous film at or near the PE melting point. The continuous PE film exhibits an ability to cut off the ion diffusion between cathode and anode, thus preventing the cell from thermal runaway. Also, a three-layered film of pure PVdF-HFP gel/composite gel/pure PVdF-HFP with a higher ionic conductivity and good mechanical strength was prepared for assembling a coin-type lithium-ion cell.

Keywords: Lithium ion secondary battery; Gel electrolyte; Shutdown; Safety

1. Introduction

Space missions require the use of high specific energy density and high reliability batteries to provide power for various applications. The lithium-ion secondary batteries with high energy density are promising for space application. Moreover, the lithium-ion polymer batteries are also considered for future small satellite use, because it can be fabricated for a flexible thin film without electrolyte leakage. However, the safety of lithium-ion battery is an important problem during operation under abusive usage [1,2], even using a polymer or gel electrolyte [3]. An abusive usage such as making short-circuit or rapid overcharging of the battery may initiate self-heating, leading to thermal runaway. Usually, self-heating reactions are initiated at a temperature near 100°C [3,4], it can even cause cell explosion when the temperature is raised to over 110°C based on our experiment result. On the other hand, almost all equipment require that batteries can be worked at temperatures of up to 80°C. To improve the safety of lithium-ion battery with gel electrolyte, it is an effective method using gel electrolyte with thermal shutdown function as internal safety device. And the thermal shutdown function of gel electrolyte can be achieved by means of dispersing the thermoplastic resin in the gel. The key point is selecting a thermoplastic resin with lower mp between 80 and 120°C, more preferably from 90 to 110°C, as was also suggested by Gee and Olsen [3].

We have successfully prepared a poly(vinylidene fluoride hexafluopropylene) (PVdF-HFP, mp: 158°C) based gel electrolyte, it shows a high ionic conductivity of millisiemens per centimeter order and good mechanical strength of ca. 4 MPa at an ambient temperature [5].

In this work, we tried to prepare a PVdF-HFP/polyethylene composite gel electrolyte with thermal shutdown function, and discuss on it for the lithium-ion secondary cell use.

2. Experimental

The PVdF-HFP/PE composite gel electrolyte was prepared as follows. First, the PVdF-HFP copolymer (Kureha, Chem. Ltd., MW: 320,000 g/mol) was dissolved in THF at ca. 50°C with stirring. Second, the PE (Aldrich Chem., mp: 90°C, named PE90; or 104–115°C, named PE115) was added into above THF solution, and heating this mixture to ca. 100°C until the PE have melted completely, was then slowly cooled to 45°C with stirring. Thus, an ultra-fine PE

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particle suspended in THF solution can be obtained. Then, adding the plasticizer of 1.0 mol/dm^3 $LiClO_4$/PC + EC or $LiPF_6$/GBL + EC (1.75 ml plasticizer/1 g PVdF-HFP) to the mixture. Finally, this PE suspension mixture was casted onto a glass petri dish to form a composite gel electrolyte film. The thickness of the composite gel film was controlled to ca. 100 μm. And the sandwich-type gel electrolyte of pure PVdF-HFP gel//PVdF-HFP/PE composite gel//pure PVdF-HFP gel was also prepared by the cast method (total thickness: ca. 200 μm).

The electrical impedance measurement was performed at open-circuit voltage in the frequency range 20–1 kHz (Solartron 1280 B Electrochemical Measurement Unit). A two-electrode cell was used for impedance measurement as described by Laman et al. [1]. The cell was placed in an oven, with the temperature controlled at a constant rate of 1°C/min, after which the gel temperature was monitored with a K-type thermocouple, which was inserted into the cell.

The SEM observation was used to check the phase transformation of the composite gel electrolyte before and after shutdown. All the gel preparation and cell assembling were carried out in a glove box cycled with Ar gas (H_2O content is less than 1 ppm).

3. Results and discussion

To obtain an optimum composition, a number of composite gel electrolytes with various compositions were prepared, and the PE90 content is varied from 0 to 54 wt.% in the composite gel. The impedance (at 1 kHz) of the resulted gel electrolyte was measured during the rise in cell temperature from ambient temperature to 150°C. The change of the impedance as a function of temperature is shown in Fig. 1. The impedance of pure PVdF-HFP gel electrolyte is decreased with increase in the temperature, and a rapid increase in impedance was not found until 150°C. According to the above results, it can be concluded that the pure PVdF-HFP gel does not possesses a thermal shutdown characteristics in the range of ambient temperature to 150°C. When the content of PE90 is over 23 wt.%, the composite gel electrolyte exhibits the ability to rapidly increase the impedance of the electrolyte, around the melting point of PE. For example, the impedance of the composite gel electrolyte with 45 wt.% PE90 can rise rapidly by about three orders around 90°C. The dimensional stability temperature ranged from ca. 90 to 100°C for the above gel electrolyte. The similar phenomenon is also observed for PVdF-HFP/PE115 composite gel electrolyte, in the range ca. 106–130°C. Concluding the action of thermal runaway for a lithium-ion cell, it is required that the composite gel electrolyte with shutdown function must be stable at high temperature for a moment, or down to ambient temperature after thermal runaway stopping. Fig. 2 shows the thermostability test results. This composite gel electrolyte shows a high stability either when kept at a high temperature of 92°C for 3 h, or down to ambient temperature. Thus, it is suggested as an internal safety device for lithium battery.

Focus attention on the thermal shutdown action, the current separator is realized with closing the pore in the single layer polymer or multilayer polymer sheet at higher temperature [1,6–8]. In the case of using the PVdF-HFP/PE composite gel electrolyte, it has a different structure from current separator, but the similar thermal shutdown action was observed. To clarify the thermal shutdown mechanism, SEM observation was employed. Fig. 3 shows the cross-sectional SEM images of PVdF-HFP/PE composite gel electrolyte before and after thermal shutdown. Before thermal shutdown, when the PVdF-HFP gel made a framework and formed into ion diffusion channels, the ultra-fine PE particles were uniformly dispersed in the PVdF-HFP gel

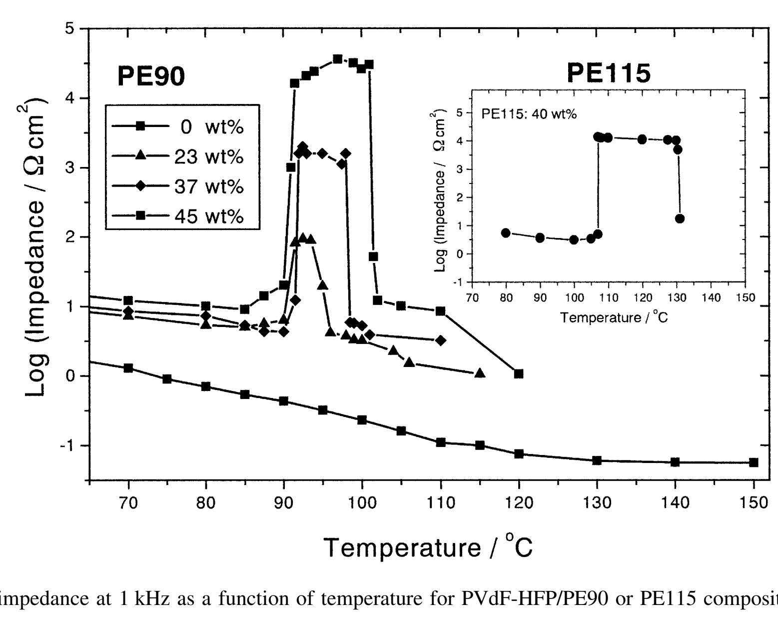

Fig. 1. The ac impedance at 1 kHz as a function of temperature for PVdF-HFP/PE90 or PE115 composite gel electrolyte.

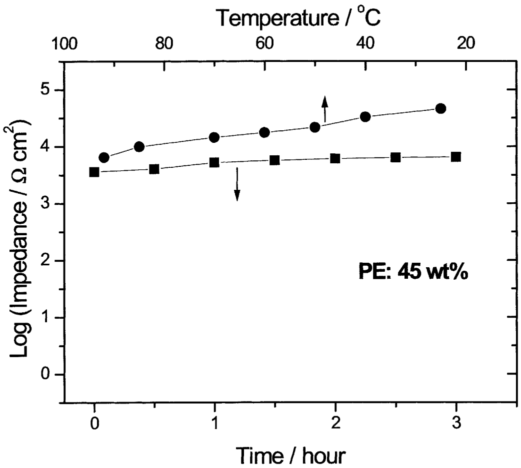

Fig. 2. Thermostability of the PVdF-HFP/PE90 (45 wt.%) composite gel electrolyte: (■) holding the temperature at 92 ± 0.5°C; (●) reducing the temperature from 92 to 25°C.

electrolyte. After shutdown, the PE particles were fused and formed a continuous film. The closed continuous PE film can cut off ion diffusion, which makes the electrode reaction stop, and prevents the cell from the thermal runaway.

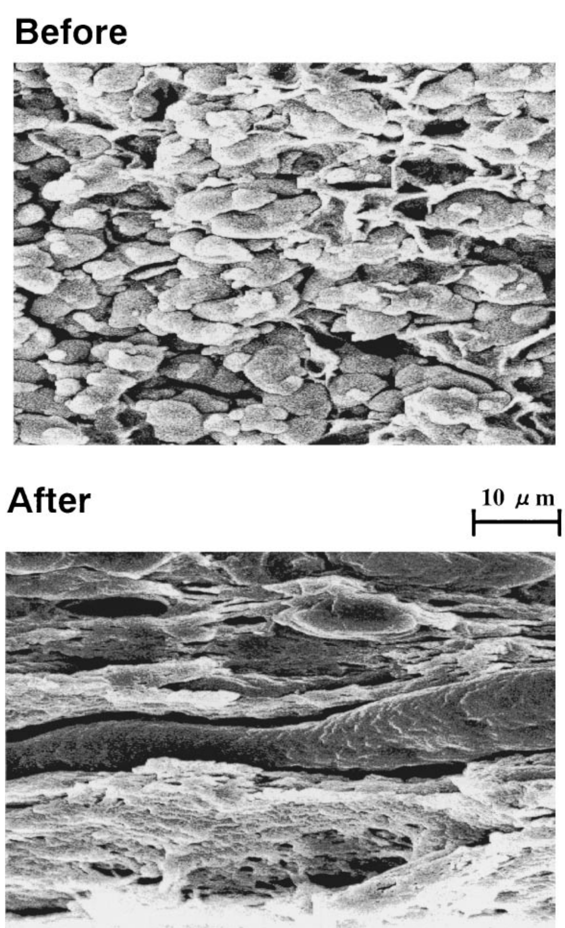

Fig. 3. SEM images of cross-section of the PVdF-HFP/PE composite gel electrolyte before and after thermal shutdown.

However, the composite gel electrolyte shows a lower ionic conductivity and poor mechanical strength. For example, the composite gel electrolyte with 37 wt.% PE90 has an ionic conductivity of 0.217 mS/cm, and a mechanical strength of 800 kPa. Thus, we prepared a three-layered film of pure PVdF-HFP gel/composite gel/pure PVdF-HFP gel for assembling a coin-type lithium-ion cell. The sandwiched gel electrolyte film also exhibits a thermal shutdown property as well as single layer composite gel electrolyte. Moreover, a coin-type lithium-ion secondary cell (2016 size, 3 mAh) is constructed with above sandwiched gel electrolyte. We found that this coin-cell can be well worked at normal condition, and exhibit a shutdown action under high temperature [9]. Also, we tried to prepare a PVdF-HFP/PE90 combined with PE115 composite gel electrolyte with a wide insulating range. These results will be reported in our following paper.

4. Conclusion

A PVdF-HFP/PE composite gel electrolyte was successfully prepared with cast method. When the PE content was over 23 wt.%, the thermal shutdown action of the composite gel electrolytes was found. Especially, the composite gel electrolyte with 37–45 wt.% PE exhibits the ability to rapidly increase its impedance by about three orders around 90°C. The composite gel electrolyte is stable when held at high temperature, or when the temperature is varied from high to ambient temperature. By SEM observation, it is clear that the PE particles were fused and formed into a continuous film at or near the PE melting point, which cut off the ion diffusion. Thus, the composite gel electrolyte can prevent the cell runaway under abusive usage. For the lithium-ion secondary cell application, a sandwich type of composite gel electrolyte with sufficient ionic conductivity and mechanical strength is also prepared. The sandwich type gel electrolyte also exhibits a good thermal shutdown property.

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