

# Thermal shutdown behavior of PVdF-HFP based polymer electrolytes comprising heat sensitive cross-linkable oligomers

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Received 1 November 2004; accepted 26 December 2004

Available online 23 March 2005

## Abstract

PVdF-HFP (polyvinylidene fluoride-hexafluoropropylene) polymer electrolytes comprising cross-linkable PEGDMA (polyethylene glycol dimethacrylate) oligomers with thermal shutdown characteristic have been developed. In contrast to the melting mechanism of polyolefin, this new polymer electrolyte possesses a thermal shutdown characteristic by a rapid cross-linking reaction of PEGDMA. The cross-linked PEGDMA network inside the PVdF-HFP matrix can provide the mechanical strength for the electrolytes, while the un-cross-linked PEGDMA oligomers serve as plasticizers for PVdF-HFP to improve the mobility of lithium ions at normal operation temperatures. In addition, the un-cross-linked PEGDMA oligomers can initiate cross-linking upon a sudden rise of temperature and thus provide thermal shutdown protection at elevated temperatures.

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**Keywords:** PVdF-HFP copolymer; Polymer electrolytes; Thermal shutdown; Cross-linking; Mechanical property

## 1. Introduction

In recent years, a lithium battery with high performance is desired for electronic devices such as notebooks, mobile telephones, digital cameras, and personal digital assistants (PDA). However, the presence of highly reactive electrodes and non-aqueous electrolytes in a fully charged lithium battery is cause for safety concern. For example, if an over-charged lithium battery experiences temperature in excess of 130 °C, it could rupture and flame [1]. At these elevated temperatures, reactions involving the active electrode materials, binder and the non-aqueous electrolytes lead to self-heating of the cell whereby the cell temperature rises automatically [1–9]. This condition, usually referred to as the *thermal run-*

*away*, could potentially lead to a catastrophic disassembly of the cell.

In order to improve its safety, a thermally activated device designed inside the lithium battery is necessary. For example, a polyolefin-based porous film has been employed to contain thermal runaway if the battery performs unusually. When the internal temperature of this battery excessively increases, this polyolefin-based porous film partially melts and its micropores are clogged, which prevents migration of ions in the liquid electrolyte. Consequently, ionic transport between the anode and cathode drastically decreases, leading to an increase in cell impedance. This prevents further reaction in the cell and shuts down the cell before explosion occurs [10–12]. Such mechanism is called *thermal shutdown* and is indispensable to the safety of a lithium battery. The lithium battery has been designed such that thermal shutdown starts at a temperature close to 130 °C when using polyethylene or at tem-

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perature close to 160 °C when using polypropylene as the separator.

However, this shutdown state can be continuously maintained only when micropores of the separator are clogged by the melted polyolefin. If the heat generated is much larger than the heat dissipated, the whole separator may be completely melted, so that the electrodes come in contact with each other directly, forming a short-circuit case. The state in which the separator is completely melted is called *meltdown*.

To overcome the unreliability of the single-layer polyolefin as battery separator, multiple-layer separator, e.g. Celgard<sup>R</sup> 2300 (PP/PE/PP), which comprises two polymeric porous membranes has been suggested [1,10–14]. One membrane is chosen to shutdown the cell based on its relatively low melting point, and the other membrane serves to maintain the separator's integrity at the shutdown temperature. These multiple-layer separators are expected to provide a wider shutdown window and are safer than the single-layer separators. Another approach is the addition of dispersed particles of inert fusible material into the polymer electrolyte, which melts at 80–120 °C to increase the impedance of the polymer electrolyte [15–18].

As an alternative to this melting mechanism to provide safety, a heat sensitive liquid electrolyte was suggested [19–21]. For example, Aurbach and co-workers [20] developed a liquid electrolyte which contains a solvent which rapidly polymerizes at temperature exceeding 100 °C to cause an increase in the viscosity and internal resistivity of the electrolyte so that the operation of the cell is terminated.

We have successfully prepared a PVdF-HFP/PEG/PEGDMA blend polymer electrolyte; it shows high ionic conductivity exceeding  $1 \times 10^{-3} \text{ S cm}^{-1}$  and good mechanical strength of ca. 50 MPa at room temperature [22–23]. In addition, the ionic conductivity of this polymer electrolyte decreases by two orders of magnitude as the cross-linked PEGDMA content reaches 50%. So this heat sensitive cross-linkable oligomers can serve as thermal shutdown device inside the polymer matrix.

In order to combine safety and performance such as high ionic conductivity and good mechanical strength, we prepared polymer electrolytes with shutdown function by blending PVdF-HFP copolymer with PEGDMA oligomers. Scheme is that one part of the oligomer which were cross-linked during film forming provide the mechanical strength for the electrolyte, and the other part of the oligomers which were un-cross-linked serve as plasticizer for PVdF-HFP copolymer. However, when the temperature rises above 100–120 °C, the un-cross-linked oligomers start to react and form a cross-linking structure in the electrolyte. This dense structure hinders the mobility of lithium ions, resulting in increased impedance of the cell so that self-heating and thermal runaway are avoided. Besides, a cross-linked PEGDMA network shows good thermal dimensional stability even at elevated temperature. Thus, this newly designed polymer electrolyte could eliminate the possibility of meltdown and is safer than the existing polyolefin-type separators.

## 2. Experimental

### 2.1. Preparation of PVdF-HFP based gel electrolytes comprising cross-linkable oligomers

PVdF-HFP copolymer (Elf Atochem Co., Kynar 2801) was dissolved in acetonitrile. After a homogeneous solution was obtained, the PVdF solution was mechanically mixed with an equal amount of liquid PEGDMA oligomer (Aldrich, MW, ca. 330) for 2 h. The resulting thick solution was cast with a doctor blade onto a Teflon plate. The plate was heated in an oven at 120, 130 and 140 °C for 10, 20 and 30 min, respectively for polymerization of the PEGDMA and evaporation of acetonitrile. Then, the freestanding membranes with different degrees of cross-linking were obtained and transferred into Ar-filled dry box (water content <10 ppm) for storage.

### 2.2. FT-IR analysis

Fourier transform-infrared spectroscopy (Bomem, DA-8.3 FTS) was used to measure the cross-linking degree of PEGDMA oligomers in PVdF-HFP based membranes. In order to improve the resolution, attenuated total reflection mode of FT-IR (ATR-FT-IR) was adopted in this study

### 2.3. Ionic conductivity and mechanical measurements

The dried membrane was soaked in 1 M LiPF<sub>6</sub>EC/DEC (1/1 v/v) containing 1% initiator (AIBN, 2,2'-azobisisobutyronitrile) for 10 min in an Ar-filled glove box. After activation, the membrane was removed from the electrolyte solution and excess electrolyte solution was wiped with a filter paper. The wetted membrane was sandwiched between two stainless-steel electrodes (SS) in a test cell. AC impedance spectroscopy (AUTOLAB) was employed to measure the ionic conductivity of the polymer electrolytes. The frequency ranged from 100 Hz to 50 kHz at a perturbation voltage of 10 mV. The shutdown ability test was carried out by monitoring the ac impedance at temperatures ranging from 30 to 180 °C for 1 h.

The tensile properties of the polymer membranes were measured by ASTM D882 procedure with a universal tensile meter (IMADA). The test specimens were 5 mm wide and 10 mm long. The tensile rate was controlled at 25 mm min<sup>-1</sup>.

## 3. Results and discussion

### 3.1. Characterization of polymer electrolytes

The degree of chemical cross-linking of PVdF-HFP/PEGDMA membranes is controlled by the casting temperature and casting time in the absence of an initiator. Thus, the membranes with different cross-linking degrees were characterized by FT-IR and the spectra are shown in Fig. 1. It is

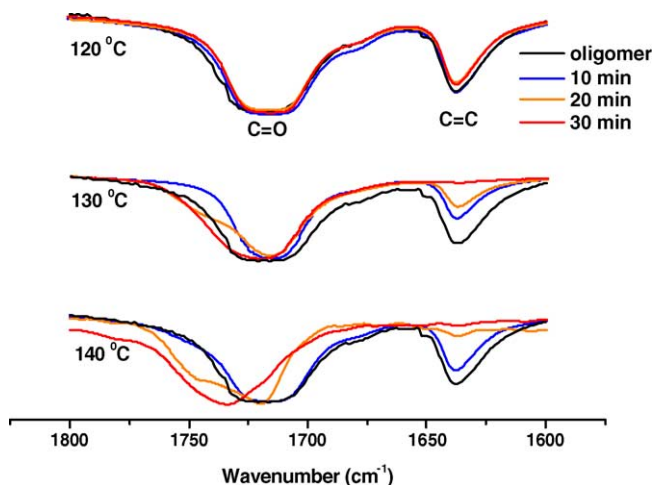
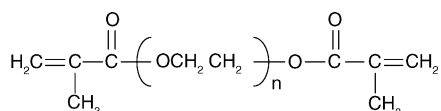


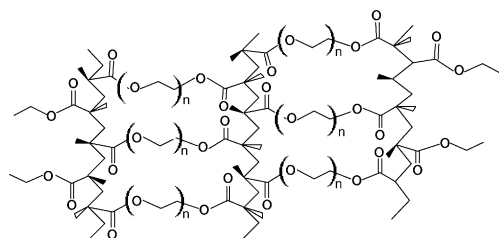
Fig. 1. FT-IR spectra of PVdF-HFP/PEGDMA prepared at different casting temperature and casting time.



Scheme 1. Molecular structure of PEGDMA oligomer.

found that C=O and C=C stretching bands of PEGDMA (see Scheme 1) appear at about 1720 and 1635  $\text{cm}^{-1}$ , respectively. Individual PEGDMA oligomers are well bonded together to form a three-dimensional network structure by radical polymerization [24,25], as shown in Scheme 2. Therefore, the C=C bands decrease as the cross-linking degree increases. It can be seen in Fig. 1, with a casting temperature at 130 and 140 °C, the C=C bands decrease as the casting temperature and casting time increase, i.e., a high cross-linking degree can be achieved via increasing casting temperature or increasing casting time. However, the C=C bands stay almost constant and are independent of the casting time at 120 °C. It implies that the C=C bonds can be broken and polymerization proceeds only when temperature is well above 120 °C. In addition, the C=O bands stay substantially constant, and shift slightly to a higher wavenumber at elevated temperature. This means C=O bonds are still retained while PEGDMA oligomers are transformed to the PEGDMA network.

In order to understand the correlation between cross-linking degree and casting temperature or casting time and



Scheme 2. Network structure of chemically cross-linked PEGDMA.

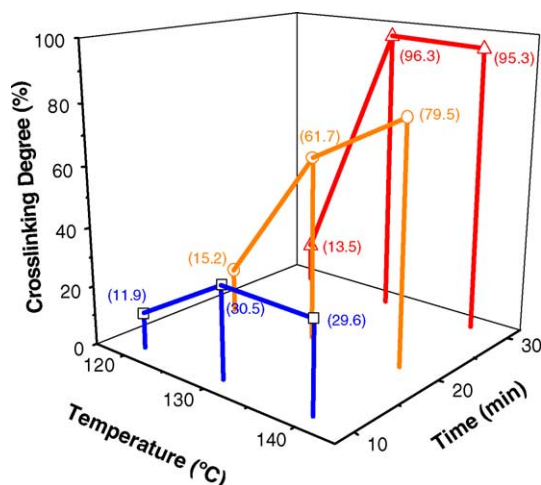


Fig. 2. The influence of casting temperature and casting time on crosslinking degree of PEGDMA in PVdF-HFP/PEGDMA membranes.

the further influence of the residual PEGDMA oligomers (uncross-linked) on PVdF-HFP membrane, quantitative analysis by FT-IR was required. The cross-linking degree can be estimated by selecting the C=O band as the reference peak, as shown in Fig. 2.

Fig. 2 depicts clearly that the higher the casting temperature or the longer the casting time during film forming, the higher the cross-linking degree. The PEGDMA oligomers are nearly completely cross-linked when the polymer membranes are prepared at 130 or 140 °C for 30 min in the absence of an initiator. By contrast, the PEGDMA oligomers show low cross-linking degree (ca. 15%) when the polymer membranes are prepared at 120 °C for 30 min. Among them, the PEGDMA exhibits a wide cross-linking degree at 130 °C, and therefore the polymerization rate of PEGDMA at this temperature is suitable to control the cross-linking degree of PEGDMA. It is worth mentioning that the PEGDMA oligomer can carry out the polymerization reaction at a lower temperature (ca. 90–100 °C) in the presence of an initiator; however, the polymerization rate of a PEGDMA is so rapid that it is hard to control the cross-linking degree using casting time.

### 3.2. Ionic conductivity

So far, we have successfully prepared PVdF-HFP/PEGDMA polymer membranes with different cross-linking degrees by controlling the casting temperature and casting time. Then, AC impedance analyzer was employed to measure the ionic conductivity of the so-obtained membranes. Fig. 3 shows the influence of the cross-linking degree of PEGDMA on the ionic conductivity of the PVdF-HFP/PEGDMA electrolytes containing 1 M LiPF<sub>6</sub> in EC/DEC (1/1 v/v). The PVdF-HFP/PEGDMA membrane with a high cross-linking degree exhibits a dense structure, which adversely affects its wettability with liquid electrolyte, hindering the mobility of lithium ions, and thereby decreasing the ionic conductivity.

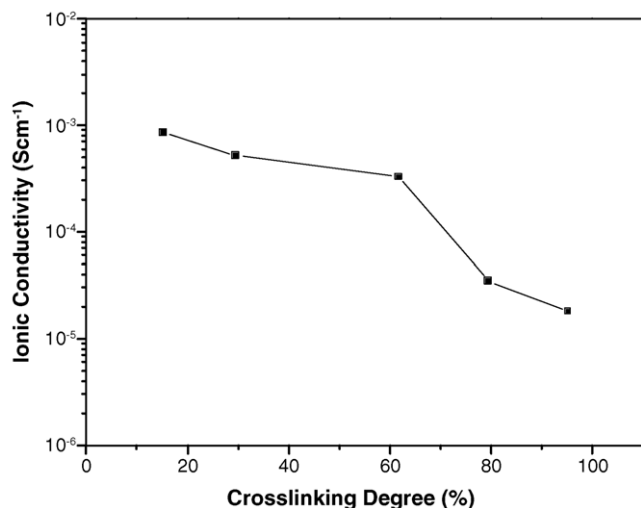


Fig. 3. Correlation between ionic conductivity of the PVdF-HFP/PEGDMA electrolytes and cross-linking degree of PEGDMA.

ity. The ionic conductivity of the PVdF/PEGDMA electrolyte with nearly complete cross-linking decreases by about two orders of magnitude when compared with that with a low cross-linking degree. So it implies that PVdF-HFP/PEGDMA is able to play a very efficient thermal shutdown role due to its inherent drastic change of ionic conductivity.

### 3.3. Mechanical properties

For fully automatic production, the polymer electrolytes should be able to withstand the stress induced by winding, stacking, rolling and folding. Fig. 4 shows the influence of the cross-linking degree of PEGDMA on the tensile modulus and the elongation of PVdF-HFP/PEGDMA membranes. It is found clearly that the tensile modulus increases with increase of PEGDMA cross-linking; however, the elongation of the membranes responds oppositely. The reinforced mechanical strength is related to the entanglement of PVdF-HFP

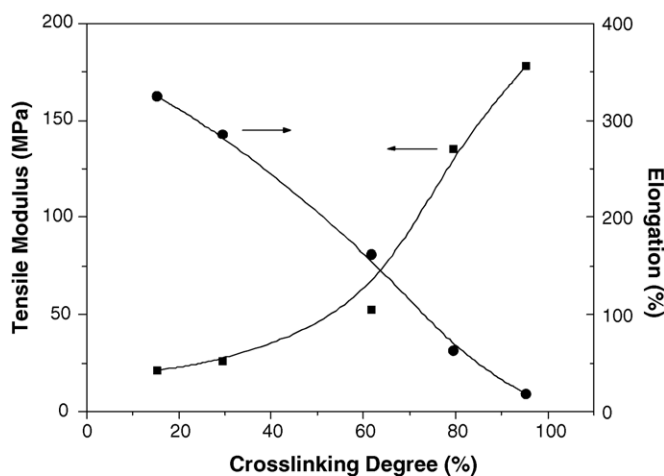


Fig. 4. The influence of the cross-linking degree of PEGDMA on the tensile modulus and the elongation of PVdF-HFP/PEGDMA membranes.

polymer chain and PEGDMA network [22–23]. The PVdF-HFP/PEGDMA membranes with low cross-linking degree (15%) show low tensile modulus (about 20 MPa) and high elongation (about 324%), implying that the un-cross-linked PEGDMA oligomer acts as plasticizer for PVdF-HFP matrix. By contrast, the membranes with a high cross-linking degree exhibit high tensile modulus (above 130 MPa) and low elongation (below 10%). Therefore, they are brittle and not suitable for large-scale manufacturing. For practical use, the membranes with about 50–70% cross-linking degree are suitable for battery manufacturing.

### 3.4. Thermal shutdown behavior

Lithium secondary batteries will initiate self-heating in abnormal situations, such as overcharging and internal/external short-circuit. Therefore, thermal shutdown by separators or polymer electrolytes is a critical feature for preventing thermal runaway. Thermal shutdown usually occurs near the melting temperature of polymer, at which the micropores of the separator are clogged, converting the ionically-conductive porous polymer membrane into a non-porous insulating layer between electrodes [7–11,26]. Fig. 5 shows the DSC thermograms for polyolefin separators including PE and trilayer (PP/PE/PP). The PE separator melts at 138 °C. The trilayer separator (PP/PE/PP) which is available in Celard<sup>R</sup> 2300 melts around 132 and 160 °C, which is related to the melting point of the PE and PP, respectively.

The impedance (at 1 kHz) of commercial polyolefin separator and the so-obtained PVdF-HFP/PEGDMA blend electrolyte was measured from ambient temperature to 180 °C, as shown in Fig. 6. As expected, the shutdown temperature of the PE separator is at about 140 °C, as is indicated by the sharp rise in impedance from 120 to 140 °C, which corresponds to the gradual melting of the PE to block the micropores. However, the PE separator undergoes meltdown at above 160 °C, i.e., the mechanical integrity of the separator

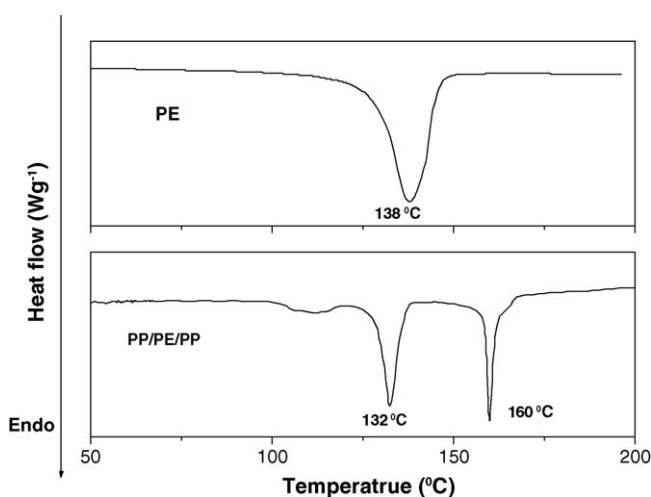


Fig. 5. DSC thermograms of polyolefin separators.



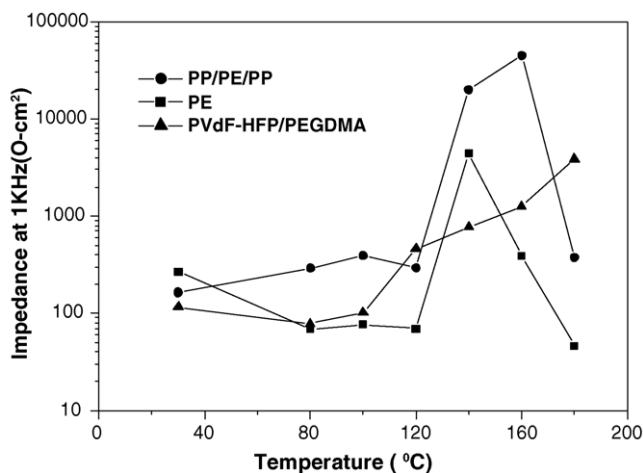


Fig. 6. Impedance of polyolefin separators (PP/PE/PP and PE) and PVdF-HFP/PEGDMA electrolyte at different temperature.

deteriorates greatly, which corresponds to the complete melting of PE. Therefore, the cell may cause internal short-circuit and create a hazard at above 160 °C. This is also reflected by the sharp drop of impedance from 140 °C to 160 °C. As for trilayer (PP/PE/PP), it shows shutdown behavior at about 140 °C and meltdown at about 180 °C. In this trilayer separator, the PE layer offers lower shutdown temperature while the PP layers provide the mechanical integrity at and above the shutdown temperature of PE.

As for PVdF-HFP/PEGDMA blend electrolyte (e.g. 60% cross-linking degree), soaked in 1 M LiPF<sub>6</sub>/EC/DEC containing 1% AIBN, the sharp impedance increase appears at 120 °C and it stays very high beyond 180 °C, as shown in Fig. 6. So the shutdown behavior of this blend electrolyte starts at about 120 °C and meltdown does not occur up to 180 °C. A successful control of thermal runaway for a lithium secondary battery requires the separators or polymer electrolytes which maintain thermal stable at high temperature for a certain period, then cool down to ambient temperature [4–6]. Besides, the thermal runaway may initiate at about 100–150 °C due to the decomposition of passivation layer on the electrodes [2–6,9]. Therefore, the PVdF-HFP/PEGDMA electrolytes which show shutdown at 120 °C and maintain thermal stability up to 180 °C should be suitable for practical application. In addition, the PVdF-HFP/PEGDMA electrolyte developed in this laboratory shows thermal shutdown behavior by another mechanism. Instead of partially melting the polymer to block die micropore as in the case of PE or PP based membranes, PVdF-HFP/PEGDMA drastically increases its impedance due to rapid polymerization of PEGDMA. So our sample will never suffer the problems of polymer meltdown and thermal instability as clearly illustrated in Fig. 6. However, so far our sample shows its highest impedance at around 3000 Ω cm<sup>-2</sup> which is lower than the maximum impedance of PP/PE/PP at 160 °C. So if we can select more suitable cross-linkable oligomer or increase oligomer content, we may further

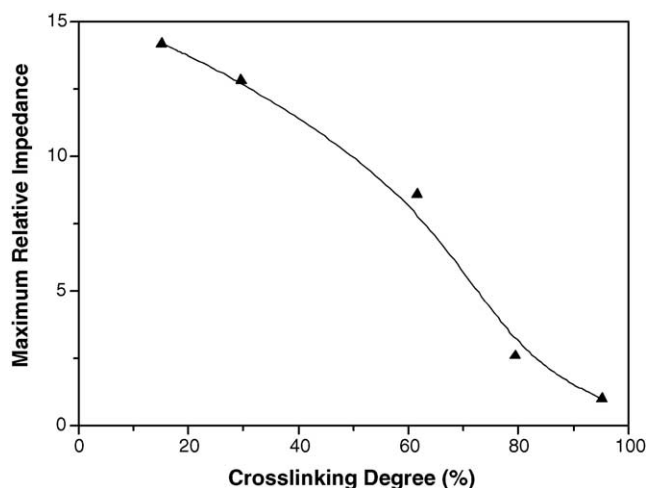


Fig. 7. Correlation between maximum relative impedance and initial cross-linking degree of PVdF-HFP/PEGDMA electrolyte. (The impedance at 100 °C serves as reference.)

improve the shutdown ability of our PVdF-HFP based electrolyte.

Fig. 7 shows the correlation between cross-linking degree of PEGDMA and the maximum relative impedance of the PVdF-HFP/PEGDMA electrolytes under different temperature. The impedance at 100 °C is used as a reference since shutdown behavior does not occur at that temperature. The blend electrolyte with lower cross-linking degree contains higher content of un-cross-linked PEGDMA oligomers in the PVdF-HFP matrix. Thus, the PVdF-HFP/PEGDMA blend electrolyte containing completely cross-linked PEGDMA oligomer does not possess the shutdown characteristic. The relative increase of impedance becomes more pronounced as the cross-linking degree of PEGDMA decreases. For example, the PVdF-HFP/PEGDMA electrolyte with ca. 30% cross-linking degree of PEGDMA shows about 13-fold increase in impedance when thermal shutdown occurs. Therefore, it can be concluded that the so-obtained polymer electrolyte shows improved tensile modulus as the cross-linking degree increases but would decrease ionic conductivity and thermal shutdown ability. Thus, an optimal condition can be obtained by careful controlling the cross-linking degree of the PVdF-HFP/PEGDMA blend electrolytes.

#### 4. Conclusions

A chemically cross-linked PVdF-HFP/PEGDMA electrolyte with a thermal shutdown characteristic has been developed successfully. The polymer electrolyte achieves the thermal shutdown by a rapid cross-linking reaction of PEGDMA instead of the melting mechanism of polyolefin; therefore, the meltdown concern can be avoided. The cross-linking degree was controlled by the casting temperature and casting time in the absence of an initiator. The cross-linked PEGDMA network reinforced the blend electrolyte, while the un-cross-

linked PEGDMA oligomer served as a plasticizer for PVdF-HFP to improve the mobility of lithium ions at normal operation temperature. Also, the un-cross-linked PEGDMA provided thermal shutdown protection at elevated temperature. The result indicates that the PVdF-HFP/PEGDMA electrolyte with ca. 60% cross-linking degree shows ionic conductivity of  $3.27 \times 10^{-4} \text{ S cm}^{-1}$  and tensile modulus of 52.68 MPa. Moreover, it shows an impedance increase by approximately one order of magnitude at 120 °C, representing thermal shutdown ability at a lower and safer temperature than the polyolefin separator. Furthermore, it maintains thermal dimensional stability well beyond 180 °C. Thus, this PVdF-HFP/PEGDMA electrolyte possesses good application potential for lithium secondary batteries.

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