

Short communication

# Effect of unreacted monomer on performance of lithium-ion polymer batteries based on polymer electrolytes prepared by free radical polymerization

Kyoung-Hee Lee<sup>a</sup>, Hong S. Lim<sup>b</sup>, Jong Hoe Wang<sup>c,\*</sup>

<sup>a</sup> Department of Applied Chemistry, Dongyang Technical College, 62-160, Kochuk-dong, Kuro-ku, Seoul 152-714, South Korea

<sup>b</sup> Energy Development Team, Corporate R & D Center, Samsung SDI Co. Ltd. 428-5, Gongse-Ri, Kiheung-Eup, Yongin-City, Kyonggi-Do, South Korea

<sup>c</sup> Korea Institute of Ceramic Engineering and Technology, 233-5, Gasan-Dong, Gueancheon-Gu, Seoul 153-801, South Korea

Received 12 May 2004; accepted 13 July 2004

Available online 11 September 2004

## Abstract

A study is made of the effect of unreacted monomer on the performance of lithium-ion polymer batteries that use cross-linked polyethylene glycol diacrylate-based polymer electrolytes prepared by free radical polymerization. At high discharge rates and low temperature, the discharge capacities of test cells containing the polymer electrolytes prepared at various concentrations of the initiator decrease as the content of the unreacted monomer in the polymer electrolytes increases. This behaviour is consistent with an increase in the interfacial resistance of the test cells with increase in the content of the unreacted monomer. The source of the high interfacial resistance is considered to be due to reaction of the unreacted monomer at the electrode surface to form a resistive film during charging for cell formation.

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**Keywords:** Polymer electrolyte; Polyethylene glycol diacrylate (PEGDA); Unreacted monomer; Interfacial resistance; Monomer decomposition; Lithium-ion battery

## 1. Introduction

Solid polymer electrolytes have attracted much attention owing to their potentially wide range of applications for solid-state batteries, electrochromic devices, and sensors [1–3]. In particular, there has been intensive efforts to develop Li-ion conductive polymer electrolytes for battery applications.

Solid polymer electrolytes with high ionic conductivity can usually be achieved by using a plasticizer additive of small organic molecules, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), which have high dielectric constants and low vapour pressures [4–6].

Cross-linked polyethylene glycol diacrylate (PEGDA) electrolytes containing a plasticizer have been studied by many researchers because these materials have high room-temperature ionic conductivity and good dimensional stability [7–9]. In general, cross-linked PEGDA-based polymer electrolytes are prepared by free radical polymerization of PEGDA monomer in the presence of liquid electrolyte. The resulting products are composed of the cross-linked polymer matrix and the liquid electrolyte, which is the main ion conductor. Unfortunately, there may also be unreacted monomer, PEGDA, in the cross-linked polymer electrolyte.

There appear to be no reports of the effect of unreacted monomers of PEGDA on the performance of Li-ion polymer batteries. Therefore, this study examines the performance of lithium-ion polymer batteries based on the PEGDA-based polymer electrolytes prepared by free radical polymerization.

\* Corresponding author. Tel.: +82 2 3282 2478; fax: +82 2 3282 2490.  
E-mail address: [jhwang@kicet.re.kr](mailto:jhwang@kicet.re.kr) (J.H. Wang).

## 2. Experimental

### 2.1. Preparation of cross-linked polymer electrolytes

Appropriate amounts of PEGDA, liquid electrolyte plasticizer and a lauroyl peroxide initiator were mixed to give a homogeneous solution. The resulting thick solution was cast on to a teflon plate. The solution was heated at 75 °C for 2 h for polymerization to make a film of the cross-linked polymer electrolyte. A 1.3 M LiPF<sub>6</sub> solution of 30:70 (by weight) ethylene carbonate:diethylene carbonate (LiPF<sub>6</sub>/EC:DEC) was used as the liquid electrolyte plasticizer. The ratio of polymer matrix to liquid electrolyte in the cross-linked polymer electrolytes was 1 to 10 by weight. All preparations of these polymer electrolytes as free-standing film were performed in a glove-box filled with argon gas.

### 2.2. Electrical measurements

A carbon|polymer electrolyte|LiCoO<sub>2</sub> cell was assembled by sandwiching a sheet of 80- $\mu$ m thick polymer electrolyte between a 73- $\mu$ m thick anode and a 70- $\mu$ m thick cathode. The cell was then enclosed in a metallized plastic bag and sealed under vacuum. All cells were assembled in a glove-box filled with argon gas.

The bulk resistance and interfacial resistance of the test cells were measured by complex impedance analysis using a Solartron 1255 frequency response analyzer coupled to an IBM PS/2 computer over a frequency from 0.1 to 100 kHz. An ac perturbation of 5 mV was applied to the cell.

Capacity ( $Q$ ) measurements were carried out by charging the cells at the 0.2C rate to 4.2 V, followed by constant-voltage charging to a C/20 rate cut-off and then discharging at various constant currents to a 2.75 V cut-off.

## 3. Results and discussion

A typical charge–discharge curve for the formation of a cell that contained a cross-linked polymer electrolyte prepared with 5 wt.% initiator is shown in Fig. 1. From such curves, plots of  $dQ/dV$  versus cell voltage were obtained.

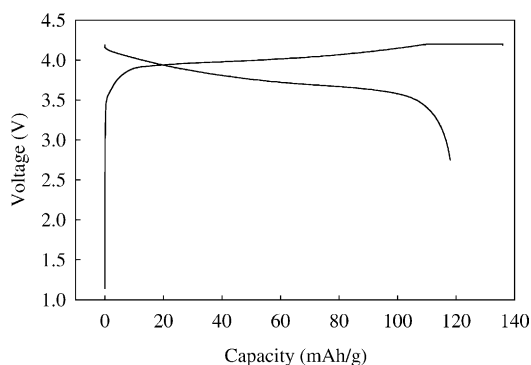


Fig. 1. Formation charge and discharge curves for carbon|cross-linked polymer electrolyte (prepared with 5 wt.% initiator)|LiCoO<sub>2</sub> cell.

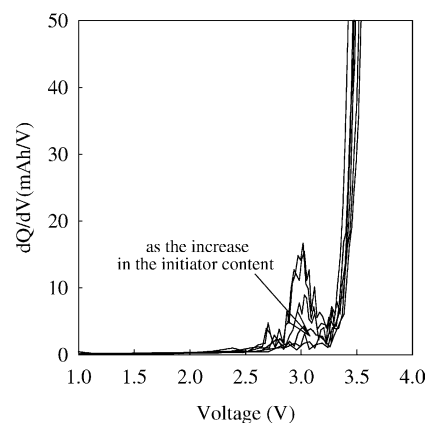


Fig. 2. A plot of  $dQ/dV$  vs.  $V$  for carbon|cross-linked polymer electrolyte|LiCoO<sub>2</sub> cells with various initiator contents.

These, in turn, were used to analyze the content of unreacted monomer in polymer electrolyte films that were prepared with various initiator contents. If unreacted monomers remain in the polymer electrolyte film, then the residuals might be decomposed at a certain voltage during the formation process and, consequently, a peak would appear in the plot of  $dQ/dV$  versus voltage.

Plots of  $dQ/dV$  versus cell voltage for test cells with various initiator concentrations are shown in Fig. 2. There are various concentrations of unreacted monomer in the polymer electrolyte films, as shown by the size of the peaks at about 3 V. The peak height as a function of initiator content is plotted in Fig. 3. The unreacted monomers appear to decompose at about 3 V. The peak height decreases as the initiator content is increased, which indicates that the content of unreacted monomer is reduced with increase in initiator concentration. It appears that there is little unreacted monomer left in the polymer electrolytes when the initiator content is 5 mol%, or more.

From these results, it can be concluded that: (i) unreacted monomer contents in the polymer electrolyte films are controlled by adjusting the content of initiator in solutions that consist of the monomer, initiator, and liquid electrolyte; and

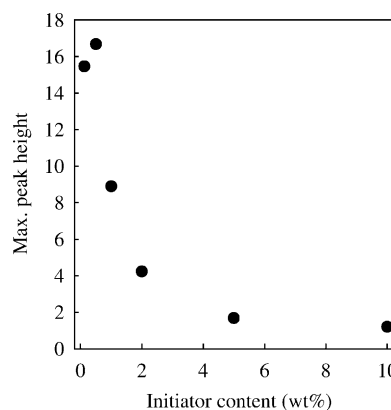


Fig. 3. Maximum peak height obtained from plot of  $dQ/dV$  vs.  $V$  as function of initiator content.

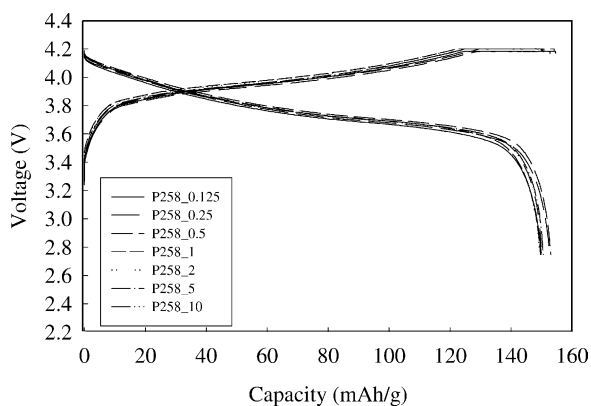


Fig. 4. Standard charge and discharge curves for carbon|cross-linked polymer electrolyte|LiCoO<sub>2</sub> cell for various initiator contents.

(ii) the unreacted monomer contents decrease after polymerization reactions as the initiator content is increased.

To demonstrate the effect of unreacted monomer PEGDA on the performance of Li-ion polymer cells, tests were conducted on cells that contained the polymer electrolytes with various concentrations of initiator. Typical standard charge–discharge curves for the cells are presented in Fig. 4 and the standard discharge capacities, which are measured at the 0.2C rate, are plotted as a function of initiator content in Fig. 5. The results show that the value of the standard discharge capacity is not affected by variation in the unreacted monomer concentration in the present range. The discharge capacities of the test cells at various discharge rates are shown as a function of initiator concentration in Fig. 6; note, the capacities are reported as percentage of the value at the 0.2C rate. The values of the discharge capacity increase as the initiator content is increased up to about 1 wt.% but level-off at higher initiator contents. The increase in discharge capacity with increase in initiator content is much higher at higher discharge rates. The discharge capacity (0.2C rate) at –20 °C is presented as a function of initiator contents in Fig. 7. These values are described as a percent value of the discharge capacity at 25 °C at 0.2C rate. The behaviour of the

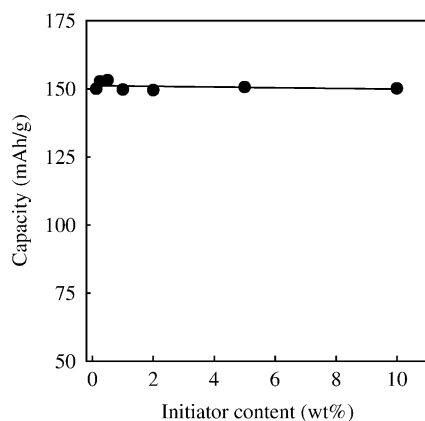


Fig. 5. Standard discharge capacities for carbon|cross-linked polymer electrolyte|LiCoO<sub>2</sub> cells as function of initiator content.

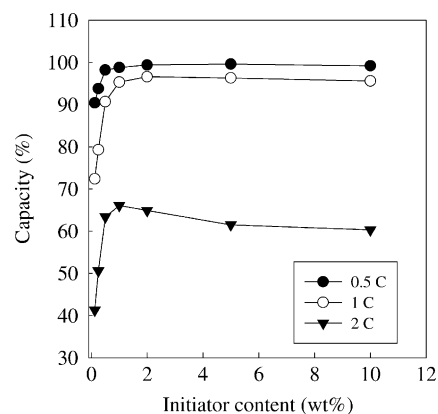


Fig. 6. Discharge capacities for carbon|cross-linked polymer electrolyte|LiCoO<sub>2</sub> cells at various discharge rates as function of initiator content.

low-temperature discharge capacity with increase in initiator content is similar to that of the discharge capacity at high rates. In summary, at high discharge rate and low temperature, the discharge capacities of the test cells containing the polymer electrolytes prepared with various concentrations of initiator increase as the initiator content is increased.

In order to find the reason for the increase in discharge capacities, especially, at high rates and low temperature, as the initiator content is increased, impedance studies were conducted on the cells. Specifically, values of the bulk resistances and interfacial resistances of the test cells were evaluated as a function of initiator content. Typical impedance spectra for the test cells at 25 and –20 °C are shown in Fig. 8(a) and (b), respectively. The values of bulk resistance and interfacial resistance were evaluated as a function of initiator content from these impedance diagrams. Plots of the bulk resistance values at 25 and –20 °C as a function of initiator content are given in Fig. 9(a) and (b), respectively. The bulk resistances increase slightly as the initiator content increases, especially, between 5 and 10 wt.%. This behaviour is expected to result from a decrease in the mobilities of the polymer matrix owing to the enhanced polymerization reaction. Nevertheless, the increase in bulk resistance with increase in initiator content is

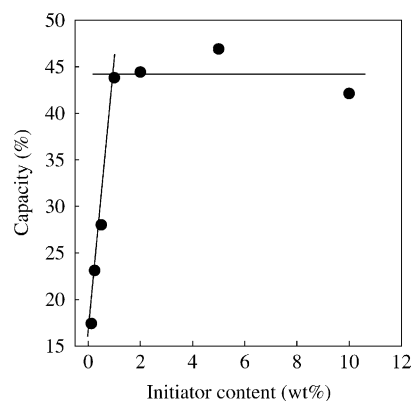


Fig. 7. Discharge capacities for carbon|cross-linked polymer electrolyte|LiCoO<sub>2</sub> cells at –20 °C as function of initiator content.

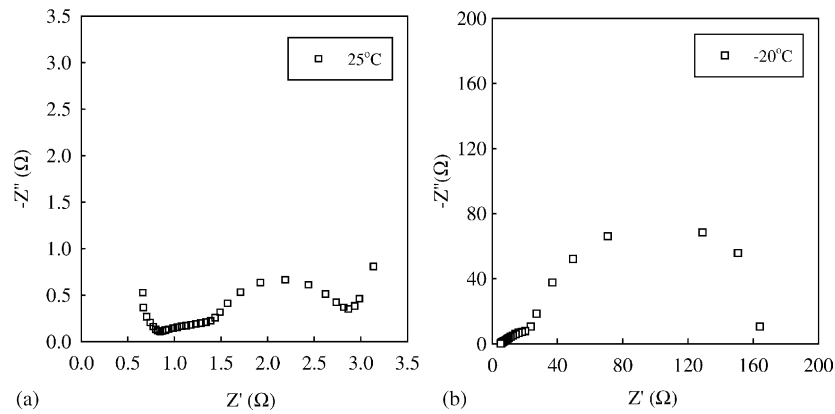


Fig. 8. Impedance diagram for carbon/cross-linked polymer electrolyte/LiCoO<sub>2</sub> cell at (a) 25 °C and (b) -20 °C.

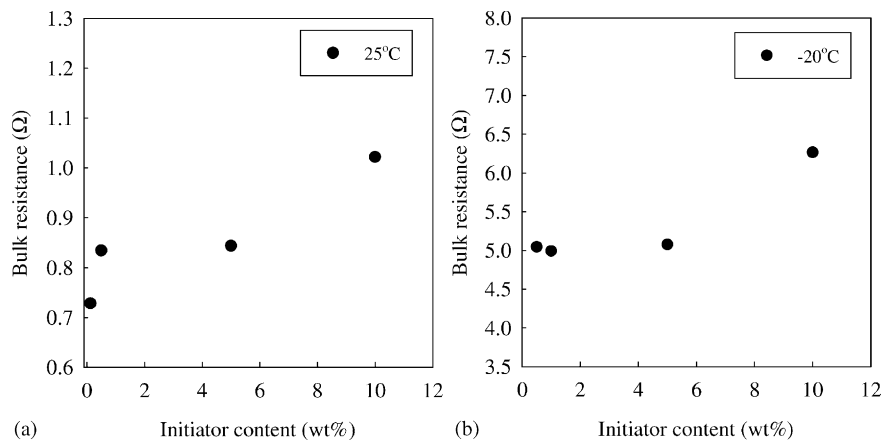


Fig. 9. Bulk resistances of the carbon/cross-linked polymer electrolyte/LiCoO<sub>2</sub> cell at (a) 25 °C and (b) -20 °C as a function of initiator content.

not quite consistent with the trend in discharge capacity over the concentration range. The interfacial resistances at the 25 and -20 °C as a function of initiator content are shown in Fig. 10(a) and (b), respectively. The interfacial resistances decrease abruptly as the initiator content is increased, especially in the lower concentration range. The dependence of the interfacial resistances is much greater than that of the bulk

resistance, such that the total resistance of the cell decreases as the initiator content increases, especially at lower concentrations of initiator. Therefore, the decrease in the interfacial resistance as the initiator content is increased is expected to be principal reason for the increase in the discharge capacities at high rates and low temperatures with the increase in initiator content.

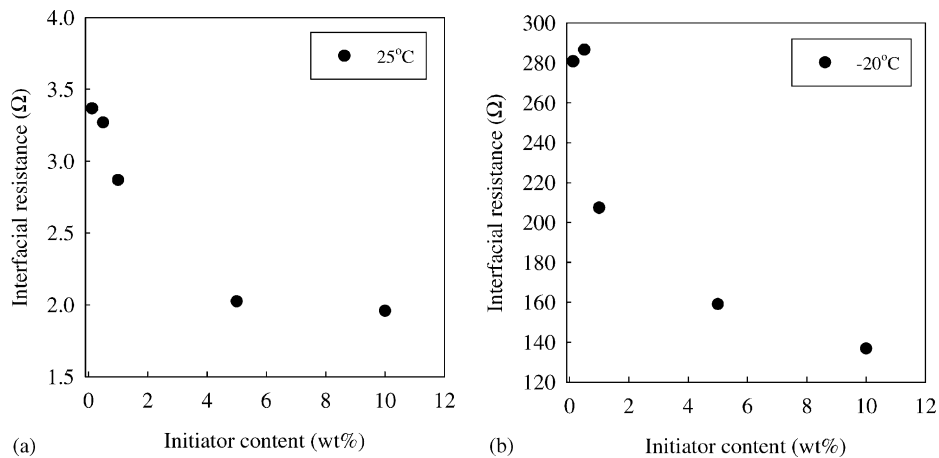


Fig. 10. Interfacial resistances of the carbon/cross-linked polymer electrolyte/LiCoO<sub>2</sub> cell at (a) 25 °C and (b) -20 °C as a function of initiator content.

Table 1

Electrical properties of two cells at various rates and low temperature; one cell contains liquid electrolyte only and the other contains liquid electrolyte with initiator but no monomer

	EC:DEC-1.3 M LiPF <sub>6</sub>	EC:DEC-1.3 M LiPF <sub>6</sub> /initiator
Standard discharge capacity at 0.2C (mAh g <sup>-1</sup> )	155	154
Discharge capacity at 0.5C (%)	98.6	98.6
Discharge capacity at 1C (%)	97.0	96.8
Discharge capacity at 2C (%)	91.3	90.0
Discharge capacity at 0.2C at -20 °C (%)	65.0	66.8

The source of the high interfacial resistances at low initiator content is thought to be due to reaction of the unreacted monomer at the electrode surface in the polymer electrolytes film to form a resistive film during charging for cell formation. As illustrated by the data in Fig. 2, unreacted monomer in the polymer electrolyte films is decomposed during the formation charge stage at about 3 V. The decomposed unreacted monomer, which is located on the electrode surface, might be a highly resistive material and, consequently, may increase the interfacial resistance.

Therefore, it can be concluded that the decomposed unreacted monomers on the electrode surface are reason for the high interfacial resistance of cells containing polymer electrolytes prepared at low initiator content; and thus, reduce the discharge capacities at high rates and low temperature.

In order to investigate the possibility of the initiator instead of the monomer being the cause of the observed variation in performance, two test cells containing liquid electrolytes were prepared. One contained the liquid electrolyte only and the other the liquid electrolytes with initiator but no monomer. The electrical properties of these cells at various rates and low temperature are compared in Table 1. There are no appreciable differences in the electrical properties of these two cells and this indicates that the initiator, lauroyl peroxide, itself has no influence on cell performance.

#### 4. Conclusions

The effects of unreacted monomer on the performance of lithium-ion polymer batteries are studied. Discharge ca-

pacities at high discharge rates and low temperature are reduced as the unreacted monomer content is increased. The increase in interfacial resistance as the unreacted monomer content is increased is expected to be the principal reason for the decrease in the discharge capacities at high discharge rates and low temperature with increase in the content of unreacted monomer. The source of the high interfacial resistance at high unreacted monomer content is considered to be due to reaction of the unreacted monomer at the electrode surface to form a resistive film during charging for cell formation.

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