



# Characterization of gel polymer electrolyte for suppressing deterioration of cathode electrodes of Li ion batteries on high-rate cycling at elevated temperature



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## ABSTRACT

As one of obvious electrolyte design technologies of Li ion batteries (LIBs) to meet durable high-rate capability at elevated temperatures for battery electric vehicles, this study assesses the superiority of gel polymer electrolyte (GPE) based on experimental results supporting its working mechanism. Our previous study indicated that degradation of cathode electrode under high-rate cycling at elevated temperature was a major cause of the decrease in performance of LIBs, and the single full cells (SFCs) with a GPE designed from dipentaerythritol hexaacrylate and methyl ether methacrylate was re-verified to have superior 3.0C cycling performance at 80 °C. The superiority of the GPE is studied from comparing mid-voltages of discharge profiles of the SFCs, observing the cross-sectional morphology of the electrodes by field emission scanning electron microscopy, assessing the interacting force among the electrolyte components by thermogravimetric analysis, and examining each resistance component of the SFCs by electrochemical impedance spectroscopy. Gel polymerization of liquid electrolyte results in a significant increase of durable high-rate capability of LIBs due to the mechanisms of not only its buffering effect on solvating process of Li<sup>+</sup> ions being extracted from the active materials during high rate operation, but also higher thermal stability of electrolyte components, lower susceptibility of the ionic conductivity of the electrolyte to a temperature change, and lower energy barrier to breakup of solvated structures during conducting of Li<sup>+</sup> ions in gel polymer matrix.

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## 1. Introduction

Recently, environmentally friendly vehicle technologies have been evaluated using Life Cycle Assessment (LCA) methodology, including the emissions coming from electricity production and the end-of-life processing of the vehicle [1,2]. According to these reports, the energy consumption of different vehicle technologies clearly showed that battery electric vehicles (BEVs) use less energy than all other vehicle technologies considered, particularly running on Li ion batteries (LIBs) charged by the electricity produced with renewable energy.

Although LIB technology is used readily in portable electronics, its application in BEVs is a relatively new and emerging technology with many technical and economic problems to resolve [3]. Therefore, government programs in many countries are encouraging the growth of the related industries from basic materials for

batteries to the complete products, BEVs with equipped LIBs [4]. Basically, current research to develop LIBs for BEV applications are similar to those of portable electronics: development of cathode and anode materials with higher capacity, design of an electrolyte with a higher oxidation potential and conductivity, and manufacturing technology of LIBs economically [5]. These technologies are also required for BEVs with higher power and a longer traveling distance.

In contrast to LIBs for portable electronics, however, research to adapt batteries to the upgrading of BEVs needs to focus on other technical problems, such as much longer cycle life, better charge/discharge performance under high rate conditions, and better durability at elevated temperatures [6]. These technologies cannot be achieved without an electrolyte design for anti-degradation methodology of the battery performance, especially at elevated temperatures. Many research groups have attempted to find solutions for these technical problems from the design of an electrolyte, finding of new electrolyte components [7] and developing of higher quality SEI layer [8]. Unfortunately, the performance of LIBs with liquid electrolyte (LE) is not so good at

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elevated temperatures because of low evaporating and boiling temperature of liquid components.

In our previous paper, the detachment of cathode materials from Al substrate was reported to be a major cause of the deterioration in the performance of LIBs at elevated temperatures [9]. This unfavorable defect of the cathode electrode was prevented by changing the electrolyte from a liquid to gel polymer type, designed with dipentaerythritol hexaacrylate (DPHA) and poly (ethylene glycol) methyl ether methacrylate (PEGMEM). The experimental results were analyzed that the gel polymer electrolyte (GPE) could suppress the detachment of the active materials of the cathode electrode due to the buffering effect on solvating process of  $\text{Li}^+$  ions being extracted from the active materials, especially from the cathode electrode. This paper reports the working mechanism of the designed GPE in LIBs in more detail, which shows better cycle life at elevated temperatures, using general analytical techniques, such as discharge curves upon 3.0 C cycling at 80 °C, field emission-scanning electron microscopy (FE-SEM) of the surface and cross-section of the cathode electrode after cycling, thermogravimetric analysis (TGA) of the GPE, and electrochemical impedance spectroscopy (EIS) of the home-made single full cells.

## 2. Experimental

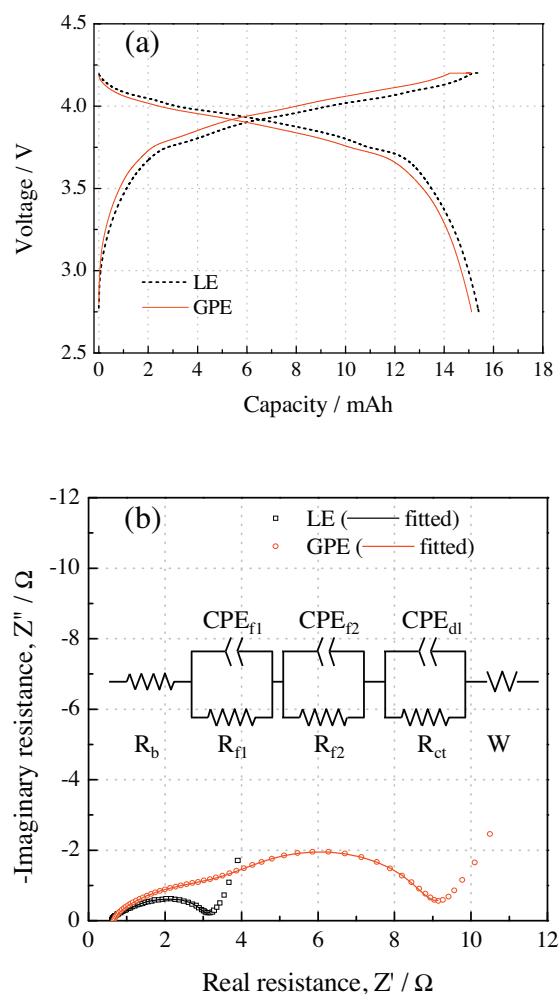
Most of these experiments were conducted under the experimental conditions reported in the previous paper [9]. The battery-grade electrolyte, 1.0 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (3/7, volume ratio), was obtained from Soulbrain Co, South Korea. The selected acrylate monomers, DPHA ( $M_n$ : 579) and PEGMEM ( $M_n$ : 1,100), were purchased from Sigma Aldrich and used as precursors of the GPE in the mixed state, 4 wt.% of DPHA: PEGMEM (=2:1), which is the best condition selected from the previous paper [9]. The cell performance of the LIBs was also conducted under the same conditions as the previous paper using home-made SFCs, 2.7 cm  $\times$  2.5 cm in size, on the pressed state by two acryl plates with a 5 mm thickness to maintain uniform cell conditions. The battery grade electrodes,  $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$  ( $x + y + z = 1$ ) coated on an Al substrate as the cathode (LNMC0 electrode), and graphite coated on a Cu substrate as the anode (graphite electrode), were obtained from SK Innovation Co., South Korea.

The electrochemical performance of the SFCs was measured in a thermostatic chamber to remove the noise caused by delicate temperature changes. The charge and discharge cycling tests were conducted on a battery cycler (WBCS3000, Wonatech Co., South Korea). As the formation process, the SFCs were charged at a constant current (CC) of 0.2 C from its open circuit voltage (OCV) to 4.2 V, followed by a constant voltage (CV) of 4.2 V to 0.02 C capacity drop (CC – CV charge), and finally discharge to 3.0 V at a constant 0.2 C rate. The performance of the SFCs was re-verified under two conditions, low rate discharges (0.2 C, 0.5 C, 1.0 C, and 2.0 C) at 25 °C and high rate discharge cycle (3.0 C, 50 times) at 80 °C. The SFCs were decomposed in a glove box to compare the electrode state after the cycling tests. The morphologies of the surface and cross-section of the LNMC0 and graphite electrodes were examined by FE-SEM (S-4200, Hitachi). The difference in the vaporization force between the LE and GPE was examined at a heating rate of 10 °C  $\text{min}^{-1}$  by TGA (Pyris, Perkin Elmer). EIS of the SFCs was performed using an IME 6ex (Zahner Elektrik, Germany) over the frequency range, 2.0 MHz  $\sim$  2.0 mHz, at a potentiostatic signal amplitude of 5 mV. In all cases, the SFCs for the EIS measurements were charged to 4.2 V and were performed in a thermostat chamber fixed at 25 °C. The equivalent circuit models for the measured impedance spectra were analyzed using  $Z_{\text{man}}$  fitting software (Ver. 2.5, Scribner Associates, Inc.).

## 3. Results and Discussions

### 3.1. Basic performance of the SFCs with electrolyte types

Fig. 1(a) is 0.2 C charge-discharge curves for the LNMC0/graphite SFCs with the LE and GPE. The SFCs with the GPE show a shorter CC region in charge curve and lower mid-voltage in discharge curve than those with the LE. Typically, LIBs with higher internal resistance show a higher mid-voltage and shorter CC region in charge profile, a voltage drop and lower mid-voltage in discharge profile, resulting in shorter charge and discharge capacities. The internal resistances of the SFCs were compared through analyzing the equivalent circuits for their EIS spectra as shown in Fig. 1(b). The high frequency intercept on the real axis is the internal resistance ( $R_s$ ) of the SFCs, which is composed of electrolyte resistance, electronic resistance of the active materials, current collectors and connection resistance. Because this research focused only on electrolyte modification to improve the high-rate



	$R_b / \Omega$	$R_{f1} / \Omega$	$R_{f2} / \Omega$	$R_{ct} / \Omega$	$W / \text{S s}^{1/2}$
LE	0.54	0.79	1.00	0.68	2.41
GPE	0.49	3.36	4.01	1.02	1.50

Fig. 1. Initial properties of the LNMC0/graphite SFCs with the LE and GPE measured at 25 °C; a) 0.2 C charge-discharge curves, b) equivalent circuit for the EIS spectra of the SFCs at 4.2 V after 0.2 C cycling and fitting parameter values.

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