



# Cycling characteristics of lithium powder polymer cells assembled with cross-linked gel polymer electrolyte



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## ABSTRACT

Lithium polymer cells composed of lithium powder anode and  $\text{LiV}_3\text{O}_8$  cathode were assembled with an in-situ cross-linked gel polymer electrolyte, and their cycling performance was evaluated. The  $\text{Li}/\text{LiV}_3\text{O}_8$  cells exhibited better capacity retention and greater rate performance than the liquid electrolyte-based cell. The stable cycling characteristics of the lithium powder polymer cells resulted from the strong interfacial adhesion between the electrodes and the electrolyte as well as the suppression of the dendritic growth of lithium powder electrode during repeated cycling.

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## 1. Introduction

In recent years, the demand for rechargeable lithium batteries with high energy density and enhanced safety has increased to meet growing needs for smaller, lighter portable electronic devices and to accommodate growing interest in electric vehicles and energy storage systems [1–4]. As a result, lithium batteries using lithium metal as a negative electrode are the focus of substantial research interest because the lithium electrode offers a very high specific capacity ( $3,860 \text{ mAh g}^{-1}$ ) [5], which is more than ten times that of the currently used carbon electrode. However, the use of lithium metal electrodes has been limited by the occurrence of dendrite growth during repeated charge and discharge cycles, as it gives rise to safety problems and gradual degradation of the cycling efficiency [6,7]. Therefore, the control of dendrite growth is very important for developing lithium metal batteries with enhanced safety and good capacity retention. In our previous studies, lithium powder instead of lithium foil was suggested as a new anode material to suppress dendritic growth, and distinct improvement in the electrochemical properties and safety of lithium powder electrodes was demonstrated [8,9]. Lithium vanadate ( $\text{LiV}_3\text{O}_8$ ) is a promising cathode active material for use in lithium metal batteries [10–15]. Based on theoretical calculations, lithium vanadate can deliver a

high specific capacity ( $280 \text{ mAh g}^{-1}$  for  $3\text{Li}^+$  insertion/deinsertion) that is nearly double that of  $\text{LiCoO}_2$ . Additionally, lithium vanadate works in a potential range in which no side reactions due to electrolyte oxidation are expected. For the successful development of lithium metal batteries, there is also a pressing need for safer, more reliable electrolyte systems. Currently, gel polymer electrolytes are considered a promising alternative to the liquid electrolytes used in lithium batteries [16–20]. As a type of gel polymer electrolyte, chemically cross-linked gel polymer electrolytes can be synthesized by an in-situ cross-linking reaction of a liquid electrolyte with cross-linking agents [20–25], a technique which has been applied to the manufacture of commercialized lithium-ion polymer batteries. In this process, an electrolyte solution containing cross-linking agents is injected into the cell and gelation is performed by heating the cell, which resolves the leakage problem while maintaining good thermal and dimensional stability as well as high ionic conductivity.

With the goal of developing high energy density lithium metal polymer cells with good capacity retention and enhanced safety, the lithium powder polymer cells composed of a lithium powder anode, a cross-linked gel polymer electrolyte and a  $\text{LiV}_3\text{O}_8$  cathode were assembled and their cycling performance was evaluated. The cross-linked gel polymer electrolytes were synthesized by in-situ chemical cross-linking in the cells, and the amount of the cross-linking agent necessary to achieve good cycling performance was suggested. The morphological analysis of the lithium powder electrode after repeated cycling demonstrated that the

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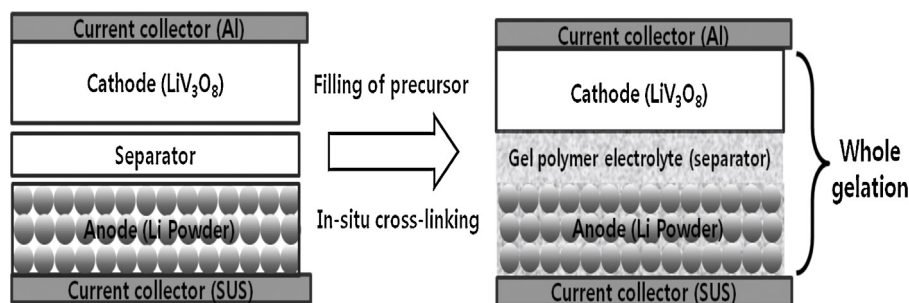


Fig. 1. Schematic presentation of lithium powder polymer cell assembled by in-situ cross-linking of a precursor electrolyte solution.

dendritic growth of lithium metal could be effectively suppressed in cross-linked gel polymer electrolytes, resulting in stable cycling characteristics.

## 2. Experimental

### 2.1. Synthesis of gel polymer electrolytes

Poly(ethylene glycol) dimethacrylate (PEGDMA,  $M_n = 550$ ) was purchased from Aldrich and used as a cross-linking agent after drying under a vacuum at  $60^\circ\text{C}$  for 24 hr. The water content in PEGDMA after vacuum drying was determined by Karl Fisher titration to be 18 ppm. PEGDMA and *t*-amyl peroxyvalate (Seki Arkema) as a thermal radical initiator were added to a liquid electrolyte to prepare the precursor electrolyte solution. The liquid electrolyte, which consisted of 1.0 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume, battery grade) containing 1 wt.% vinylene carbonate (VC), was kindly supplied by Soulbrain Co. Ltd., and used without further treatment. VC was added as a solid electrolyte interphase (SEI) forming agent. In order to optimize the content of the cross-linking agent, PEGDMA was dissolved with different concentrations (0, 2.0, 4.0, 6.0 and 8.0 wt.%) in the liquid electrolyte. The cross-linked gel polymer electrolyte was then prepared by a radical-initiated reaction of the precursor electrolyte solution at  $90^\circ\text{C}$  for 20 min.

### 2.2. Electrode preparation and cell assembly

Lithium powders were prepared by the droplet emulsion technique [8,9,26]. A mixture of molten lithium and silicone oil was sheared at approximately 25,000 rpm to produce an emulsion. As the emulsion was cooled to room temperature, the liquid lithium droplets solidified to form solid powders. The lithium powders were compacted by pressing to form an electrode. The  $\text{LiV}_3\text{O}_8$  electrode was prepared by coating a water-based slurry containing 80 wt.% lithium vanadate (GfE, Germany), 15 wt.% Ketchen black and 5 wt.% carboxymethyl cellulose (CMC) on Al foil. The electrode was roll pressed to enhance particulate contact and adhesion to the current collector. The lithium powder polymer cell was assembled by sandwiching the polypropylene (PP) separator (Celgard 2400) between the lithium powder anode and the  $\text{LiV}_3\text{O}_8$  cathode. The cell was enclosed in a pouch bag, injected with the gel electrolyte precursor and then vacuum-sealed. The cell assembly was performed in a dry box filled with argon gas. After cell assembly, the cells were maintained at  $90^\circ\text{C}$  for 20 min to induce in-situ thermal curing of the gel electrolyte precursor within the cell. The in-situ cross-linking enabled bonding of the separator firmly to the lithium powder anode and  $\text{LiV}_3\text{O}_8$  cathode together in the cell, as illustrated in Fig. 1.

### 2.3. Measurements

The morphologies of the electrodes were examined using a scanning electron microscope (SEM, JEOL JSM-6300). Fourier transform infrared (FT-IR) spectra were recorded on JASCO 460 IR spectrometer in the range of  $400\text{--}4000\text{ cm}^{-1}$ . The ionic conductivity of the liquid electrolyte was measured by a Cond 3210 conductivity meter (WTW GmbH, Germany), and the ionic conductivity of the cross-linked gel polymer electrolyte after thermal curing was determined from AC impedance measurements. AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over a frequency range of 100 Hz to 100 kHz with an amplitude of 10 mV. Charge and discharge cycling tests of the lithium powder polymer cells were conducted at a constant current over a voltage range of 2.0–3.6 V with battery test equipment (WBCS 3000, Wonatech) at room temperature. To observe the morphological changes of the lithium powder electrodes, the cells were disassembled after 100 cycles in a glove box and the electrodes were washed with dimethyl carbonate to remove the residual electrolyte. After drying in an argon-filled glove box, the morphology of the lithium powder electrodes was characterized using a field emission scanning electron microscope.

## 3. Results and discussion

The cross-linked gel polymer electrolytes were synthesized by thermal curing of the liquid electrolyte with different cross-linking agent contents at  $90^\circ\text{C}$  for 20 min. Fig. 2-(a) shows the photo images of the cross-linked gel polymer electrolytes cured with different amounts of PEGDMA. As the content of PEGDMA increased at intervals of 2.0 wt.%, the electrolyte solution became highly viscous and finally non-fluidic, indicating that PEGDMA with multiple oligo(ethylene oxide) acrylate functional groups effectively induced the thermal cross-linking reaction. Gel polymer electrolytes without liquid flow were obtained at PEGDMA contents greater than 6 wt.%, as shown in Fig. 2-(a). Ionic conductivities of the gel polymer electrolytes after thermal curing were measured as a function of the PEGDMA content, and the results are shown in Fig. 2-(b). The ionic conductivity of the base liquid electrolyte was  $7.0 \times 10^{-3}\text{ S cm}^{-1}$ . The ionic conductivities of the gel polymer electrolytes decreased with increasing PEGDMA content, since the thermal curing with cross-linking agent increased the viscosity of the resulting electrolytes and produced the three-dimensional electrolyte polymer networks. The large decrease in the ionic conductivity with increasing PEGDMA content from 4.0 to 6.0 wt.% can be ascribed to the abrupt reduction of ionic mobility due to the formation of cross-linked polymer electrolytes with high cross-linking density. Because the complete gelation of the liquid electrolyte failed at PEGDMA contents less than 6 wt.%, a gel electrolyte precursor containing 6.0 or 8.0 wt.% PEGDMA was applied to the lithium powder polymer cells. In order to confirm the chemical cross-linking reaction of PEGDMA, FT-IR analysis was carried out

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