



Reversible thixotropic gel electrolytes for safer and shape-versatile lithium-ion batteries

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HIGHLIGHTS

- A new class of gel electrolyte with reversible thixotropic property is demonstrated.
- The gel electrolyte consists of (fluoropolymer/cellulose derivatives) and liquid electrolyte.
- A form factor-free pouch-type cell can also be assembled with the gel electrolyte.

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ABSTRACT

All-solid-state lithium-ion batteries (ASLBs) are receiving considerable attention due to their safety superiority and high energy density (achieved by bipolar configuration). Inorganic solid electrolytes are explored as a key-enabling material of the ASLBs. However, their critical challenges, including grain boundary resistance, interfacial instability with electrode materials and complicated processability, remain yet unresolved. Here, we demonstrate a new class of gel electrolyte with reversible thixotropic transformation and abuse tolerance as an effective and scalable approach to address the aforementioned longstanding issues. The gel electrolyte consists of (fluoropolymer/cellulose derivative) matrix and liquid electrolyte. The reversible thixotropic transformation is realized via sol-gel transition based on Coulombic interaction of the polymer matrix with liquid electrolyte. This unusual rheological feature allows the gel electrolyte to be printed in various forms. In addition, the gel electrolyte shows low crystallinity, thus playing a viable role in delivering high ionic conductivity. Based on understanding of rheological/electrochemical characteristics of the gel electrolyte, we fabricate a form factor-free pouch-type cell assembled with the gel electrolyte using sequential screen-printing process. The resultant cell shows exceptional safety upon exposure to various harsh abuse conditions, along with decent electrochemical performance.

1. Introduction

Lithium-ion batteries (LIBs) have been extensively explored since their successful commercialization in the early 1990s. Based on the ceaseless development of the battery components including electrodes, electrolyte and separator, along with progress of cell assembly process, LIBs have succeeded in achieving the high energy and high power

densities to fulfil stringent requirements of various mobile electronics [1–3]. However, LIBs are now faced with serious safety concerns about unexpected ignition or explosion, which is mainly ascribed to flammable organic liquid electrolytes [4–6]. Especially, considering that newly emerging applications such as wearable electronics and electric vehicles are vulnerable to safety failure, we are in urgent need of non-flammable battery materials. In this regard, all-solid-state lithium-ion

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batteries (ASLBs) in which liquid electrolytes are replaced with inorganic solid electrolytes, have been considered as a promising alternative to address the safety issues [7,8]. It is highly expected that the solid electrolytes are non-flammable and enable the battery system to ultimately operate in the wide range of voltage and temperature minimizing the deterioration of battery performance [9–11]. Furthermore, the use of solid electrolyte can achieve high energy density through efficient space utilization by bipolar stacking of electrode layers and also allow for flexible cell design which lies far beyond typical cylindrical or prismatic forms [12,13].

Until now, a variety of inorganic solid electrolytes such as oxide- or sulfide-based ones, have been investigated for potential use in ASLBs [8]. Although they have shown promising results particularly in ionic conductivity, their intrinsic drawbacks, including relatively low ionic conductivity, poor air-compatibility, narrow electrochemical stability, and so on have been not yet fully resolved [7]. Moreover, the grain boundary resistance arising from the solid-solid interface still remains a critical obstacle to commercialization of ASLBs [14,15]. In this regard, the polymeric or gel electrolytes have continuously attracted much attention as a competent alternative or a complementary material of the inorganic solid electrolytes [14,16]. In particular, the gel electrolyte shows decent ionic conductivity because of liquid-like ion transport mechanism and intimate interfaces with electrode materials due to their mechanical softness and good wettability, which can be suggested as an appealing solid-state electrolyte for realization of the ASLBs [17,18].

For the facile and multi-purpose use of the gel electrolyte, easy fabrication without complex synthesis and development of seamless assembly are indispensably needed. Thus, in comparison to a conventional gel electrolyte wherein the polymer matrix is swelled by injected liquid electrolyte, the gel electrolyte proposed herein, which can be solidified physically or chemically from homogeneous and viscous sol solution, is expected to allow for solution-based processes such as spraying and printing, thereby enabling conformal contact with electrodes. In addition, this gel electrolyte is expected to provide exceptional design flexibility of cells [19]. Therefore, how to simply prepare the sol electrolyte solution and how to easily define the starting point of gelation from sol state are key-enabling technologies for effective utilization of the gel-based solid-state electrolyte.

Herein, we present a new class of gel electrolyte with reversible thixotropic transformation and abuse tolerance to address the aforementioned issues. Salient features of the gel electrolyte include high ionic conductivity of $\sim 10^{-2} \text{ S cm}^{-1}$, design diversity, decent mechanical strength, and facile scalability. Viscous solution obtained from simple blending of polymers and liquid electrolytes shows the gelation behavior within controlled time scale, resulting in a self-standing ion-conductive film. And, this sol-gel transition, called as shear stress-driven thixotropy or shear-thinning behavior with a time interval, can be reversibly controlled by tuning shear stress, which implies the availability of viscosity control for the uniform and conformal coating, irrespective of solution's viscoelastic states. In virtue of this unique rheological behavior, gel electrolytes with desired forms can be successfully realized through various printing techniques. We expect that the thixotropicity originating from the controlled Coulombic interaction (dissociated salt (cationic and anionic) species and polymers) and the high ionic conductivity of this gel electrolyte (comparable with that of liquid electrolyte) might be closely related with the gelation process. Eventually, with this thixotropic gel electrolyte, curved pouch-type LIBs with E, T, R, I-shaped hole are fabricated by sequential screen-printing process, providing reasonable charging/discharging profile and stable cycle performance. Also, the resultant pouch-type cell exhibits stable electrochemical operation even upon exposure to harsh abuse conditions such as distortion, twisting, scission, and even hole-punching.

2. Experimental

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP)

(KynarFlex 2801, Arkema), hydroxypropylcellulose (HPC) ($M_w \sim 80,000$, Aldrich), *N*-methyl-2-pyrrolidone (NMP) (Aldrich), acetone (Aldrich), and lithium electrolyte solution (Enchem Co. Ltd.) of 1.0 M LiPF₆ dissolved in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (3:7 v/v) were used as provided. PVdF-HFP and HPC were mixed in NMP/acetone mixture (1:1 w/w) wherein the weight ratio of PVdF-HFP:HPC:(NMP/acetone) is 7:3:30. After enough stirring using a planetary centrifugal mixer (Thinky, ARE-310), the lithium electrolyte solution (1.0 M LiPF₆ in EC/DMC) was additionally mixed for samples with various blending ratios (0–700 wt% based on the polymer weight added) to yield the sol solution. The above prepared sol solution turned to gel state with elapsed time, but after stirring for several minute, viscous sol solution was again restored. For the stirring process, the planetary centrifugal mixer was used. The stirring was performed at 1500 rpm for 5 mn to obtain viscous sol solution with viscosity of $\sim 20,000$ cP. After that, the stencil printing process was conducted using the customized masks. Also, a planetary centrifugal mixer was used to obtain the uniform dispersion of TiO₂ in gel electrolyte.

The commercially available LiCoO₂ (Umicore, $D_{50} = 10 \mu\text{m}$), Super P carbon black (Timcal), and PVdF (Aldrich) were used. For the fabrication of cathode electrode, the slurry of LiCoO₂, Super P, PVdF (92:4:4 wt%) in NMP/acetone mixture (1:1 v/v) was coated on an Al current collector using doctor blade apparatus. For the anode, the slurry consisting of pitch-coated natural graphite (Carbonix), Super P carbon black (Timcal), and PVdF (Aldrich) (90:5:5 wt%) in the NMP/acetone mixture was coated on a Cu current collector. The electrode was used after thoroughly drying at 120 °C. The fabrication procedures of the pouch-type 5.5 × 5.5 cm² LIB assembled with the stencil-printed gel polymer electrolytes were described in other publication [20].

The Fourier-transform infrared spectroscopy (FT-IR) (Nicolet iS50, Thermo Fisher Scientific Instrument) was used for molecular interaction analysis in gel system. The structural analysis of gel electrolyte was performed by X-ray diffraction (XRD) pattern using an X-ray diffractometer (X'pert Pro, Philips, $\lambda = 1.54,056 \text{ \AA}$) equipped with a Cu target and accumulative detector. The rheological properties were investigated using a rheometer (Haake MARS 3, Thermo Electron GmbH). The microstructural images were obtained from a scanning electron microscopy (SEM) (Hitachi S-4800). Ionic conductivity of the gel electrolytes was determined from complex impedance spectra measured using a frequency response analyzer (Solartron HF 1225 Gain-Phase Analyzer) in the frequency range of 10^{-1} – 10^5 Hz. A conductivity cell (2 cm × 2 cm) comprising two stainless steel electrodes on each side of the gel electrolyte film was used. Temperature dependence data of ionic conductivity were also obtained over the range of -10 °C to 90 °C. Microtensile testing machine (Instron 8848, Instron) was used for measuring the stress-strain response.

3. Results and discussion

To fabricate the gel electrolyte with reversible thixotropicity, polymers (fluoropolymers and cellulose derivatives) were mixed with liquid electrolyte. First, PVdF-HFP and HPC were dissolved in NMP/acetone (1:1 v/v) solvent mixture. And, liquid electrolyte (1.0 M LiPF₆ in EC/DMC 3:7 v/v) was added and stirred to form homogeneous solution (Fig. 1a). Just after blending, this sol solution showed fluidic behavior with an apparent viscosity of $\sim 20,000$ cP. After several hours, the sol turned into a gel with a viscosity of 80,000 cP, revealing the formation of long-range internetwork structure (Fig. 1b and c). It is notable that this sol-gel transition enables the fabrication of a self-standing lithium-conductive film through simple stencil printing technique (Fig. 1b). In addition, the 3D-structured gel electrolytes (e.g., car- or fish-shaped) were fabricated (Fig. 1b). These results suggest that the thixotropic gel electrolyte can be exploited in the development of complex-shaped ionic devices as well as the power sources with various form factors.

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