



# Development of all-solid-state lithium battery using quasi-solidified tetraglyme–lithium bis(trifluoromethanesulfonyl)amide–fumed silica nano-composites as electrolytes



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## HIGHLIGHTS

- ▶ Quasi-solid-state electrolyte containing G<sub>4</sub>/LiTFSA are prepared.
- ▶ Quasi-solid-state electrolyte has solid-like appearances.
- ▶ Quasi-solid-state electrolyte has liquid-like conductivity and diffusivity.
- ▶ All-solid-state cell exhibited noticeable charge–discharge performance.
- ▶ Concentration polarization resistance limited the power density.

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## ABSTRACT

A quasi-solid-state electrolyte consisting of tetraethylene glycol dimethyl ether (tetraglyme, G<sub>4</sub>)/lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) mixtures together with fumed silica nanoparticles was prepared for use as the electrolyte of an all-solid-state lithium rechargeable battery. Via the liquid route, we have succeeded in fabricating a quasi-solid-state electrolyte regardless of the high concentration of G<sub>4</sub>/Li-TFSA such as 75 vol%. It was found that the conductivities, the self-diffusion coefficients and the structure of the G<sub>4</sub>/Li-TFSA complex in the quasi-solid-state composite are essentially similar to those of the bulks regardless of the solid-like appearance. Compared to the quasi-solid-state electrolytes containing the conventional room temperature ionic liquids (RTILs), the ones containing the equimolar G<sub>4</sub>/LiTFSA complex exhibited a higher stability to the lithium electrodes. The all-solid-state lithium rechargeable battery was assembled using LiCoO<sub>2</sub> and lithium metal as the cathode active material and anode, respectively. The all-solid-state cells showed noticeable charge–discharge and cycle performances. In the cut-off voltage range of 4.3–3.4 V, it achieved high initial discharge capacities of 130, 110 and 90 mAh g<sup>-1</sup> at 0.05, 0.1 and 0.2 C, respectively. Even after one hundred charge–discharge cycles, the discharge capacities remained high at 105, 100 and 95 mAh g<sup>-1</sup>, respectively.

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## 1. Introduction

Development of a solid-state electrolyte is one of the key issues for the research and development of the future generation batteries. This is because a class of materials enables the assembly of all-solid-state cells allowing the flexible design of the devices, enhancing both the energy and power densities [1]. However,

among the solid-state electrolytes including both organic and inorganic compounds, the materials having a sufficient lithium ionic conductivity as well as stabilities in the voltage range for the battery operation are limited to a few cases [1–3].

On the other hand, room temperature ionic liquid (RTIL)–Li-salt mixture is recognized as one of the candidate electrolyte materials [4–6]. This is because this class of materials has a high ionic conductivity and wide potential window, low volatility and high stability. Recently, Watanabe's group proposed a new family of electrolytes for the lithium rechargeable battery, i.e., the equimolar complex of triethylene glycol dimethyl ether (triglyme,

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G3) or tetraethylene glycol dimethyl ether (tetraglyme, G4) with Li-salts [7–12]. Based on extensive investigations of the physicochemical properties over a wide range of Li-salt compositions, they revealed whether the equimolar mixtures of glyme and Li-salt behaved as a concentrated solution or ionic liquid solvent depending on the anion species' Lewis basicity. When the lithium salts with a weak Lewis basic, anion such as lithium bis(trifluoromethanesulfonyl)amide (LiTFSA), are mixed with glyme in an equimolar concentration, the mixture forms the equimolar complex, [Li(glyme)]TFSA, and thus behaves like RTILs [11]. They assembled lithium-ion rechargeable cells consisting of LiCoO<sub>2</sub> [7], LiFePO<sub>4</sub> [12] and sulfur [9] as the cathodes, and lithium as the anode, and confirmed excellent charge–discharge and cycle performances.

Another interesting property of the RTIL is the interaction with a second media such as solid surfaces [13–28]. RTIL–Li-salt–oxide mixtures change their states depending on the mixing ratios. For instance, the addition of silica [17–19] and fumed silica nanoparticles [18,24–28] leads to a composite of gels and quasi-solids with increasing the volume ratio of the oxides. By using the quasi-solid-state electrolytes based on RTIL–solid mixtures, various electrochemical devices such as fuel cells, dye-sensitized solar cells, electric double layer capacitors, and lithium-ion rechargeable batteries have been developed to date [26–28]. Recently, we investigated the ion dynamics, the stability and the electrolyte performances of a quasi-solid-state electrolyte containing conventional RTILs, such as 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)amide (EMI-TFSA), *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)amide (DEME-TFSA) and *N*-methyl-*N*-propyl piperidinium bis(trifluoromethanesulfonyl)amide (PP13-TFSA). When LiCoO<sub>2</sub> and lithium are used as the cathode active material and anode, respectively, our all-solid-state lithium rechargeable batteries exhibited good charge–discharge cycle performances [28].

In this study, we fabricated the quasi-solid-state electrolyte using the RTIL-like equimolar G4/LiTFSA complexes and fumed silica nanoparticles for use as the electrolyte of the all-solid-state lithium rechargeable cell. The performance of the quasi-solid-state composite was examined in terms of its ionic conductivity and self-diffusion coefficients. The lithium symmetric cells were assembled to investigate the stabilities of the quasi-solid-state electrolyte to lithium electrodes. The all-solid-state lithium-ion battery was assembled using LiCoO<sub>2</sub> and lithium metal as the cathode and anode, respectively. The charge–discharge characteristics and the cycle performances were also evaluated.

## 2. Experimental

### 2.1. Preparation of specimen

LiTFSA powder (>99%, Kishida Chemical Co., Ltd.) was dissolved into G4 (99%, Sigma–Aldrich Co.) at the desired molar ratios. These were used without further purification, but opened in an argon-filled glove box. The molar ratios of G4 to LiTFSA were 1, 2 and 8. The resultant liquids were further mixed together with fumed silica nanoparticles (390 m<sup>2</sup> g<sup>−1</sup> specific surface area and 7 nm diameter, Sigma–Aldrich Co.) in methanol for at least 3 h. The quasi-solid-state white powder was then obtained by evaporating the methanol on a hot plate at which the temperature was kept at 323 K until the methanol was completely evaporated. Before mixing in methanol, the powder of fumed silica was dried in an oven at the temperature of 333 K for more than several days and then it was quickly transferred to and stored in the argon-filled glove box. A self-standing electrolyte sheet was obtained by further mixing the powder of polytetrafluoroethylene (PTFE, Teflon6-J, Du Pont–Mitsui

Fluorochemicals Co., Ltd.) with the quasi-solid-state powder at 5 wt%. The PTFE powder was used as-received, but stored in the argon-filled glove box. The powders of the quasi-solid-state electrolyte and PTFE were weighed in the desired weight ratios and mixed using an agate mortar and an agate pestle for a few minutes until the mixtures were the self-standing transparent sheets. We also prepared the electrolyte sheets soaked in the individual G4/LiTFSA liquids. The compositions of the resultant quasi-solid-state composite powder, the self-standing electrolyte sheet and soaked in the G4/LiTFSA liquids were denoted as 75 vol% G4/LiTFSA–fumed silica (or composite), 95 wt% (75 vol% G4/LiTFSA–fumed silica)–PTFE (or composite–PTFE) and 95 wt% (75 vol% G4/LiTFSA–fumed silica)–PTFE soaked in the G4/LiTFSA liquids (or composite–PTFE (soaked)), respectively.

### 2.2. Evaluation of viscosity

The viscosity of the G4 and G4/LiTFSA mixtures were evaluated using a viscometer (DV-II+ Pro, Brookfield Engineering, Inc.) with a corn spindle (CPE-40) at 308 K.

### 2.3. Evaluation of conductivity

The electrical conductivities of the G4/LiTFSA and the apparent conductivities of the uniaxially pressed body of 75 vol% G4/LiTFSA–fumed silica with a 400 μm thickness and 10 mm diameter, 95 wt% (75 vol% G4/LiTFSA–fumed silica)–PTFE with a 200 μm thickness and 10 mm diameter, 95 wt% (75 vol% G4/LiTFSA–fumed silica)–PTFE soaked in the G4/LiTFSA liquids with a 200 μm thickness and 10 mm diameter and seven sheets of separators (#3501, Celgard LLC, denoted by separators) of 200 μm thickness and 16 mm diameter were evaluated by the two-probe ac technique. Fig. 1 shows schematic illustrations of the experimental setup and configuration for the electrical conductivity measurements of (a) the bulk and (b) the composite. A quartz tubular type holder, having two compartments, was used in this study. The individual compartment is sealed from ambient gas by O-rings. The inner quartz tube has a gas flow channel to the outer one near the bottom of the holder. A thermocouple with an alumina tube is attached near the specimen. Two potential and current probes, four in total, are inserted into the specimen and connected near the specimen in order to negate the resistance of the lead wire. The Al<sub>2</sub>O<sub>3</sub> tube associated with the thermocouple is connected to the outer quartz tube by springs so that the specimen is always exposed by the mechanical pressure. The quartz holder is placed in a water bath to control the temperature.

The liquids of G4/LiTFSA mixture, i.e., “bulk” specimen, were poured into a quartz vessel of approximately 1.3 cm<sup>3</sup>. The platinum plate electrodes having platinum lead wires were inserted into the sides of the vessel as shown in Fig. 1(a). It was placed in the “lower space” of a quartz tubular type holder. The composite powder was uniaxially pressed at 0.5 ton cm<sup>−2</sup> to a 400 μm in thickness and 10 mm diameter, i.e., the “composite”, was sandwiched between platinum plate electrodes with Al<sub>2</sub>O<sub>3</sub> disc supports and an applied mechanical pressure uniformly from springs. It was then placed in the “upper space” of the quartz tubular type holder. The measurements were conducted in flowing argon at 100 cm<sup>3</sup> min<sup>−1</sup>. The “composite–PTFE” and “composite–PTFE (soaked)”, having 200 μm thickness and 10 mm diameter, were placed in a 2032-type coin cell. The stainless steel case and spacer were used as electrodes. The specimens were connected to an electro-analytical system consisting of a potentiostat/galvanostat and a frequency response analyzer (VersaSTAT-400, Princeton Applied Research). The

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