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Ionic Conductivity and Mechanical Properties of Slide-Ring Gel Swollen with Electrolyte Solution Including Lithium Ions

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ABSTRACT

Polymer gel electrolytes with both high ionic conductivity and mechanical ductility are produced using a slide-ring (SR) gel swollen with an electrolyte solution (ES) composed of propylene carbonate (PC) and lithium salt. The SR gel was derived from polyrotaxane (PR), in which cyclic molecules known as cyclodextrins (CDs) are threaded on the axial polymer chain of polyethylene glycol (PEG) capped by bulky ends, through intermolecular crosslinking between the CDs. The molar conductivity of the SR gel electrolyte with a high swelling ratio and small crosslinking density was more than 95% for pristine ES, and the activation energy and potential window of the SR gel electrolyte was close to that of pristine ES. The compressive properties of the SR gel electrolyte were also investigated; the Young's modulus of the SR gel electrolyte decreased with the crosslinking density and the SR gel electrolyte with a low crosslinking density was not fractured under compression to almost half of the original thickness.

1. Introduction

In the last decade, the characteristics of lithium ion batteries, such as high voltage, high energy density, and long cycle life, have been improved and lithium ion batteries have been used in various applications. Increasing safety requirements has led to the extensive adoption of pseudo-solidified electrolyte solutions (ESs) using polymer matrices. So, pseudo-solidified ESs using polymer matrices with high retention for ESs and thus free from a leakage, and with sufficiently high ionic conductivity have been developed [1–9]. Polyethylene oxide (PEO) [10–18], polypropylene oxide (PPO) [14,15], polyacrylonitrile (PAN) [19–41], polymethyl methacrylate (PMMA) [10,26,34,42–60], and polyvinilidene fluoride-hexafluoropropylene (PVdF-HFP) [10,51,61–80] have been investigated for application as pseudo-solidified ESs using polymer matrices. Polymer gel electrolytes using PEO and PPO, which are chemically cross-linked random copolymers of EO and PO, have room temperature conductivities greater than $10^{-3}\,\mathrm{S\,cm^{-1}}$; however, this is significantly smaller than that of pristine ESs because the polymer gel network disturbs lithium cation transport [81]. In contrast, pseudo-solidified electrolytes that employ PVdF-HFP, PAN or PMMA, which are porous membranes containing an ES, had ionic conductivity greater than $3.0 \times 10^{-3}\,\mathrm{S\,cm^{-1}}$, which is sufficient for commercial use, in addition to good thermal and electrochemical stability. Furthermore, the transport properties of the lithium cations in these pseudo-solidified ESs are similar to that of pristine ESs, so that the ion dynamics are not significantly hindered by the polymer matrix [10,19–81].

On the other hand, polymer gel electrolytes containing a large quantity of ES generally have poor mechanical strength; therefore, it is difficult to achieve both high ionic conductivity and sufficient mechanical strength with these materials. Therefore, considering the exponential spread of lithium ion battery applications such as vehicles and cell phones, polymer gel electrolytes with both high ionic conductivity and high mechanical strength should be rigorously investigated.

This research is directed at the use of the slide-ring (SR) gel reported by Okumura and Ito [82] to achieve polymer gel electrolytes with both high ionic conductivity and mechanical ductility, which is an index of mechanical strength. The SR gel is made from polyrotaxane [83–86] (PR), in which cyclic molecules, cyclodextrins (CDs), are threaded on an axial polyethylene glycol (PEG) polymer chain capped by bulky end groups (Scheme 1(a)), through intermolecular crosslinking between the CDs. The CDs

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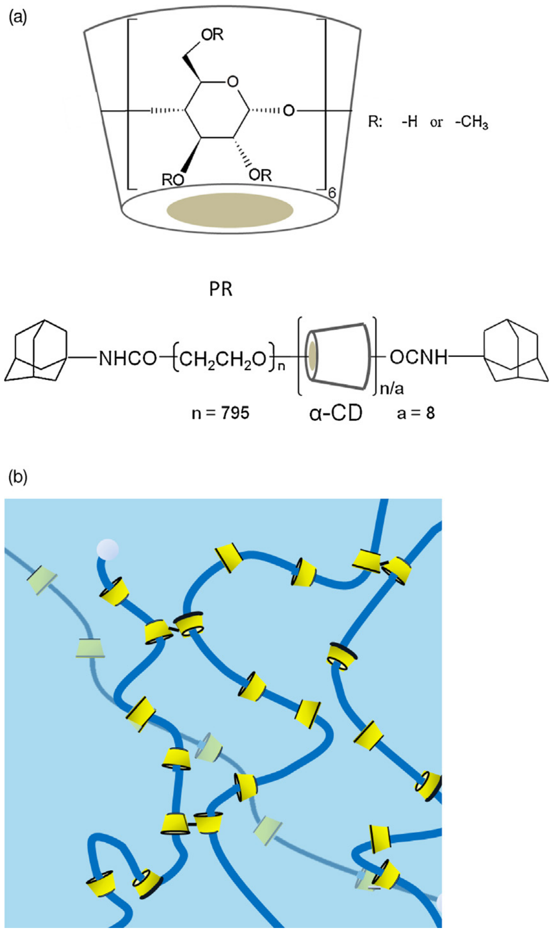

Scheme 1. (a) Structure of CD and PR, (b) Structure of SR-gel.

form mobile cross-linking junctions that slide along the PEG, so that these SR gels exhibit unique characteristics such as unique swelling and mechanical properties [82,87–90] (Scheme 1(b)).

We have recently reported the ionic conductivity of SR gels swollen with ionic liquids (ILs) [91]. The molar conductivity of SR gels swollen with ILs that have a high swelling ratio was more than 92% that of pure IL. SR gels swollen with ILs also have high ionic conductivity. With increasing crosslinking density, the swelling ratio and molar conductivity decreased due to an increase in the disturbance of ion transport by the polymer network [91]. In the present article, we report the ionic conductivity of SR gels containing lithium ES with various crosslinking densities of the SR gel to clarify the ion transport of ES in the SR gel network. Furthermore, we report compressive measurements of SR gels containing lithium ES to investigated the mechanical properties of the SR gel network in lithium ES.

2. Experimental

2.1. Preparation of SR gels

2.1.1. Materials

PR, in which α-CDs are threaded by PEG ($M_w = 35,000$), was purchased from Advanced Softmaterials Co., Ltd. According to the information provided by the manufacturer, the number of α-CD rings included in a single PR molecule is estimated to be ca. 98 from ^{1}H nuclear magnetic resonance spectroscopy (NMR) measurements, which corresponds to a stoichiometric α-CD to ethylene oxide unit ratio in the inclusion complex of 1:8.1 (inclusion ratio = 24.7%). To prepare methylated polyrotaxane (MePR) [92–95], dehydrated dimethyl sulfoxide (DMSO; Wako Pure Chemical Industries, Ltd.), potassium *t*-butoxide (*t*-BuOK; Sigma–Aldrich Co.) in tetrahydrofuran (THF), and iodomethane (Tokyo Chemical Industry Co., Ltd.) were used without further purification. Divinyl sulfone (Tokyo Chemical Industry Co., Ltd.) was used as a crosslinker without further purification. In addition, dehydrated DMSO, dehydrated dimethyl formamide (DMF) and chloroform were used to wash the SR gels. All of these compounds were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

A mixture of liquid propylene carbonate (PC; Wako Pure Chemical Industries, Ltd.) and lithium bis(trifluoromethanesulfonyl) imide (LiTFSI; Tokyo Chemical Industry Co., Ltd.) was used as the ES without further purification.

2.1.2. Preparation of MePR

MePRs were prepared with degrees of substitution (DS) at 27.5 and 74.2%. PR (600 mg, 4.61×10^{-6} mol) was dissolved in dehydrated DMSO (24 mL) under a dry N_2 atmosphere and then 1.0 M solutions of *t*-BuOK (1.62 mL for DS of 27.5%; 5.78 mL for DS of