



Improvement of charge/discharge properties of oligoether electrolytes by zwitterions with an attached cyano group for use in lithium-ion secondary batteries



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ABSTRACT

Zwitterions with a cyano group on the side chain (CZ) were synthesized. Although the addition of CZ caused a slightly negative effect on viscosity, ionic conductivity, limiting current density, and lithium transference number, the oxidation limit of PEGDME/lithium bis(trifluoromethylsulfonyl)amide (LiTfSA) composites was improved to over 5 V. For charge/discharge testing using Li|electrolyte|LiCoO₂ cells, the cycle stability of PEGDME/LiTfSA with CZ in the voltage range of 3.0–4.6 V was much higher than that of PEGDME/LiTfSA. Incorporating a small mole fraction of CZ into PEGDME-based electrolytes prevented an increase in the interface resistance between the electrolyte and cathode with increasing numbers of the cycle.

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1. Introduction

Polymer electrolytes have been vigorously studied for battery applications over the last three decades [1] because they are superior to conventional organic liquid electrolytes in terms of leakage, volatility, and processability. Since poly(ethylene oxide) (PEO) can solubilize alkali metal salts, as a result of the dipole moment of the ether oxygen, and transport ions along the main chain, it is a good candidate for use as a solid polymer electrolyte [2]. Some problems must be addressed before PEO can be utilized as a promising electrolyte material. PEO exhibits a low ionic conductivity (below 10^{-4} S cm⁻¹) at room temperature due to the crystallinity. It also has a cation transference number below 0.4 because of interaction between the cation and ether segments [3,4]. Several researchers attempted to solve these problems by evaluating various PEO derivatives. For example, building comb-like anionic structures and attaching them to the PEO chain is

effective for improving ionic conductivity [5,6] and lithium ion transference number [7,8].

Additives have been actively studied to improve the properties of the PEO matrix. For example, plasticizers [9,10] and inorganic fillers [11,12] have been evaluated as additives that can improve ionic conductivity, lithium ion transference number, and interfacial resistance between the electrode and electrolyte. In recent years, ionic liquids (ILs) have been studied as plasticizers for PEO matrixes [13]. Although the addition of ILs to PEO matrixes improves ionic conductivity, the lithium ion transference number is still low owing to the migration of IL itself along the potential gradient [14].

On the other hand, zwitterions, which have a positive and negative charge in the same molecule, are one of potential electrolyte material additives that can help transport ions effectively [15–17]. Some electrochemical properties of electrolyte materials have been improved by the addition of zwitterions. Tiyapiboonchaiya et al. reported that ionic conductivity was improved by adding zwitterions to a polymer gel electrolyte [18]. Byrne et al. also reported that ionic conductivity was improved by the addition of zwitterions and inorganic nanofillers [19]. The

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addition of zwitterions to ILs led to an increase in the diffusion coefficient of lithium ions, the formation of solid electrolyte interphases (SEIs) on electrodes, and the improvement of coulombic efficiencies for the lithium plating-stripping reaction [20].

Recently, we found that the oxidation limit of poly(ethylene glycol)dimethyl ether (PEGDME)/lithium bis(trifluoromethylsulfonate)amide (LiTFSA) was raised to 5 V by adding a small amount of a zwitterion with an oligoether on the side chain [21]. In general, high-voltage active cathode materials such as LiCoO_2 and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [22–24] cannot be applied to lithium-ion batteries with PEO-based electrolytes because the oxidation limit of the PEO chains is $\sim 4\text{ V}$ [25–27]. Zwitterions are interesting alternative additives for PEO-based electrolytes. In this study, we focused on zwitterions with cyano groups that showed a dissociation effect for lithium salts due to its interaction with cations [28]. It is also known that the introduction of a cyano group into an IL structure leads to the formation of SEIs on electrodes [29]. According to the knowledge, zwitterions with cyano groups would improve the electrochemical and charge-discharge properties of oligoethers. We synthesized a novel zwitterion with a cyano group on the side chain, and added the zwitterion to an oligoether, poly(ethylene glycol) dimethyl ether (PEGDME), matrix as model compounds for polymer electrolyte to investigate the effect of the zwitterion and cyano group on the electrochemical properties of PEGDME-based electrolytes.

2. Experimental

2.1. Materials

Poly(ethylene glycol)dimethyl ether (PEGDME) ($M_n = 1000\text{ g mol}^{-1}$) and 1-(2-hydroxyethyl)imidazole (97.0%) were purchased from Sigma-Aldrich. PEGDME was dried at 60°C *in vacuo* before use. Potassium hydroxide (86.0%) and acrylonitrile (99.0%) were purchased from Kanto Chemical Co., Inc. Propanesultone ($>99.0\%$) was purchased from Tokyo Chemical Industry Co., Ltd. and was distilled *in vacuo* before use. Dehydrated acetonitrile was purchased from Wako Pure Chemical Industries, Ltd. 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonate)amide ([C₂mim][TFSA]) (99.0%) was purchased from Iolitec GmbH and was dried *in vacuo* at 60°C before use. Lithium bis(trifluoromethylsulfonate)amide (LiTFSA) (99.8%) was purchased from Kishida Chemical Co., Ltd. and was dried at 120°C *in vacuo* before use. Li foils (thickness: 0.4 mm, diameter: 16 mm) were purchased from Honjo Metal Co., Ltd. Poly(vinylidene difluoride) (PVDF) (#1120) was purchased from Kureha Battery Materials Japan Co., Ltd. Acetylene black was purchased from Denki Kagaku Kogyo Co., Ltd. Lithium cobalt oxide (average particle diameter: $1.02\ \mu\text{m}$) was purchased from Kusaka Rare Metal Ltd.

2.2. Synthesis of 3-(2-(1H-imidazol-1-yl)ethoxy)propanenitrile

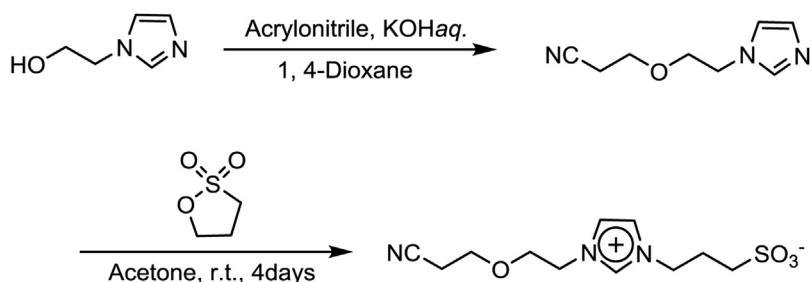
3-(2-(1H-imidazol-1-yl)ethoxy)propanenitrile was synthesized using a previously published procedure [30]. 2-(1H-imidazol-1-yl)ethanol (5.00 g, 44.6 mmol) and 25 wt% KOH(aq) (1.25 mL) were added into 1,4-dioxane (5 mL). Then, acrylonitrile (2.60 g, 49.1 mmol) was added dropwise to the solution over 30 min. The solution was stirred at room temperature for 24 h. The solvent and acrylonitrile were removed by using a rotary evaporator. The residual liquid was dissolved in chloroform, and the chloroform solution was washed with water and saturated aqueous NaCl. Then, the organic layer was dried over MgSO_4 . The solvent was removed by a rotary evaporator, and the residue was purified by column chromatography (aluminium oxide, activated (Kanto Chemical Co., Inc.)) (eluent: chloroform/methanol (v/v)=50/1). The product obtained was colorless liquid (3.10 g, 18.8 mmol, 42%). $^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 2.57\text{--}2.59$ (t, $J = 6.2\text{ Hz}$, 2H), $3.62\text{--}3.64$ (t, $J = 6.3\text{ Hz}$, 2H), $3.74\text{--}3.77$ (t, $J = 5.1\text{ Hz}$, 2H), $4.13\text{--}4.15$ (t, $J = 5.1\text{ Hz}$, 2H), 7.00 (m, 1H), 7.04 (m, 1H), 7.52 (s, 1H). $^{13}\text{C NMR}$ (CDCl_3 , 500 MHz): δ (ppm) = 18.84, 46.90, 65.83, 70.58, 117.64, 119.47, 129.26, 137.44.

2.3. Synthesis of 3-(1-(2-(2-cyanoethoxy)ethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (CZ)

3-(1-(2-(2-cyanoethoxy)ethyl)-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (CZ) was synthesized using a previously published procedure [15]. 3-(2-(1H-imidazol-1-yl)ethoxy)propanenitrile (9.92 g, 60.1 mmol) was dissolved in acetone (25 mL). An equimolar amount of propanesultone (7.33 g, 60.1 mmol) was added dropwise into the solution over 30 min. The supernatant was then removed by decantation. The residue was dissolved in methanol. Then, acetone was added into the solution, and the precipitate was collected by filtration. A colorless crystal product was obtained (13.5 g, 46.8 mmol, 78%) (Scheme 1). $^1\text{H NMR}$ (D_2O , 500 MHz): $\delta = 2.28\text{--}2.33$ (quin, $J = 7.3\text{ Hz}$, 2H), $2.71\text{--}2.73$ (t, $J = 5.9\text{ Hz}$, 2H), $2.88\text{--}2.91$ (t, $J = 7.4\text{ Hz}$, 2H), $3.71\text{--}3.74$ (t, $J = 5.85\text{ Hz}$, 2H), $3.89\text{--}3.91$ (t, $J = 4.8\text{ Hz}$, 2H), $4.34\text{--}4.37$ (t, $J = 7.1\text{ Hz}$, 2H), $4.40\text{--}4.42$ (t, $J = 4.8\text{ Hz}$, 2H), 7.55 (s, 2H). $^{13}\text{C NMR}$ (D_2O , 500 MHz): δ (ppm) = 18.21, 25.07, 47.24, 49.90, 49.24, 65.36, 68.31, 119.87, 122.36, 122.97. Analytical calculations for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}_4\text{S}$ (%): C, 45.98; H, 5.96; N, 14.62; S, 11.16; experimentally produced product (%): C, 46.04; H, 5.95; N, 14.65; S, 11.23.

2.4. Preparation of composites

A given amount of PEGDME, LiTFSA, and CZ was dissolved in dehydrated acetonitrile, and these mixtures were stirred at r.t. for 24 h. Then, the solvent was removed by using a rotary evaporator. The residue was dried *in vacuo* at 60°C . The molar ratio of ethylene oxide unit to the lithium salt was fixed at 8. PEGDME/LiTFSA/CZ(x)



Scheme 1. Synthesis of CZ.

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