



Gel polymer electrolyte for lithium-ion batteries comprising cyclic carbonate moieties



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HIGHLIGHTS

- Synthesis of a new polymer matrix comprising cyclic carbonate moieties.
- Polymer matrix is able to retain huge amounts of liquid electrolyte.
- Gel polymer electrolyte displays high conductivity and good mechanical stability.
- Gel polymer electrolyte shows good performance in NCM/graphite full cells.

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ABSTRACT

A polymer system based on oligo (ethylene glycol) methyl ether methacrylate (OEGMA) and cyclic carbonate methacrylate (CCMA) was chosen as matrix to realize high-performance gel polymer electrolytes due to the fact that both monomers are able to interact with the liquid electrolyte, thus, retaining it inside the matrix. Additionally, OEGMA enables high flexibility, while CCMA provides mechanical stability. The polymer displays a high thermal stability up to 200 °C and a glass transition temperature below room temperature (5 °C) allowing an easy handling of the obtained films. By immobilizing the liquid electrolyte 1 M LiPF₆ in EC:DMC 1:1 w:w in the polymer host a gel polymer electrolyte with a high conductivity of 2.3 mS cm⁻¹ at 25 °C and a stable cycling behavior with high capacities and efficiencies in Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O₂ (NCM)/graphite full cells is obtained. The investigated gel polymer electrolyte is identified as promising electrolyte for lithium-ion batteries, because it combines good electrochemical properties comparable to that of liquid electrolytes with the safety advantage that no leakage of the flammable electrolyte solvents can occur.

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1. Introduction

Lithium-ion batteries – characterized by their high discharge voltage of about 3–4 V and their unbeatable specific energy of 150 Wh kg⁻¹ – are already the favored battery system for the portable market [1,2]. Moreover they have succeeded in entering the sustainable vehicle market [3]. Despite the unique features they offer, lithium-ion batteries have not yet reached the technological level needed for a large-scale commercialization for electric and hybrid-electric vehicles. Recent studies focus on the improvement of energy density and safety, which comes along with the development of materials for the various battery components [4]. While the electrode material stands out due to high capacity and

durability, the electrolyte needs to have a high ionic conductivity at a broad temperature range of use [5]. Furthermore, properties like a wide electrochemical stability window and environmental friendliness are indispensable for future developments.

Commercial lithium-ion battery electrolytes usually contain a lithium salt, typically LiPF₆, which is dissolved in mixtures of cyclic and linear carbonates as solvents [6,7]. Despite the positive features like high conductivity and stability in a wide temperature range, these electrolytes show some issues, especially concerning large-scale applications for electromobility and stationary energy storage.

Using liquid electrolytes leads to safety hazards such as fire and explosion, which can be caused by leakage of liquid electrolyte comprising highly flammable linear carbonates as solvent [8]. Solid polymer electrolytes, which consist of a polymer (e.g. polyethylene oxide) in which a lithium salt is dissolved, would be an ideal candidate to make batteries safer, but this advantage goes along with a considerably reduced conductivity [9]. To combine the

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positive properties of liquid and solid polymer electrolytes, gel polymer electrolytes have been introduced. They consist of a liquid electrolyte, which is immobilized in a polymer matrix. Therefore, leakage can be avoided [10]. Recently, our group reported on the preparation of statistical co-polymer membranes via UV-induced free radical polymerization comprising oligo (ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) as monomers. Due to its ethylene glycol side chains, OEGMA is able to interact with the liquid electrolyte [11], whereas BnMA was used to enhance the mechanical stability of the gel polymer electrolyte. Gel polymer electrolytes based on this co-polymer showed promising performances in lithium-ion batteries as well as in high power devices [12,13].

In this paper a polymer host based on OEGMA and cyclic carbonate methacrylate (CCMA) is synthesized and gelled using the state-of-the-art liquid electrolyte 1 M LiPF₆ in ethylene carbonate (EC):dimethyl carbonate (DMC) 1:1. CCMA was chosen as monomer as it displays a similar structure like the solvents of the liquid electrolyte. Therefore, it is assumed that CCMA is able to interact with the liquid electrolyte, which would be beneficial for the liquid electrolyte uptake capacity as well as for the ability to retain the liquid electrolyte inside the polymer matrix. Apart from thermal and electrochemical investigations of the gel polymer electrolyte, the applicability in lithium-ion batteries is evaluated.

2. Experimental

2.1. Chemicals

Glycerol 1,2-carbonate ($\geq 90\%$) was obtained from TCI, triethylamine ($\geq 99.6\%$), ethyl acetate (EtOAc, 99%) and pentane ($\geq 99\%$) from VWR International and methacryloyl chloride ($\geq 95\%$) and benzophenone (BNP, $\geq 99\%$) from Acros Organics. Butylated hydroxytoluene (BHT, $\geq 99\%$) was purchased from Fluka and oligo (ethylene glycol) methyl ether methacrylate ($M_n = 300 \text{ g mol}^{-1}$) from Sigma–Aldrich.

2.2. Monomer synthesis

Cyclic carbonate methacrylate (CCMA) was synthesized according to a slightly modified method described by Kilambi et al. (see Scheme 1) [14]. Glycerol 1,2-carbonate (3.54 g, 0.030 mol, 1.00 eq.), triethylamine (4.44 mL, 0.032 mol, 1.07 eq.) and EtOAc (30 mL) were introduced into a three-neck flask, which was constantly purged with argon. To maintain the reaction temperature at a low level, the flask was immersed in an ice-water bath. The dropping funnel was charged with methacryloyl chloride (2.71 mL, 0.028 mol, 0.93 eq.) in ethyl acetate (5 mL) and the solution was added dropwise within two hours. Afterward, the reaction mixture was stirred over night at RT. For purification the reaction mixture was filtered, washed several times with NaHCO₃ solution (sat.), 1 wt % -HCl solution and NaCl solution (sat.) and dried over Na₂SO₄. After the gentle removal of the solvent using a rotary evaporator, the crude product was purified by column chromatography starting with pentane:EtOAc 3:1 and increasing to 0:1. After freeze-drying a yellowish, very viscous liquid was obtained as the final product (76%). Due to the highly reactive nature of CCMA all used solutions

and solvents were kept cool and BHT was added to inhibit polymerization during purification. The final product was stored in a freezer.

MS: calculated: 186.16 g mol⁻¹, found: 209.0425 [M + Na⁺], 395.0950 [2M + Na⁺].

¹H NMR (400 MHz, CDCl₃) [ppm] $\delta = 6.17$ (s, 1H, C=CH₂), 5.68 (s, 1H, C=CH₂), 5.01 (m, 1H, CH), 4.61 (t, 1H, CH₂ cyclic carbonate), 4.44 (m, 1H, CH₂ cyclic carbonate), 4.36 (m, 2H, CH₂-O), 1.97 (s, 3H, CH₃); ¹³C NMR (101 MHz, CDCl₃) [ppm] $\delta = 166.62$ (C=O methacrylate), 154.38 (C=O cyclic carbonate), 135.12 (C=CH₂), 127.29 (CH₂=C), 73.79 (CH cyclic carbonate), 66.05 (CH₂-O), 63.42 (CH₂ cyclic carbonate), 18.14 (CH₃). ATR-IR [cm⁻¹]: 2959 (s, CH₃, CH₂), 1792 (w, C=O cyclic carbonate), 1718 (m, C=O), 1640 (m, C=C), 1296 (w, ester), 1060 (w, ester), 811 (m, C=CH₂), 712 (m, C=CH₂).

2.3. Polymer synthesis

The polymers were prepared by mixing CCMA and 0.2 wt% BNP for the CCMA-homopolymer and OEGMA and CCMA in different molar ratios and 0.2 wt% BNP for the co-polymers, respectively. The well-stirred mixtures were then drawn into a film by coating a certain amount between two quartz glass plates using Mylar[®] foil type A (DU PONT FILMS) and a spacer to obtain a constant thickness of about 300 μm . The polymerization was performed using UV-light (UVACUBE 100, Hoenle) for one hour. After polymerization the films were dried in a glass oven (BÜCHI Labortechnik) under reduced pressure at 120 °C over night.

2.4. Gel polymer electrolyte preparation

Gel polymer electrolytes were prepared by gelling polymer disks with diameters of 7–10 mm with appropriate amounts of liquid electrolyte (1 M LiPF₆ in EC:DMC 1:1 w:w, LP30, Merck, battery grade, conductivity: 10.7 mS cm⁻¹ [7]) to obtain a polymer:liquid electrolyte ratio of 1:5.5 corresponding to a composition of 15 wt% polymer and 85 wt% liquid electrolyte. To ensure complete soaking all disks were allowed to gel in sealed glass vessels for at least 24 h.

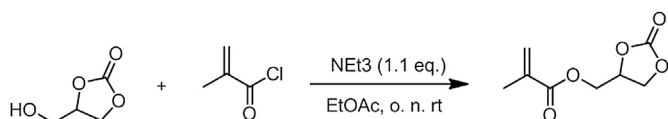
2.5. Thermal characterization

For Thermogravimetric Analysis (TGA) of the synthesized polymers and gel polymer electrolyte, a TGA Q5000 (TA Instruments) was used. Each sample was heated from room temperature to 600 °C with a heating rate of 5 K min⁻¹.

DSC measurements were carried out using a DSC Q2000 (TA Instruments). 10 mg of the polymer was put in a closed aluminum can. The sample was cooled from room temperature to -150 °C followed by an increase in temperature up to 120 °C with a heating rate of 10 K min⁻¹ in a nitrogen atmosphere. Three cooling and heating cycles were conducted for every sample.

2.6. Electrochemical characterization

The conductivity of the gel polymer electrolytes was investigated in a sealed lab-made cell employing two stainless steel electrodes with a distance of 600 μm , which was assembled in an argon filled glove-box (MBraun, O₂ and H₂O content lower than 1 ppm). The temperature dependent conductivity of the gel polymer electrolyte between 5 °C and 55 °C was measured using a Solartron 1260 impedance analyzer, which was connected to a Solartron 1287A potentiostat/galvanostat and an environmental simulation chamber (MK 53, Binder GmbH). All measurements were performed in a frequency range of 10 Hz to 10 MHz with a voltage amplitude of 5 mV. The given conductivities are an average of three measurements.



Scheme 1. Synthesis of the monomer cyclic carbonate methacrylate (CCMA).

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