



## Short communication

## Methacrylate based gel polymer electrolyte for lithium-ion batteries

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## H I G H L I G H T S

- ▶ Methacrylate based gel polymer electrolytes as promising electrolyte for lithium-ion batteries.
- ▶ Methacrylate based gel polymer electrolytes display high conductivity and good mechanical stability.
- ▶ Methacrylate based gel polymer electrolytes allow performance comparable to that obtained using conventional electrolytes.

## A R T I C L E I N F O

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## A B S T R A C T

A methacrylate based gel polymer electrolyte (GPE) was prepared and electrochemically investigated. The polymer was synthesized as a statistical co-polymer of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) by free radical polymerization. The ethylene glycol side chain of OEGMA should be able to interact with the liquid electrolyte, thus keeping it inside the GPE, whereas BnMA was used to enhance the mechanical stability of the GPE. Such a polymer was able to retain liquid electrolyte up to 400% of its own weight, while the mechanical stability of the GPE was still high enough to be used as separator in lithium-ion batteries. The GPE displayed a conductivity of  $1.8 \text{ mS cm}^{-1}$  at  $25^\circ\text{C}$  and an electrochemical stability window comparable to that of a standard liquid electrolyte. When used in lithium-ion batteries, such a GPE allowed a performance comparable to that obtained using conventional liquid electrolytes. Therefore the reported electrolyte was identified as a promising candidate as electrolyte for lithium-ion batteries.

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## 1. Introduction

Today's main applications of lithium-ion batteries are in portable electronic devices. Recently, they have been also considered for application in transportation [1], such as electric vehicles (EVs) or hybrid electric vehicles (HEVs), and for stationary energy storage systems [2,3].

In state of the art lithium-ion batteries usually liquid electrolytes consisting of a lithium salt (e.g.  $\text{LiPF}_6$ ) dissolved in a mixture of organic carbonates are used [4,5], which display a low boiling point and flash point and are prone to leakage. Moreover, this hazardous potential increases with increasing battery size. To avoid the risk of electrolyte leakage solid polymer electrolytes (SPEs), which consist of a lithium salt dissolved in a polymer matrix, have been developed. Among these electrolytes, the ones based on poly(ethylene oxide) (PEO) have been widely investigated and showed the best properties. [6] These electrolyte systems enable the construction of

light-weighted and flexible all-solid-state batteries in various forms and shapes [7]. Additionally, the costs for the separator can be saved, as the mechanical stability of SPEs is high enough to avoid electronic contact between the anode and cathode. Unfortunately, SPEs suffer from low conductivity at ambient temperatures (in the range of  $10^{-6}$  to  $10^{-4} \text{ S cm}^{-1}$ ) which limits their application to higher temperatures [8,9]. Beside their low conductivity, also the oxidative stability of PEO has been reported to be only 3.8 V vs.  $\text{Li/Li}^+$  which limits the cathodes that can be used with these electrolytes to those operating at 3 V [10].

To combine the advantage of liquid electrolytes (high ionic conductivity) with those of SPEs (no separator needed, avoiding cell leakage) GPEs have been introduced [11]. In these systems a liquid electrolyte is immobilized into a polymer matrix. Therefore, high conductivities can be achieved, while the mechanical stability of the system remains high enough to be used as separator in lithium-ion batteries. Different polymers have been investigated as host systems, e.g. poly(methyl methacrylate), poly(acrylonitrile), poly(vinylidene fluoride) or co-polymers of these systems [12–17].

Among the many polymers investigated in this context methacrylate based systems have the advantage of wide availability, low

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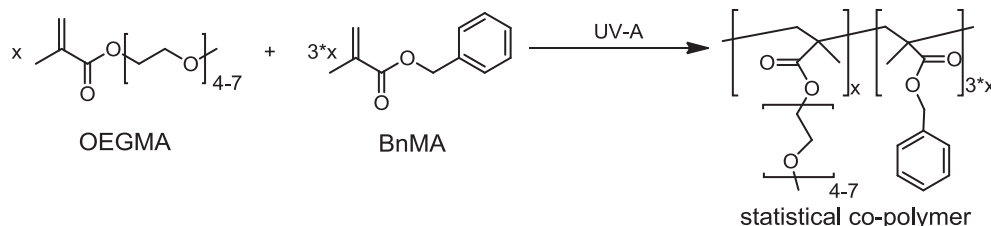


Fig. 1. Polymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) by UV light.

toxicity and good electrochemical stability [18,19]. Additionally, polymethacrylates can be synthesized by irradiation with UV-light, which is a fast and cheap synthesis method. Recently, methacrylate based polymer membranes containing ethylene oxide side chains have attracted some attention [20–22]. These systems display high conductivities and good electrochemical stabilities. However, the applicability of these polymer membranes has just been shown in lithium metal systems in combination with lithium iron phosphate (LFP) as cathode material up to a potential of 4.0 V.

In this paper we report on the preparation, electrochemical characterization and application of GPEs with high ionic conductivity and good mechanical stability. The polymer matrix of this GPE was synthesized by UV-induced photopolymerization of two different methacrylate monomers, oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and benzyl methacrylate (BnMA) (Fig. 1). OEGMA was chosen because the ethylene glycol side chains should be able to interact with the liquid electrolyte, thus keeping it inside the polymer avoiding cell leakage. On the other hand, BnMA was used to enhance the mechanical stability of the GPE. The polymer membranes obtained by this method are able to retain liquid electrolyte up to 400% of its own weight, while the mechanical stability of the obtained GPE is still high enough to be used as separator in lithium-ion batteries. The applicability of this electrolyte was proven in LFP/graphite and  $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$  (NCM)/graphite full cells.

## 2. Experimental

### 2.1. Polymer synthesis

In Fig. 1 the reaction equation of the considered synthesis is shown.

The monomers OEGMA (Sigma–Aldrich, average  $M_n = 300$ ) and BnMA (Sigma–Aldrich, 96%) were mixed in a molar ratio of 1:3. 0.2 wt% of the radical starter benzophenone (Acros Organics, 99%) were dissolved in the solution and the reaction mixture was polymerized by irradiation with UV light (UVACUBE 100, Hoenle AG) for 1 h. During irradiation, the mixture was placed between two Mylar foils and a constant film thickness of 300 or 600  $\mu\text{m}$  was adjusted. After polymerization the membranes were dried over night in a glass oven (Büchi Labortechnik AG) at 120 °C under vacuum.

After punching out polymer discs with a diameter of 7–10 mm the polymer membranes were gelled with 1 M  $\text{LiPF}_6$  in EC:DMC 1:1 (LP30 Merck, battery grade) by adding an appropriate amount of electrolyte to the polymer. The electrolyte was soaked into the polymer over night in sealed glass vessels. Polymer:liquid electrolyte ratios ranging from 60 wt% polymer content and 40 wt% liquid electrolyte up to 20 wt% polymer content and 80 wt% liquid electrolyte have been investigated.

### 2.2. Electrochemical characterization

The conductivity of the GPEs was investigated in a sealed cell between two stainless steel electrodes with a distance of 300  $\mu\text{m}$ .

Electrode preparation and assembling of the cell was carried out in an argon filled glove box (MBraun,  $\text{O}_2$  and  $\text{H}_2\text{O}$  content lower than 1 ppm). The influence of the polymer:liquid electrolyte ratio was determined at 25 °C. The temperature dependant conductivity between 5 °C and 55 °C was investigated for a composition of 20 wt% polymer:80 wt% liquid electrolyte in an environmental simulation chamber (MK 53, Binder GmbH). All conductivity measurements have been performed using a Solartron 1260 impedance analyzer, connected to a Solartron 1287A potentiostat/galvanostat, in a frequency range from 1 MHz to 10 Hz.

All tests with active materials were performed in three-electrode cells (Swagelok) with lithium as reference electrode to monitor the electrode potentials. For electrochemical stability measurements a GPE consisting of 20 wt% polymer and 80 wt% liquid electrolyte was placed between a lithium counter (12 mm diameter) and a Pt working electrode (1 mm diameter) inside a Swagelok cell with lithium as reference electrode. The stability was determined by cyclic voltammetry using a Solartron 1287 potentiostat with a scan rate of 1  $\text{mV s}^{-1}$  in a potential range from open circuit potential (OCP) to 6.5 V vs.  $\text{Li/Li}^+$  for the anodic sweep (=oxidation) and from OCP to 0.1 V vs.  $\text{Li/Li}^+$  for the cathodic sweep (=reduction).

For constant current charge/discharge cycling, anodes and cathodes of the same capacity have been chosen, whereas for cyclic voltammetry experiments the capacity of the working electrode was only 70% of the counter electrode capacity to ensure that the current is not limited by the counter electrode. In order to ensure an optimal contact between the particles of the electrode and the GPE, the electrodes were pre-wetted with liquid electrolyte. After the cells were connected to a battery tester Series 4000 from MACCOR, Inc. they were allowed to rest for 6 h before the constant current cycling started. LFP/graphite cells were cycled in a voltage range between 2.8 and 4.1 V. Herein 1C corresponded to current density of 0.4–0.6  $\text{mA cm}^{-2}$ . For NCM/graphite full cells the voltage range was between 2.8 and 4.2 V and 1C corresponded to a current density of 1.75  $\text{mA cm}^{-2}$ . Cyclic voltammetry measurements on LFP and graphite working electrodes were performed using a scan rate of 50 and 30  $\text{mV s}^{-1}$ , respectively.

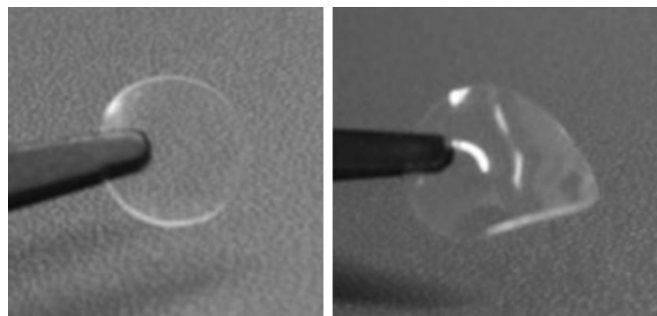


Fig. 2. Photographs of the polymer membranes before and after gelling.

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