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Semi-interpenetrating polymer network of poly(methyl methacrylate) and ether-modified polysiloxane

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ABSTRACT

Solid polymer electrolyte membranes are prepared as *semi*-interpenetrating networks (*semi*-IPN) by solution casting technique composed of poly(methyl methacrylate) (PMMA) as polymeric host matrix, polysiloxane-*comb*-propyloxymethoxytriglycol (PSx) as ion conducting component and lithium bis(trifluoromethane)sulfonimide (LiTFSI) as conducting salt. The resulting *semi*-IPN (*net*-poly(methyl methacrylate))-*sipn*-(polysiloxane-*comb*-propyloxymethoxytriglycol), is investigated using differential scanning calorimetry (DSC), Fourier transform infrared (FTIR) spectroscopy and impedance spectroscopy (IS). DSC measurements show two glass transitions ($T_{g\text{-PSx}}$, $T_{g\text{-PMMA}}$) indicating an independent coexistence of the PMMA host matrix and the PSx conducting component. FTIR spectroscopy reveals interactions between Li^+ ions and the ether-functionality of PSx, whereas PMMA does not interact with the Li^+. In order to distinguish PMMA and PSx contributions to the ionic transport, the effective ionic conductivity of PSx was calculated. The ionic conductivity of the *semi*-IPN is 3.1×10^{-6} S cm^{-1} at room temperature.

1. Introduction

Secondary lithium ion batteries containing polymer electrolytes have received considerable attention in lithium battery development [1–4]. Polymer electrolytes represent a promising alternative to commercially used liquid electrolytes due to higher thermal decomposition temperatures and reduced flammability [2]. Different classes of polymer electrolytes like solid polymer electrolytes [5], gel polymer electrolytes [6,7] and hybrid electrolytes containing inorganic fillers such as Al_2O_3 [8], TiO_2 [9] or SiO_2 [10,11] have already been reported in numerous reviews. Requirements for polymer electrolytes in lithium batteries are good mechanical stability and high lithium ion conductivities [1,12]. Hybrid electrolytes and solid polymer electrolytes attract particular attention due to their compatibility to lithium metal anodes and thus reduced the formation of dendrites [6]. Furthermore, by adding nanocomposite materials to polymer host matrices a hybrid inorganic–organic system is formed which enhances the ionic conductivity and provides simultaneously mechanical, thermal and chemical stabilities [9,13–16].

A further approach to fulfill such requirements is by combining two polymers with different functions into a single network in order to form an interpenetrating network (IPN) [17–19]. A chemical or physical cross-linked polymeric host system such as poly(vinylpyrrolidone) (PVP) [20], poly(vinyl chloride) (PVC) [21] or poly(methyl methacrylate) (PMMA) [22] provides a three dimensional network with large free volume and high mechanical stability. It can act as a component for dissolving another polymeric component at the same time, provides and enhances the ion mobility of dissolved salts. Poly(ethylene oxide) (PEO) is most often used as ion dissolving and conducting polymer component, so far [22,23]. However, ether-modified polysiloxanes can reach much higher ionic conductivities at temperatures below 60 °C as compared to PEO itself due to higher segmental mobility caused by the flexibility of the Si–O–Si backbone and very low glass transition temperature [24,25]. Furthermore, poly(methylhydrosiloxane) (PMHS) 1 as a precursor polymer can be easily modified with various side chains by substitution or addition reactions in order to enhance salt solubility and ion mobility [25,26].

Here, we report a novel heterogeneous *semi*-IPN composed of PMMA as a polymeric host system and the ether-modified polysiloxane-*comb*-propyloxymethoxytriglycol (PSx) as an embedded ion conducting component, (*net*-PMMA)-*sipn*-PSx and lithium bis(trifluoromethane)sulfonimide (LiTFSI) for usage as polymer electrolyte membrane in lithium ion batteries. The distribution of PSx was examined by scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX). Interactions between the *semi*-IPN and Li^+ were investigated by Fourier transform infrared (FTIR) spectroscopy. The thermal stability was analyzed by differential scanning calorimetry (DSC). Moreover, the ionic conductivity of the polymer membranes was examined by impedance spectroscopy (IS). In order to increase the understanding of intermolecular interactions in the *semi*-IPN systems (*net*-PMMA)-*sipn*-PSx-LiTFSI, mixtures of PMMA/LiTFSI, PSx/LiTFSI were also investigated to distinguish the

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different contributions of each component to the overall performance of the *semi*-IPN.

2. Experimental

2.1. Experimental procedures

Semi-IPNs consisting of PMMA (Aldrich) as host network, PSx as an intercalating conducting component and LiTFSI (Aldrich) as conducting salt were investigated. Triethyleneglycolallylmethylether **2** was synthesized according to literature [27] and applied as a grafted side chain to the polysiloxane backbone (Fig. 1). The platinum-catalyzed functionalization of **1** was made via the well-known hydrosilylation [28].

Membranes have been prepared by solution casting technique using tetrahydrofuran (THF) as solvent. Since PSx is a macromolecular liquid, the composition of (*net*-PMMA)-*sipn*-PSx membranes was first optimized with regard to the PSx content to obtain a good mechanical stability and ionic conductivity of the resulting polymer electrolyte membranes. Furthermore, the LiTFSI concentration was varied. In general, 0.8 mL of a cast solution consisting of PMMA/PSx (0.5 g), LiTFSI and THF (2.5 mL) was poured into a petri dish (0.4 cm diameter). After evaporation of THF at 40 °C under vacuum (10^{-2} mbar) for 5 h, the resulting membranes were dried at 60 °C in high vacuum (10^{-5} mbar) for additional 3 days.

2.2. Characterization methods

SEM-EDX measurements were carried out in order to investigate the distribution of PSx in the *semi*-IPN. The dried membranes were sputter coated with carbon at a pressure of 4×10^{-5} bar and analyzed with SEM (JSM-6510, JEOL, Germany).

Glass transition temperatures (T_g) of the samples have been determined by DSC (NETZSCH DSC 204) measurements using NETSCH software (v6.1.0). All samples were sealed into an aluminum can and analyzed in a temperature range of −100 to 150 °C with 10 °C/min heating rate and a three cycle mode. For interpretations the third cycle was used.

FTIR technique (IR-21 Prestige, Shimadzu, Japan) was carried out using transmission mode from $\tilde{\upsilon} = 400$ to $4700\ \text{cm}^{-1}$. The spectral resolution was set to $4\ \text{cm}^{-1}$, and 80 scans per sample were recorded and averaged to obtain a single spectrum. Evaluation was made using IRsolution software (Shimadzu, v1.50). FTIR spectra were baseline corrected using a multi-point approach; the vibrational mode with the highest absorbance was normalized to 1 absorbance unit whereupon the baseline was corrected once again using a two-point approach for visual improvement only. For PMMA containing systems the C═O vibrational mode ($\tilde{\upsilon} = 1729\ \text{cm}^{-1}$) was used for normalization, and for PSx C–O–C vibrations at $\tilde{\upsilon} = 1109\ \text{cm}^{-1}$. In some cases, traces of physisorbed moisture were detected due to the preparation of samples in air atmosphere.

Ionic transport properties of polymer membranes were determined by IS in a measurement setup of a combined multiplexer instrument (Agilent Technologies E5250A) with two matrix switches (E5252A 10 × 12). Preparation of impedance cells was carried out in a dry room (Munters GmbH, Germany) at a temperature of 21 °C. The dew point inside the dry room was measured to be −62 °C (±2 °C, H_2O: 5–10 ppm). The samples were measured in an inert gas atmosphere between two stainless steel electrodes in a temperature range from 90 to −20 °C at an alternating voltage of 40 mV over a frequency range of 20 Hz to 1.7 MHz. The data was recorded using ZPlot and analyzed with ZView v3.1c (Scribner Associates, Inc.).

3. Results and discussion

3.1. SEM analysis

In order to investigate the miscibility of PSx in a PMMA host system, SEM-EDX analyses were conducted. Fig. 2 displays a membrane with 40 wt.% PMMA and 60 wt.% PSx. The distribution of silicon from the Si–O-backbone of PSx is highlighted in red and indicates an inhomogeneous structure of (*net*-PMMA)-*sipn*-PSx.

3.2. DSC analysis

In Table 1 glass transition temperatures obtained from DSC measurements are summarized for pure PMMA electrolyte membranes, pure PSx liquid electrolytes and for (*net*-PMMA)-*sipn*-PSx, as well as for (*net*-PMMA)-*sipn*-PSx-LiTFSI electrolyte membranes with various amounts of LiTFSI. The labels $T_{g\text{-PSx}}$ and $T_{g\text{-PMMA}}$ indicate the specific glass transition temperature of the materials. Pure PSx exhibits one single glass transition at −94 °C. The addition of LiTFSI to pure PSx causes an increase of $T_{g\text{-PSx}}$. Ionic interactions or ionic cluster formation in the amorphous region of the polymer usually resembles physical crosslinking [29]. Therefore, the segmental motion of polymer chains is inhibited leading to higher glass transition temperatures and a decrease of ionic transport. Fig. 5 displays the effect that $T_{g\text{-PSx}}$ increases almost gradually upon the addition of salt because of the increased number of ion–polymer and ion–ion interactions [29].

Contrary to the liquid PSx/LiTFSI electrolytes, in PMMA/LiTFSI electrolyte membranes, $T_{g\text{-PMMA}}$ decreases with increasing amounts of LiTFSI. Regarding the two conformational states of the TFSI-anion, *transoid* with C2 symmetry and *cisoid* with C1 symmetry [30–32], the highly flexible anion contributes to formation of an amorphous PMMA structure and inhibits intermolecular interactions within the PMMA network. The lack of binding sites for Li^+ prevents physical-crosslinking and additionally, weakens cohesion of the PMMA network. As a result, the network becomes more flexible and $T_{g\text{-PMMA}}$ decreases consequently. Excess of LiTFSI tends to self-aggregate which causes a decrease of T_g with salt concentrations higher than 20 wt.%, as reported by CHANG et al. for PVP-*co*-PMMA-$LiClO_4$ networks [29].

In (*net*-PMMA)-*sipn*-PSx membranes the T_g for each polymer component, $T_{g\text{-PMMA}}$ and $T_{g\text{-PSx}}$, were recorded. Since glass transition of pure PMMA occurs at a temperature of 118 °C, the addition of the liquid PSx to PMMA has an impact on $T_{g\text{-PMMA}}$, decreasing it significantly down to 63 °C. This phenomenon is caused by the crystalline structure of PMMA [33] which is disturbed by the addition of the liquid PSx. As a result, the rigid PMMA network becomes more flexible with increasing content of PSx and $T_{g\text{-PMMA}}$ decreases consequently (Fig. 3c). In contrast,

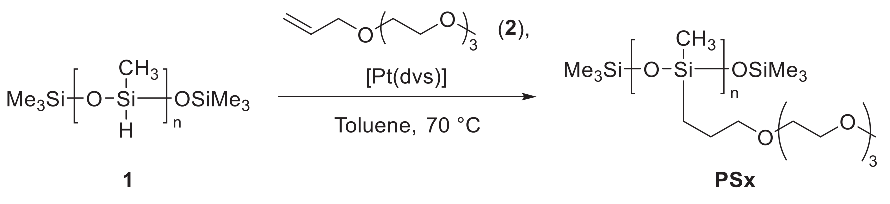

Fig. 1. Synthesis of ether-modified PSx.