

Characterization of *semi*-interpenetrating polymer electrolytes containing poly(vinylidene fluoride-co-hexafluoropropylene) and ether-modified polysiloxane



Eva Cznotka ^{a,*}, Steffen Jeschke ^{a,b,1}, Hans-Dieter Wiemhöfer ^{a,*}

^a Institute for Inorganic and Analytical Chemistry, University of Münster, Correnstr. 28/30, 48149 Münster, Germany

^b Department of Applied Physics, Chalmers University of Technology, SE-41296 Gothenburg, Sweden

ARTICLE INFO

Article history:

Received 22 December 2015

Received in revised form 12 February 2016

Accepted 18 February 2016

Available online 10 March 2016

Keywords:

Polymer network

Solid polymer electrolytes

Differential scanning calorimetry

ABSTRACT

This work presents a detailed study of a *semi*-interpenetrating polymer network (*semi*-IPN) consisting of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP), polysiloxane-*comb*-propyl(triethylene oxide) (PSx) and lithium bis(trifluoromethane)sulfonimide (LiTFSI) prepared by a solution casting technique. According to differential scanning calorimetry (DSC), formation of the PVDF-HFPs crystalline phase is inhibited by the PSx which results in a significant improvement of tensile strain. A homogeneous distribution of PVDF-HFP and PSx in the membrane is analyzed using micro-FTIR mapping. Since no peak-shift due to mixing of PVDF-HFP and PSx was observed in FTIR second derivative analysis, computational models were applied to investigate the intermolecular interactions between the constituting domains of different polarity. An influence of PVDF-HFP on the Li⁺ transport in the ion-conducting PSx was determined by calculating the effective conductivities. The highest ionic conductivity of $7.7 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature was reached with 15 wt.% LiTFSI. The electrochemical stability window ranges from 0.5 V to 4.6 V vs. Li/Li⁺ reference electrode.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Solid polymer electrolytes (SPEs) are promising materials to overcome current problems in battery technology such as leaks, flammability and internal shorting caused by use of organic, liquid components [1, 2]. Different types of SPEs such as gelled SPEs [3–5], porous SPEs [6,7] and dry SPEs [8] have already been reported in literature. First research approaches on SPEs go back to the early seventies, where poly(ethylene oxide) (PEO) was launched by Wright as the first SPE [9]. Due to high crystallinity and poor motion performance of the PEO backbone, the conductivities are quite low in the magnitude of $10^{-7} \text{ S cm}^{-1}$ at room temperature and have already caused a problem for practical use [9, 10]. A fast ion transport in SPEs is predominantly due to the existence of amorphous phases and low glass transition temperatures (T_g) which induces a good polymer chain flexibility [11]. Modified polysiloxanes have already been proven to be a suitable alternative to PEO with lower glass transition temperature and conductivities close to those required for practical use ($10^{-3} \text{ S cm}^{-1}$) [12–14]. However, polysiloxanes show low mechanical stability [12]. To overcome this

problem, the formation of interpenetrating polymer networks (IPNs) is a promising technique where two or more polymer networks are at least partially interlaced on a molecular scale [15]. A *semi*-IPN is a special type of IPN consisting of linear or branched polymers which can be separated from the host network without breaking chemical bonds [15–17].

Due to its high thermal stability, chemical resistance and mechanical strength, PVDF is a suitable polymer to act as a stabilizing host matrix [18]. PVDF based membranes are already applied in different fields such as wastewater treatment [19], vacuum membrane distillation [20] or as active separator in lithium ion batteries [21,22]. However, PVDF shows high crystallinity in the range between 35% and 70% which impairs the properties as SPE [18]. In general, a suppression of crystallinity of polymers can be realized by (a) cross-linking; (b) polymer alloys such as interpenetrating networks; and (c) co-polymerization [23]. Several co-polymerizations of PVDF were carried out [24] by forming *semi*-crystalline copolymers such as poly(vinylidene fluoride-co-trifluoroethylene) (PVDF-TrFE) [25], poly(vinylidene fluoride-co-chlorotrifluoroethylene) (PVDF-CTFE) [26] or poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) with a reduced degree of crystallinity compared to neat PVDF. For application as electrolyte material in lithium ion batteries, PVDF-HFP has attracted the most attention as a gel polymer electrolyte [27–32] rather than as a solid polymer electrolyte. However, research on PVDF-HFP-based SPEs usually involves PEO, e.g. PVDF-HFP/PEO blend membranes

* Corresponding authors.

E-mail addresses: eva.cznotka@wwu.de (E. Cznotka), hdw@uni-muenster.de (H.-D. Wiemhöfer).

¹ Authors considered equal.

Table 1

Porosity (*P*) determination of membranes with different PVDF-HFP, PSx and LiTFSI compositions.

PVDF-HFP [wt.%]	PSx [wt.%]	LiTFSI [wt.%]	<i>P</i> [%]
<i>Variation of (net-PVDF-HFP)-sipn-PSx</i>			
90	10		4 ± 0.3
80	20		5 ± 0.5
70	30		7 ± 1.1
60	40		11 ± 0.5
50	50		18 ± 0.1
40	60		26 ± 0.2
<i>Variation of LiTFSI in semi-IPNs</i>			
38	57	5	24 ± 0.2
36	54	10	26 ± 0.6
34	51	15	26 ± 0.7
32	48	20	25 ± 0.1
30	45	25	24 ± 0.6

prepared by Malik et al. which were analyzed concerning their thermal degradation [33]. Elmér et al. produced PVDF-HFP based membranes with a cross-linked PEG-grafted polymethacrylates and LiTFSI which offer ionic conductivities of 10^{-5} S cm⁻¹ at room temperature [34].

In the herein presented work a novel SPE based on PVDF-HFP combined with an ion-conducting polysiloxane-*comb*-propyl(triethylene oxide) (PSx) in form of a *semi*-IPN ((*net*-PVDF-HFP)-*sipn*-PSx-LiTFSI) is prepared and investigated. During preparation, different amounts of lithium bis(trifluoromethane)sulfonimide (LiTFSI) were added and SPE-membranes were prepared by solution casting technique. Thermal and morphological properties were analyzed by DSC. Due to the amphiphilic nature of PSx with its ether-moieties and the rather unpolar siloxane-backbone, computational methods were applied to gain insights into the intermolecular interactions of ether/PVDF and siloxane backbone/PVDF as well as their energetic aspects, in order to support experimental FTIR investigations. Furthermore, SEM-EDX and micro-FTIR mapping were applied to visualize the distribution of the *semi*-IPN ingredients. The ionic conductivity as well as the electrochemical

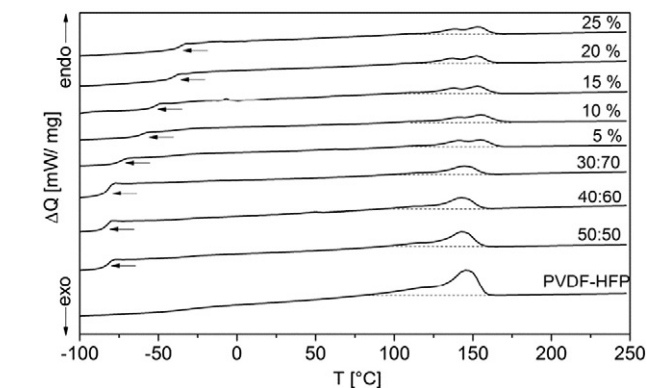


Fig. 2. DSC thermograms for pure PVDF-HFP films, (*net*-PVDF-HFP)-*sipn*-PSx films with different ratios (50:50; 40:60; 30:70) and *semi*-IPN with different LiTFSI concentrations.

stability of the *semi*-IPN system was investigated to determine its application as SPE in lithium-ion batteries.

2. Experimental

2.1. Preparation of *semi*-IPNs

Liquid polysiloxane-*comb*-propyl(triethylene oxide) (PSx) was prepared according to the literature [35,36]. *Semi*-IPNs were made by solution casting technique using PVDF-HFP (Sigma-Aldrich, $M_w \sim 4 \times 10^5$, bimodal distribution) as a host network, PSx as a conducting component and LiTFSI (Sigma-Aldrich) as a conducting salt. These components were dissolved in anhydrous acetone and poured into a Petri dish. After complete evaporation of acetone the membranes were dried at 80 °C under vacuum (10^{-2} mbar) for 5 h and then stored at 80 °C in high vacuum (10^{-5} mbar) for additional 2 days. Due to membrane mechanical stability reasons, a ratio of 40:60 wt.% for PVDF-HFP:PSx was chosen in (*net*-PVDF-HFP)-*sipn*-PSx and *semi*-IPNs. Membrane preparation

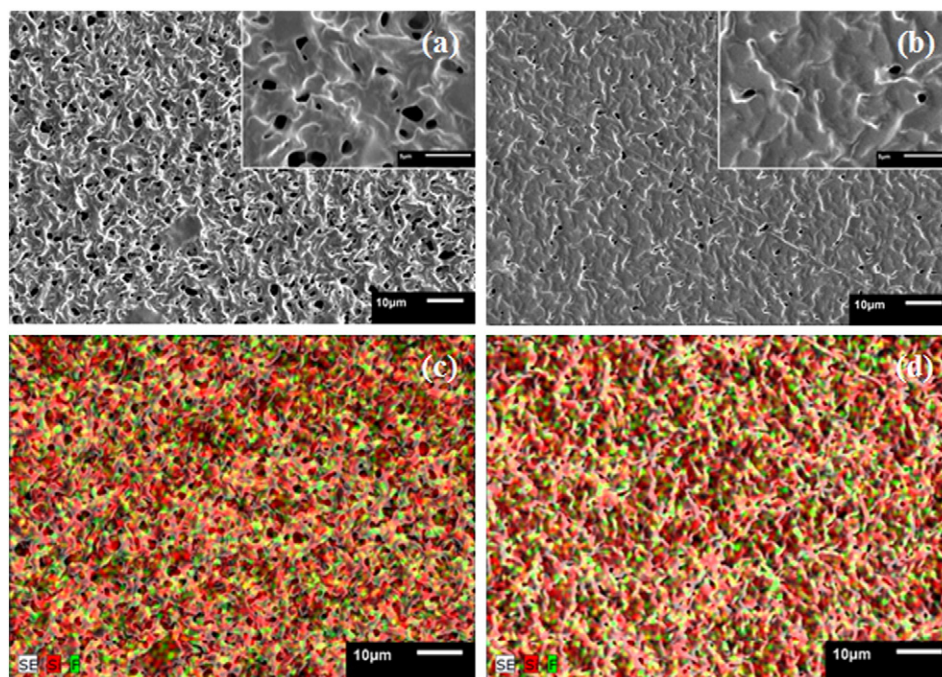


Fig. 1. SEM images of (*net*-PVDF-HFP)-*sipn*-PSx membranes of the a) upper surface and b) bottom surface and corresponding SEM-EDX images of the c) upper surface and d) bottom surface.

Download English Version:

<https://daneshyari.com/en/article/1296150>

Download Persian Version:

<https://daneshyari.com/article/1296150>

[Daneshyari.com](https://daneshyari.com)