



Electrospun-sodiumtetrafluoroborate-polyethylene oxide membranes for solvent-free sodium ion transport in solid state sodium ion batteries



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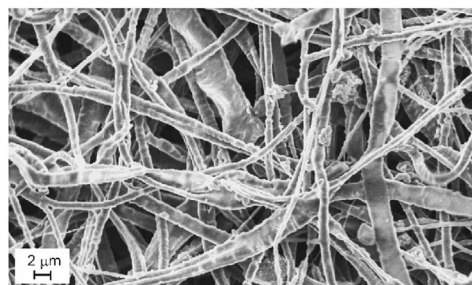
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HIGHLIGHTS

- Hybrid polymer-salt membranes were fabricated by electrospinning.
- Ion conductivities up to $10^{-4} \text{ S cm}^{-1}$ were realized for those membranes.
- A conduction mechanism was determined for the ion transport in the hybrid system.
- Na-based membranes show similar conductivities that comparable Li-membranes.
- Plasticizer in Na membranes does not significantly improve the conductivity.

GRAPHICAL ABSTRACT

Na-ion conducting, electrospun PEO:NaBF₄ membrane.



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ABSTRACT

Electrospinning is used to fabricate sodium ion conducting fiber membranes composed of polyethylene oxide (PEO), sodium tetrafluoroborate (NaBF₄), and succinonitrile (SN) as plasticizer.

As compared to conventionally prepared lithium electrolyte membranes with identical composition (PEO:SN:LiBF₄), those membranes exhibit conductivities up to $10^{-4} \text{ S cm}^{-1}$ at 328 K (activation energy $\sim 36 \text{ kJ mol}^{-1}$, 36:8:1 membrane), which favors such systems as a solid-state electrolyte alternative for batteries. The conduction mechanism is evaluated and the ion mobility are examined. We identified the segment mobility of the polyethylene oxide as the main driving force for the enhanced ion mobility in the membranes. The introduction of SN has only a minor influence on the conductivity and segment mobility at room temperature, but extends the anion and cation mobility to temperatures below ambient. For the 36:8:1 (PEO:SN:NaBF₄) membrane we found the highest ion mobility of all membranes under investigation. A comparison of the present sodium membranes with lithium systems of the same composition shows that the overall performance of the sodium systems is comparable. Taking plasticizer-free sodium membranes into account they perform even better than the lithium containing counterparts, and plasticizer-modified membranes show only half an order of magnitude lower conductivities than comparable lithium ones.

1. Introduction

Polymer electrolytes are frequently used in rechargeable batteries as a save alternative to liquid electrolytes [1,2] or separators [3]. Beside

the polymer matrix they contain a salt which delivers the mobile ion species. Important is the grade of dissociation of the salt, the tendency and ability of the mobile ion to coordinate with the polymer and also the number of suitable and accessible coordination sites within the

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polymer matrix [4]. In some cases, additives are needed to increase the polymer flexibility and ion mobility, in order to tune the ion conductivity as one of the key parameters of the system. Such plasticizer additives tend to increase the segment mobility of the amorphous polymer matrix which then enables an improvement of the ion mobility in the system (solid lubricant) [5–7].

Another possible application for ion conductive polymers in the field of batteries are separator membranes in liquid and all solid state batteries, either as gel electrolytes (GE) [8], containing a liquid electrolyte or as solid polymer electrolyte (SPE) [1] without any additional solvent. While ions are predominantly conducted via the liquid electrolyte in GE, the ion transport must be fully realized within the polymer phase in a SPE. Advantages of such SPEs are the flexibility of the battery cell (like for GE), a good solubility for alkaline salts and a reasonable mechanical stability [9–12].

Although the vast majority of studies in the field of rechargeable batteries has been devoted to Li based systems, the notion that the availability of Li may be limited has triggered research on alternative metals recently. Na based systems may evolve as a promising and sustainable substitute in the future [13]. In most of the cases, such SPE membranes are fabricated by solution casting or hot pressing methods where the polymer and the salt are dissolved and the solvent is removed afterwards. One prominent polymer amongst many others is polyethylene oxide (PEO). An advantage of PEO is that it can be successfully used as polymer matrix in SPE's in contact to metallic sodium. Unfortunately, sodium melts at 98 °C which represents the upper temperature in solid state battery applications. Another drawback of PEO-based SPE's (applied as thin-film electrolytes of 10–20 μm) is their poor ionic conductivity of 10^{-7} to 10^{-5} S cm⁻¹ [11]. In order to overcome this limitation, the temperature has been raised to temperatures larger than 80 °C, to provide enough conductivity for applications. Together with the melting point of sodium this aspect drastically narrows the operation window for applications. Thus, strategies have to be developed to significantly improve the room temperature conductivity of sodium polymer electrolytes. One possibility, which is not in the focus of this article, is the usage of hybrid ceramic-polymer electrolytes (e.g. Li₇La₃Zr₂O₁₂ (LLZO) for Li systems) where an ion conductive solid is added to the polymer electrolyte [14].

PEO/Li salts SPE's have been frequently examined in the past decades for Lithium ion battery applications, pioneered by *Armand* and *Wright* with PEO:LiBF₄ [15–17]. An interesting review article summarizing the recent developments of crystalline and polymer electrolytes in Lithium chemistry can be found elsewhere [18]. The knowledge gained in Lithium battery technology concerning the polymer electrolytes and conductive salts has been partially transferred to Sodium battery science [11]. Many Sodium-salts have been tested in liquid, polymer and gel electrolytes. Some examples are NaClO₄, NaBF₄, NaPF₆, NaTF (Na[CF₃SO₃]) or NaTFSI (Na[N(CF₃SO₂)₂]), beside others. If solid polymer electrolytes (SPE), without the usage of any liquid electrolyte, comes into play, the prototype of polymer used is PEO.

As early as 1981, *Armand* et al. and *Papke* et al. [19–21] reported on the synthesis and characterization of NaBF₄@PEO SPE's. Solution casting was used to fabricate membranes which showed conductivities of 1×10^{-7} S cm⁻¹ at 303 K and 7×10^{-5} S cm⁻¹ at 363 K [21]. The formation of crystalline (PEO)_xNaBF₄ adducts were identified as the reason for the overall low conductivity due to trapping of sodium ions in these phases. In 1983, *Shriver* et al. reported, that the conductivity is significantly larger in amorphous than in crystalline PEO [22] and that breaking the Na⁺–O interaction within a given PEO chain is favored rather than a hop from one chain to the other. Later on, other salts acting as a sodium source were tested. *Hashmi* et al. found conductivities of 5×10^{-6} S cm⁻¹ for a NaPF₆@PEO sample (PEO:NaPF₆ molar ratio of 15:1) at room temperature [23]. In a recent study, new fluorine-free SPE were reported [24]. Here, percyano-substituted organic salts like sodium pentacyanopropenide (NaPCPI), sodium 2,3,4,5-tetracyanopropenide (NaTCP) and sodium 2,4,5-tricyanoimidazolate

(NaTIM) were tested as additives to PEO. Reasonable high ionic conductivities of $1 \cdot 10^{-6}$ to $7 \cdot 10^{-4}$ S cm⁻¹ were found for hot-pressed 10:1 and 50:1 disks (molar ratios of PEO:salt) at temperatures between 293 and 353 K. Due to toxicity and safety issues such cyano compounds might be non-beneficial.

An example for a working sodium/sulfur solid state battery using PEO:salt SPE's has been reported in 2007. Solution casted PEO:NaTF in a 9:1 M ratio was used [25] resulting in a capacity of 166 mAhg⁻¹ at the 10th cycle. At 90 °C the PEO:NaTF SPE showed a conductivity of $3.4 \cdot 10^{-4}$ S cm⁻¹.

Recently, electrospinning has been used to fabricate LiBF₄@PEO membranes of different compositions and with SN as a plasticizer additive [26]. Compared with solution casted membranes, the overall performance of the electrospun membranes was significantly improved. An increase of the Li ion conductivity of two orders of magnitude for the different membrane types from $1 \cdot 10^{-6}$ S cm⁻¹ [27] to $2 \cdot 10^{-4}$ S cm⁻¹ (at 298 K) has been observed. Inspired by this finding the question arose if electrospun membranes containing sodium ions show the same trend and if electrospinning has a comparable optimization potential for sodium conducting systems. Therefore, we conducted a series of experiments with electrospun NaBF₄@PEO membranes, including the usage of SN as a plasticizer. Membranes of different compositions were fabricated and selected electrochemical properties were determined.

2. Experimental section

2.1. Preparation of the PEO:NaBF₄ and PEO:SN:NaBF₄ membranes

The spinning solution was prepared by dissolving PEO ($M_w \approx 300\,000$, Sigma-Aldrich, dried at 333 K in vacuo) in acetonitrile (Sigma Aldrich, anhydrous > 98%), resulting in a 1.6 M solution. NaBF₄ (Alfa Aesar, 98%, dried at 333 K in vacuo) and succinonitrile (Sigma Aldrich, 99% dried at 333 K in vacuo) in different amounts were added according to the compositions given in Table 1 and stirred for 24 h under argon atmosphere.

The electrolyte membranes were prepared using a home-built electrospinning (ES) apparatus (described elsewhere [26]) with a stainless steel needle (inner diameter: 0.9 mm), a flow rate of 3 mL h⁻¹, an applied voltage of 17 kV, and 12 cm working distance between needle and flat collector. After the spinning process all membranes were dried in vacuo, punched up into small foils and were subject to detailed analyzes.

2.2. Membrane characterization

The morphology of the membranes was characterized using scanning electron microscopy (SEM) (Zeiss model EVO MA10). By adjusting secondary electron mode and accelerate voltage of 3 kV, SEM pictures were recorded.

For X-ray diffraction (XRD) the punched out samples were placed between Scotch Magic Tape and measured in a flat-bed sample holder using a STOE STADIP diffractometer (Cu K_{α1} radiation, $\lambda = 1.54051$ Å).

The thermal characterization was performed on a Netzsch F3 Maia differential scanning calorimeter (DSC) in a temperature range of 113–523 K and a heating rate of 10 K/min under constant argon flow.

Table 1
Composition of PEO:SN:NaBF₄ membranes.

Sample (PEO:SN:NaBF ₄)	PEO (in mol%)	SN (in mol%)	NaBF ₄ (in mol%)
18:0:1	94.7	0	5.3
36:0:1	97.3	0	2.7
18:3:1	82.0	13.5	4.5
36:8:1	80.0	17.8	2.2

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