



Preparation and electrochemical performance of polyphosphazene based salt-in-polymer electrolyte membranes for lithium ion batteries



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HIGHLIGHTS

- Stable solvent-free polymer electrolyte membranes.
- Total ionic conductivity 0.16 mS cm^{-1} at 30°C .
- Compatibility with metallic lithium electrodes, stable SEI, no degradation.
- Electrochemical stability window from 0 V up to 4.7 V vs. Li/Li^+ .

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ABSTRACT

This work presents a detailed study of the electrochemical performance of polyphosphazene based electrolyte membranes consisting of a linear polymer with $-(\text{N}=\text{PR}_2)-$ units, grafted with ethylene oxide side chains of the type $\text{R} = -(\text{OCH}_2\text{CH}_2)_3\text{OCH}_3$ and containing LiTFSI and LiBOB as dissolved lithium salts. The average molecular weight was 10^5 g mol^{-1} . Mechanical stability was achieved by UV induced in-situ cross-linking of the thin polymer electrolyte films. Favorable properties of this type of polymer electrolytes are the good thermal and electrochemical stability of the electrolyte membranes, the broad electrochemical stability window ranging between 0 V and 4.7 V versus the Li/Li^+ reference and a very good interface stability at lithium metal electrodes where a stable SEI was formed during initial contact. Total ionic conductivities up to $10^{-4} \text{ S cm}^{-1}$ were measured at 30°C . The transference numbers of lithium ions at 50°C ranged between 0.06 and 0.07 and hence are lower by a factor of about three as compared to other typical polymer electrolytes. Nevertheless, the partial lithium ion conductivity estimated from the product of total conductivity and lithium ion transference number is as high or slightly higher compared to PEO based polymer electrolytes.

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1. Introduction

In recent years, the demand for more efficient and safer lithium ion batteries has increased, due to the growing interest in mobile devices and electric vehicles. Polymer gel electrolytes are already in use in lithium polymer batteries, e.g. based on poly(ethylene oxide) (PEO) or poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) swollen with liquid electrolytes like LiPF_6 containing EC/DMC mixtures [1,2]. The early investigations in the field of polymer electrolytes can be divided into solvent-free polymer electrolytes and gel polymer electrolytes (GPE). Since the first publications on salt solutions in PEO and their possible use as electrolytes [3–5], these and other solvent free polymer electrolytes have been considered as attractive candidates for battery applications, due to

their safety, absence of volatility and less or negligible inflammability as compared to liquid electrolytes [2,6]. Mechanically stable cross-linked polymer electrolytes allow safe separation of anodes and cathodes, preventing short-circuits and dissolution of electrode components. Although solvent-free polymer electrolytes are often denoted as solid polymer electrolytes, the expression solid polymer is not correct as the corresponding polymers are used above their glass transition temperature and, thus correspond more to highly viscous fluids. In fact, as extensively reviewed [2,7], the ion transport is closely coupled to the segmental motion of the polymer molecules explaining also the observed non-Arrhenius temperature dependence of the conductivity which is well described by a Vogel–Fulcher–Tammann (VTF) equation in close analogy to the temperature dependence of the reciprocal viscosity of the polymer fluids.

As early as 1984, strongly improved ionic conductivities were demonstrated by choosing polyphosphazenes grafted with

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oligoethylene oxide side chains as solvents for lithium salts [8,9]. The advantage of oligoether grafted polyphosphazenes is their complete amorphous property together with an extremely low glass transition temperature which favors a high ionic mobility and solubility [10–14] and makes them attractive for a low temperature battery application. Recent experiences with good stability and performance of polyphosphazene based electrolytes in lithium ion cells as well as with lithium metal electrodes lead us to start more thorough investigations of their electrochemical behavior. The very good thermal and chemical stability of corresponding organo-modified polyphosphazenes and the availability of a convenient synthetic route towards high purity polymers by a living cationic polymerization were further arguments [15–17]. This work aims at the preparation and investigation of mechanically stable salt-in-polymer electrolyte membranes based on an oligoether grafted polyphosphazene with respect to electrochemical properties and stability versus lithium metal.

Furthermore, ion or mixed conducting inorganic polymers can be used as additives or binders in electrode structures by stabilizing the network of active particles and supporting the ion transport in such three-dimensional structures [18–20].

2. Experimental

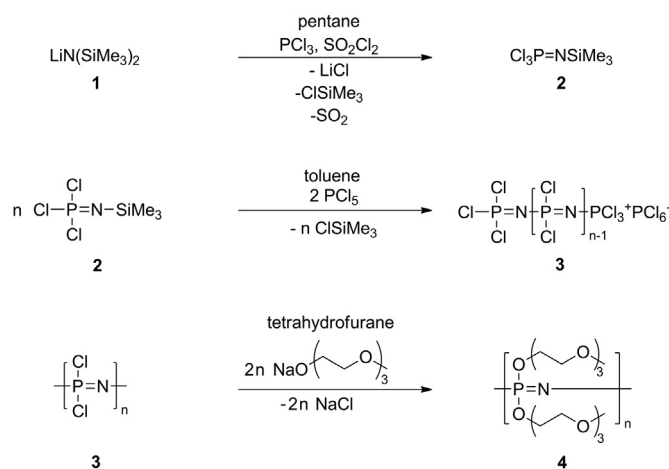
2.1. Materials

All reactions were carried out under a dry nitrogen gas atmosphere using standard vacuum-line Schlenk techniques. Tetrahydrofuran (99.5%, VWR), *n*-pentane (98%, Baker) and toluene (99.7%, VWR) were freshly distilled from sodium benzophenone prior to use. Sulfuryl chloride (SO₂Cl₂ 98%, Aldrich), phosphorous trichloride (PCl₃, 99%, Merck KGaA) and 2-(2-(2-Methoxyethoxy)ethoxy) ethanol (C₇H₁₆O₄, 99% Merck KGaA) were freshly distilled before use. Sodium hydride (NaH, 60% w/w dispersed in mineral oil, Aldrich), lithium bis(trimethylsilyl)amide (LiN(Si(CH₃)₃)₂, 97%, Aldrich) and phosphorous pentachloride (PCl₅, sublimated under vacuum) were stored under argon in a glove box. Lithium bis(trifluoromethanesulfonyl)imide (LiN(SO₂CF₃)₂, purum, Aldrich) and lithium bis(oxalato)borate (LiB(C₂O₄)₂; 97%; Chemetall GmbH) were exclusively stored and handled in a dry room with water contents lower than 20 ppm and used as received. Chloroform-*d* (99.8 atom% D, Aldrich), lithium foil (Chemetall GmbH, 99.99%), platinum (Chempur, 99.99%, Ø = 2 mm) and nickel (Alfa Aesar, 99.98%) were used as received. Celite 545® (Merck KGaA) and the molecular sieve 4 Å (VRW) were dried at 140 °C for 48 h minimum before use. The dialysis tubes (Reichert Chemietechnik, molecular weight cut off 12,000–14,000 g mol⁻¹) for polymer purification were washed and cleaned with distilled water before use.

2.2. Synthesis and membrane preparation

The synthesis of the monomer Cl₃P=NSiMe₃ was done in a dry Schlenk line under inert argon according to a synthetic route described by Wang et al. [16,21] with minor modifications [17]. Poly[dichlorophosphazene] (**3**) was synthesized from this monomer via living cationic polymerization using the route developed by Allcock et al. [22]. The final nucleophilic substitution of chlorine using the corresponding sodium alcoholate leads to the desired poly[bis 2-(2-(2-methoxyethoxy)ethoxy)ethoxy phosphazene] MEEEP (**5**) according to Scheme 1.

119.5 mmol of lithium bis(trimethylsilyl)amide (**1**) were dissolved in 300 mL of dry pentane. Freshly distilled phosphorous trichloride (114.6 mmol) was added drop wise within 30 min, while keeping the reaction temperature permanently at –15 °C. The reaction mixture was stirred for 30 min. Then sulfuryl



Scheme 1. The first two reactions describe the route to the precursor polymer (**3**) by the living cationic polymerization with PCl₅ as initiator; the third line describes the subsequent functionalization by nucleophilic substitution yielding MEEEP (**4**).

chloride (106.1 mmol) was added drop wise under equal reaction conditions. After 30 min of stirring lithium chloride was precipitated, filtrated through Celite® and washed with 60 mL of dry *n*-pentane. After solvent evaporation the phosphoranimine monomer Cl₃P=NSiMe₃ (**2**) was vacuum distilled at 22 °C and 10⁻³ mbar. The monomer was received as a clear liquid with yields up to 70%. Afterward, phosphorous pentachloride was dissolved in dry toluene with concentration of about 11 mmol L⁻¹. The freshly prepared solution was added quickly to the monomer/toluene solution. The initiator-monomer ratio was 350:1. The polymerization product poly[dichloro-phosphazene] (**3**) was identified in the reaction mixture after 48 h by ³¹P NMR. After solvent evaporation, the transparent, viscous precursor polymer (**3**) was received. ³¹P NMR (400 MHz, CDCl₃, 300 K): δ (ppm) ~ –17.97.

3.6 g (150 mmol) of sodium hydride was suspended in 120 mL tetrahydrofuran and cooled to 0 °C. The freshly distilled 2-(2-(2-methoxyethoxy)ethoxy)ethanol was added drop wise and the suspension was stirred for 1 h under hydrogen gas evolution. Then 8.7 g (74.9 mmol) of precursor polymer (**3**) dissolved in 50 mL tetrahydrofuran was added to the meanwhile clear solution and stirred for 24 h, while sodium chloride precipitated. Excess solvent was removed in a rotary evaporator. The product was purified in a dialysis tube (molecular weight cut off = 12,000–14,000 g mol⁻¹) against distilled water. After a final evaporation of water and drying at 50 °C under vacuum for 2 h, the highly viscous, yellow honey like poly[bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy phosphazene)] MEEEP (**4**) (*M*_w = 1.4979 · 10⁵ g mol⁻¹, polydispersity index PDI = 1.32) was received in a yield of 24.7 g (66.5 mmol, 88%). ¹H NMR (400 MHz, CDCl₃, 300 K): δ (ppm) = 3.32 (3H, s), 3.58 (8H, m), 4.00 (2H, s), 3.49 (2H, m). ¹³C NMR (101 MHz, CDCl₃, 300 K): δ (ppm) = 59.06 (s), 65.13 (s), 70.86–70.29 (m), 72.09 (s). ³¹P NMR (400 MHz, CDCl₃, 300 K): δ (ppm) = –8.19 (s).

The salt-in-polymer electrolyte membranes were prepared by a solution casting technique as described in Ref. [23]. A solution of MEEEP (**4**) in tetrahydrofuran was mixed with different amounts of LiTFSI or LiBOB, as well as 5 wt% benzophenone. After stirring for 2 h the solvent was evaporated and then dried for at least 48 h at 70 °C under vacuum. Karl–Fischer titration revealed a remaining water content below 5 ppm. The homogeneous mixtures were sandwiched between two Mylar® foils and pressed to the thicknesses of ~350 μm. Solid, flexible and transparent membranes were received after 10 min of UV-irradiation. Using 5 wt% benzophenone, a cross-linking degree of 10% was obtained as referred to

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