



# Enhanced Lithium-Ion Transport in Polyphosphazene based Gel Polymer Electrolytes



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## ABSTRACT

A detailed electrochemical study is presented of the lithium ion transport in polyphosphazene based gel polymer electrolytes. The polyphosphazene poly[bis(2-(2-methoxyethoxy) ethoxy) phosphazene (MEEP) was chosen for the polymeric network. In combination with liquid electrolytes (organic carbonates with lithium bis(oxalato) borate and lithium(hexafluoro) phosphate) gel polymer electrolyte membranes with very good ionic conductivities of  $2.3 \text{ mS cm}^{-1}$  at  $30^\circ\text{C}$  and high lithium transference numbers of 0.31 at  $90^\circ\text{C}$  were prepared. The investigated electrolytes exhibited very good interface stability at lithium metal electrodes during long term lithium plating/stripping experiments with up to 500 cycles. Discharge rate investigations on full cells consisting of lithium metal | MEEP gel polymer |  $\text{LiFePO}_4$  delivered high capacities of  $140 \text{ mAh g}^{-1}$  at a discharge rate of 5 C.

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## 1. Introduction

In the past, a growing interest in mobile devices and electric vehicles has advanced the research on more efficient lithium batteries. Key factors are higher specific capacities and output voltages, longer cycle life and improved safety. Approaching these problems, the use of polymer electrolytes has been intensively studied in recent decades [1–3]. However, due to the limited ionic conductivity of solid salt-in-polymer solutions, there are many current publications presenting new types of gel polymer electrolytes [4–8]. Cross-linked polymeric networks trap the liquid component whereby leakage of the liquid component is prevented and high ionic conductivities of  $1 \text{ mS cm}^{-1}$  at room temperature can be achieved.

For fast charging and discharging of a lithium cell, high current densities have to be used. Therefore, a high lithium transference number, besides ionic conductivity, is an important parameter for a sufficient lithium ion transport through the battery electrolyte.

In 1984, high ionic conductivities were reported for linear polyphosphazene polymers grafted with (oligoethylene oxide)-type side chains [9,10]. Today it is known that the high ionic conductivity of those polymer electrolytes is mainly aroused by anion transport through the polymer network [11–14]. The partial negatively charged nitrogen and the oxygen atoms of the side chains strongly coordinate lithium ions which is why the lithium

transference numbers at ambient temperatures are very low ( $<0.1$ ). This makes the solid salt in polymer electrolytes unfeasible for fast charging lithium cells. Anyway, the good electrochemical and thermal stability, as well as the performance with lithium metal anodes [11] make the polyphosphazene-based electrolytes attractive, if this problem can be addressed.

This work aims at the preparation of oligoethylene oxide functionalized polyphosphazene poly[bis(2-(2-methoxyethoxy) ethoxy) phosphazene] (MEEP) based gel polymer electrolytes with an enhanced lithium ion transport. Therefore lithium[bis(oxalato) borate] (LiBOB) and lithium(hexafluoro) phosphate ( $\text{LiPF}_6$ ) based liquid electrolytes are used as gelling agents. As reported before, the addition of liquid electrolyte into the polyphosphazene matrix enhances the ionic conductivity, as well as the lithium transference number [15] but is still improvable. Therefore, this work presents a detailed study of the prepared MEEP based gel polymer electrolytes using different compositions of MEEP: liquid electrolyte and varying lithium salt concentrations.

The performance of the improved gel polymer electrolyte was tested with temperature dependent discharge rate performance tests in  $\text{Li}|\text{LiFePO}_4$  cells using the gelled polymer as electrolyte and separator at the same time.

## 2. Experimental

### 2.1. Materials

Ethylene carbonate, dimethyl carbonate and diethylene carbonate were used as received (99.9%, Merck KGaA) and stored

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under Argon in a glovebox. Tetrahydrofuran (99.5%, VWR), *n*-pentane (98%, Baker) and toluene (99.7%, VWR) were freshly distilled from sodium benzophenone prior to use. Sulfuryl chloride (SO<sub>2</sub>Cl<sub>2</sub> 98%, Aldrich), phosphorous trichloride (PCl<sub>3</sub>, 99%, Merck KGaA) and 2-(2-Methoxyethoxy) ethanol (C<sub>5</sub>H<sub>12</sub>O<sub>3</sub>, 99% Merck KGaA) were freshly distilled before use. Sodium hydride (NaH, 60% w/w dispersion form in mineral oil, Aldrich), lithium bis(trimethylsilyl) amide (LiN(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, 97%, Aldrich), phosphorous pentachloride (PCl<sub>5</sub>, sublimated under vacuum) and lithium bis(oxalate) borate (LiB(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>; 97%; Chemetall GmbH) and lithium (hexafluoro) phosphate (LiPF<sub>6</sub>, 99.99%, Aldrich) were stored under Argon in a glovebox. 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<sup>®</sup> (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 12,000–14000 g/mol) for polymer purification were washed and cleaned with deionized water before use.

Sodium carboxymethyl-cellulose (Na-CMC, WALOCEL<sup>™</sup> CRT 2000 PPA 12, Dow Wolff Cellulosics), lithium iron phosphate (LiFePO<sub>4</sub>, P2, Süd-Chemie) and carbon black (Super P<sup>®</sup>, Timcal) were used as received.

## 2.2. Electrode preparation

The preparation of the LiFePO<sub>4</sub> electrodes was performed using the commonly used doctor blade method. The slurry contains of 150 mg Na-CMC, 300 mg carbon black and 2.6 g LFP P2 in 7 mL water. Finally the slurry was dispersed with a high energy stirrer (T 18 ULTRA-TURRAX<sup>®</sup>, IKA) for 1 h at 5000 rpm. An etched aluminum foil was (5 wt.% KOH, 60 °C, 60 s, *d* = 20 μm) coated with the slurry using a doctor blade (wet film = 120 μm, dry film = 22–24 μm). The obtained sheets were dried in the oven at 80 °C for 15 h, stamped into discs of 12 mm diameter and dried for 48 h (120 °C at 10<sup>-3</sup> mbar). The composition of the LFP cathodes was 85 wt.% LFP P2, 10 wt.% Super P and 5 wt.% Na-CMC with a load of ~2.85 mg · cm<sup>-2</sup> ≅ ~2.42 mg cm<sup>-2</sup> LFP (theoretical capacity C<sub>theo</sub> = 165 mAh g<sup>-1</sup>).

## 2.3. Polymer synthesis

Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (MEEP) was synthesized via nucleophilic substitution of the chlorine atoms in [NPCl<sub>2</sub>]<sub>n</sub> which was synthesized with a four step synthesis route by Wang et al. [16,17] with minor modifications [18] through a living cationic polymerization [19]. The detailed preparation route for oligoether functionalized polyphosphazene based solid salt-in-polymer solutions, as well as first electrochemical properties of polyphosphazene based gel polymer electrolytes have already been published elsewhere [11,15].

## 2.4. Gel polymer membrane preparation

The chemical structures of the polymer and the compositions of the liquid electrolytes are summarized in Table 1.

In this work all gel polymer electrolyte membranes were prepared by swelling a cross-linked MEEP membrane with the favored amount liquid electrolyte. The cross-linked polymer membranes were made via a solution casting technique as described in [20]. A desired amount of MEEP (~1 g) was mixed with 5 wt.% benzophenone. The homogeneous mixtures were sandwiched between two Mylar<sup>®</sup> foils and pressed to the desired thickness of 200 μm–300 μm. Solid membranes were received after 12 min of UV-irradiation. With 5 wt.% benzophenone a cross-linking degree of 10% was obtained, referred to the (NPR<sub>2</sub>) monomer units. Round discs of 10 mm diameter were cut out. The required amounts of liquid electrolyte (60 wt.% referred to the MEEP membrane) were added and the membranes were allowed to swell within 12 h in a sealed glass vessel. For the gel polymer electrolytes with higher salt concentrations, 37.5 mol% of the respective lithium salt was dissolved in the MEEP network in advance and the salt containing membranes were swollen afterwards with the liquid electrolyte (60 wt.% referred to the MEEP + Li-salt membrane). The resulting mechanically stable gel polymer membranes (Fig. 1) were placed between lithium foils for further electrochemical analysis. For discharge rate analysis the LiFePO<sub>4</sub> electrode was pre wetted with a very small amount of liquid electrolyte to ensure good electrolyte infiltration in the porous cathode structure. All cells were assembled in a dry room with humidity values <10 ppm H<sub>2</sub>O.

## 2.5. Electrochemical characterization

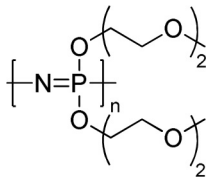
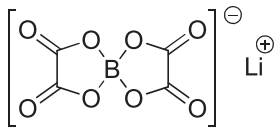
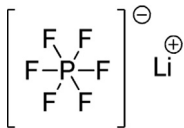
The ionic conductivity of the gel polymer electrolyte membranes was determined by impedance spectroscopy in a temperature range from 30 °C to 90 °C. The impedance was measured with a frequency response analyzer Autolab PGStat302 N (Metrohm). The membranes were measured between two lithium electrodes in the frequency range from 1 MHz to 1 Hz with an AC amplitude of 10 mV. The ionic conductivity σ<sub>total</sub> was calculated according to:

$$\sigma_{total} = \frac{d \cdot A^{-1}}{R_{0,el}} \quad (1)$$

with *d* as the GPE membrane thickness (typically 200 μm or more), the contact area *A* = 1.13 cm<sup>2</sup> and *R*<sub>0,el</sub> as the ohmic electrolyte resistance. The latter was measured by frequency dependent AC impedance before the polarization experiment by taking the real part of the impedance at a medium frequency where the imaginary part has a minimum.

The lithium transference number was determined using a recently described improved steady-state potentiostatic polarization method [21]. Symmetric two-electrode Swagelok<sup>®</sup>-cells with

**Table 1**  
Chemical structures of the used polymer and lithium salts.

Polymer	Liquid Electrolyte 1	Liquid Electrolyte 2
		
MEEP	Lithium [bis(oxalate) borate] 0.7 M in EC/DMC (1:1 by weight)	Lithium (hexafluoro) phosphate 0.7 M in EC/DEC (3:7 by weight)

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