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Performance of polyphosphazene based gel polymer electrolytes in combination with lithium metal anodes

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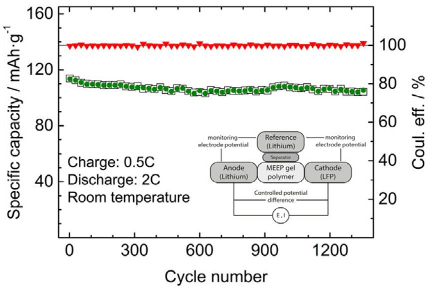
HIGHLIGHTS

- Electrochemical stability window 0 V –4.4 V versus Li/Li$^+$.
- Long term cycling stability in contact with lithium metal anode.
- 1350 cycles for a full cell with lithium anode without dendrite formation.
- MEEP based gel polymer: partial lithium ion conductivity of 0.1 mS cm^{-1} (50 °C).

GRAPHICAL ABSTRACT



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ABSTRACT

This work presents a detailed study of the electrochemical performance of a polyphosphazene based gel polymer electrolyte in a lithium metal polymer cell. The polyphosphazene MEEP was chosen because of its favorable properties, such as good thermal and electrochemical stability versus lithium metal. In combination with a liquid electrolyte, consisting of 0.7 mol L^{-1} LiBOB in EC/DMC, a high ionic conductivity of ~9·10^{-4} S cm^{-1} at 30 °C was achieved. The electrochemical stability window ranges between 0 V and 4.4 V vs. Li/Li$^+$ reference electrode. The gel polymer was drop coated onto the electrode materials and cross-linked to achieve high mechanical stability. The gel polymer showed a very good interface stability at lithium metal electrodes in the prepared full cells, where a stable SEI was formed during initial contact. The full cell tests delivered a stable cycling behavior with more than 1300 cycles and capacities higher than 110 mAh g^{-1} at high discharge rates of 2C$_D$, without any indication for short circuits caused by lithium dendrites.

1. Introduction

Due to the rising interest of applications for lithium secondary batteries which provide higher output voltage, higher specific capacity and longer cycle life, polymer electrolytes have been intensively studied in recent decades [1–3]. For secondary batteries like lithium/sulfur or lithium/air batteries, lithium metal is still a desirable anode material due to its low weight, low cost and high specific capacity. The use of lithium metal is still challenging because of its safety issues caused by lithium dendrite growth during charging and thus its use in secondary batteries is still considered critically.

For lithium/polymer batteries several polymers like poly(ethylene oxide) (PEO) [4], polyacrylnitrile (PAN) [5,6], poly(methyl methacrylate) (PMMA) [7] or poly(vinylidene fluoride) (PVDF) [8,9] have been studied, but the ionic conductivity at lower temperatures is too low and thus inadequate for practical use at higher current

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densities. Therefore, the attention has turned to gel polymer electrolytes (GPEs). When cross-linked, the liquid component is incorporated into the polymer matrix and thereby preventing leakage of the liquid electrolyte and exhibiting high ionic conductivities from 10^{-4} to 10^{-3} S cm^{-1} at room temperature.

In this work we focus on the electrochemical properties of a new polyphosphazene based gel polymer electrolyte, especially in combination with lithium metal anodes. As polymer matrix poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene (MEEP) was used. The combination with a liquid electrolyte made of 0.7 mol L^{-1} lithium bis[oxalato]borate (LiBOB) in an ethylene carbonate/dimethylcarbonate (1:1 by weight) mixture lead to the gel polymer electrolyte. MEEP fulfills several requirements as a polymer matrix in gel polymer electrolytes [10], which are (a) easy production at low cost [11], (b) thermal stability [12], (c) good compatibility with the liquid electrolyte, resulting in good mechanical strength of the product [13] and (d) good electrochemical stability towards reduction and oxidation [14]. The functionality of the MEEP based gel polymer in direct contact to lithium metal and the examination of the gel polymer | lithium interface were investigated in full cells, using lithium iron phosphate (LFP) as cathode material and metallic lithium as anode.

2. Experimental

2.1. Materials

Ethylene carbonate (99.9%, *Merck KGaA*) and dimethyl carbonate (99.9% *Merck KGaA*) were directly used. Tetrahydrofurane (99.5%, *VWR*), *n*-pentane (98%, *Baker*) and toluene (99.7%, *VWR*) were freshly distilled from sodium benzophenone prior to use. Sulfuryl chloride (SO_2Cl_2 98%, *Aldrich*), phosphorous trichloride (PCl_3, 99%, *Merck KGaA*) and 2-(2-Methoxyethoxy)ethanol ($C_5H_{12}O_3$, 99% *Merck KGaA*) were freshly distilled before use. Sodium hydride (NaH, 60% w/w dispersion form in mineral oil, *Aldrich*), lithium bis(trimethylsilyl)amide ($LiN(Si(CH_3)_3)_2$, 97%, *Aldrich*), phosphorous pentachloride (PCl_5, sublimated under vacuum) and lithium bis(oxalato)borate ($LiB(C_2O_4)_2$; 97%; *Chemetall GmbH*) were stored under Argon in a glove box. 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 (*Reichelt 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. Polymer synthesis

The synthesis of the polyphosphazene MEEP proceeds according to a four step synthesis route by Wang et al. [15,16] with minor modifications [17] and a living cationic polymerization reaction, firstly reported by Allcock et al. [18]. Nucleophilic substitution of the chlorine atoms in $[NPCl_2]_n$ with sodium alcoholates leads to the desired MEEP. The detailed reaction route, thermal and electrochemical properties of a similar oligoether functionalized polyphosphazene was already published before [19].

119.5 mmol of lithium bis(trimethylsilyl)amide 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 below −5 °C. The reaction mixture was stirred for 30 min. Then sulfuryl 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 $Cl_3PNSiMe_3$ 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} in toluene. The freshly prepared solution was added quickly to a monomer/toluene solution, thus an initiator-monomer ratio of 350:1 was reached. The polymerization product poly[dichloro-phosphazene] $[NPCl_2]_n$ was identified after 48 h by ^{31}P NMR. After solvent evaporation the transparent, viscous $[NPCl_2]_n$ was received. ^{31}P NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) ~ −17.97.

3.6 g (150 mmol) of sodium hydride was suspended in 120 mL tetrahydrofurane and cooled to 0 °C. The freshly distilled (2-(2-methoxyethoxy)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 $[NPCl_2]_n$ dissolved in 50 mL tetrahydrofurane were added to the 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 an evaporation of water and drying at 70 °C under vacuum for 2 days, the highly viscous, yellow honey like poly[bis(2-(2-methoxyethoxy)ethoxyphosphazene] (MEEP) was received in a yield of 24.7 g (66.5 mmol, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = 3.33 (3H, s), 3.49 (8H, m), 4.03 (2H, s), 3.61 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$, 300 K): δ (ppm) = 59.06 (s), 65.13 (s), 70.86–70.29 (m), 72.09 (s). ^{31}P NMR (400 MHz, $CDCl_3$, 300 K): δ (ppm) = −8.34 (s).

2.3. Electrode preparation

Sodium carboxymethyl-cellulose (Na–CMC, WALOCEL™ CRT 2000 PPA 12, *Dow Wolff Cellulosics*), lithium iron phosphate ($LiFePO_4$, P2, *Süd-Chemie*) and carbon black (Super P®, *Timcal*) were used as received. The preparation of electrodes was performed using the doctor blade method. At first the slurry was prepared by dissolving ~0.15 g Na–CMC in 3 mL water (*Millipore*, 2 h stirring). To the obtained binder solution 300 mg carbon black was added followed by 15 h stirring. Afterward 2.6 g LFP P2 (theoretical capacity C_{theo} = 170 mAh g^{-1}) and 3 mL water was added and stirred until the suspension was homogeneous. Finally the slurry was dispersed with a high energy stirrer (T 18 ULTRA-TURRAX®, *IKA*) for 1 h at 5000 rpm. Aluminum foil was etched in 5 wt.-% KOH (60 °C, 60 s, *d* = 20 μm), cleaned with purified water and then directly coated with the slurry using a doctor blade (wet film = 120 μm, dry film = 22–24 μm). The sheets were dried in an oven at 80 °C for 15 h, stamped into discs of 12 mm diameter and dried for 48 h (120 °C at 10^{-3} mbar). The electrode composition was 85 wt.-% LFP P2, 10 wt.-% Super P and 5 wt.-% Na–CMC and had a load of ~2.85 mg cm^{-2} ≙ ~2.42 mg cm^{-2} LFP.

2.4. MEEP gel polymer preparation and drop coating

In a dry room (H_2O content < 10 ppm), a mixture of MEEP (including 5 wt.-% benzophenone as cross-linker) with the liquid electrolyte (LE) made of 0.7 mol L^{-1} LiBOB in EC/DMC (1:1) was stirred for 2 h to ensure complete homogenization. The electrodes (LFP and metallic lithium) were drop coated with 40 μL of the prepared electrolyte solution. While cooling the coated electrodes with dry ice, the polymer was simultaneously cross-linked by UV-irradiation within 7 min. The thickness of the gel polymer electrolyte coating was ~300 μm. Using smaller amounts of the electrolyte solution in the drop coating process leads to thinner coatings. Anyway, a relatively thick electrolyte coating was used to enhance safety and long-term cycling capability by lowering the