

Chemically controlled protective film based on biphenyl derivatives for high potential lithium battery



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ABSTRACT

High potential cathodes are of strong interest to improve lithium-ion battery performances, nevertheless, no compatible electrolyte above 4.5–4.8 V vs Li⁺/Li was found yet. The main strategies involved the use of protective film inhibiting and/or delaying electrolyte degradation. In this context, we focused on the use of adapted modified biphenyls to form a protective film at the positive electrode. Particularly phosphate biphenyl derivatives oxidation permits to produce a protective film which significantly decreases the self-discharge without compromising the lithium intercalation kinetic.

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1. Introduction

Lithium ion batteries are the most competitive power sources for high capacity energy storage, thanks to their high energy density and power capability. In order to improve the performances of the cell in term of energy density or to replace graphite electrode which induces security issue for high-power applications, numerous researches are dedicated to the elaboration of high potential cathodes. Potentials up to 4.9 V vs Li⁺/Li can be reached in LiMn_{2-x}M_xO₄ (LMN) spinel oxides (M = Ni, Fe) [1,2] but this potential is incompatible with the use of regular LiPF₆/carbonate electrolytes which are oxidized close to 4.5 V vs Li⁺/Li [3] on non-active electrodes (i.e. platinum, glassy carbon, etc.). In addition, when operating with active positive electrode materials and carbon used as electronic conductor, the catalytic oxidation of the electrolyte at lower potential than an inactive electrode is observed [3]. Upon cycling in a LiPF₆-based electrolytes, most positive electrodes are covered by highly resistive LiF, Li_xPF_y, Li_xPO_yF₂ fluorophosphates and organic and polymeric materials [4–8]. This high reactivity leads to a rapid self-discharge process (up to 80% per month) using LiNi_{0.4}Mn_{1.6}O₂ as positive electrode [9]. Several additives are used in literature to overcome the electrolyte instability. The oxidation of additives at lower potential than that of the electrolyte induces the formation of conducting layers [10,11] or insulating ones [12–14] which reduce the reactivity of the electrolyte and improve the capability retention of the cell. In these cases polymeric material deposited

(borate, polycarbonate and phosphorous derivatives respectively) onto the active surface of the electrode lower or suppress the decomposition of both solvent and salt in the electrolyte without harming to the lithium exchange.

Following the same strategy, we focused on the use of functionalized biphenyl derivatives in order to decrease the reactivity of the positive active material LiMn_{1.6}Ni_{0.4}O₄ toward electrolyte and then to limit the self-discharge. Indeed, polymeric controlled film can be achieved through oxidation of biphenyl function [15,16] at a potential consistent with the use of high potential positive electrode. In addition, in order to introduce polar function with solvation ability toward Li⁺, highly chemical stable phosphate group was chosen as additional functional group. Thanks to the two additives properties, polymeric material issued from oxidation of biphenyl derivatives should exhibit a protective effect and prevent high polarization induces by a non-solvating film at the electrode surface. The effect of the phosphate group position on the aromatic ring on the electrochemical properties of the additives was examined. In addition, the electrochemical properties of the resulting polymeric film was evaluated on platinum electrode and then for the more relevant additive on LiMn_{1.6}Ni_{0.4}O₄ electrode.

2. Experimental

2.1. Synthesis

¹H NMR (300.12 MHz) spectra were run on Bruker Advance 300 spectrometer and obtained from CDCl₃ (δ_H: 7.26 ppm). Multiplicities are reported as follows: ddt = doublet of doublet of triplet, dt = doublet of triplet, dq = doublet of quadruplet, ds^t = doublet of

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sextuplet, t = triplet, tt = triplet of triplet, m = multiplet, coupling constants J are reported in Hz.

2.1.1. General procedure (Scheme 1)

To 150 mL tetrahydrofuran (THF) containing the phenolic derivative, NaH was added at room temperature and under argon. After 2 h reaction, the solution was cooled at 0 °C and chlorophosphate derivative was added. After 2 h at 0 °C, the mixture was maintained at 40 °C during 48 h. After addition of 10 mL of an aqueous solution of NaHCO₃ (0.1 mol L⁻¹), the product was extracted with dichloromethane. The organic phases were evaporated, and the product was purified by column chromatography on silica gel with dichloromethane/methanol (99/1) as eluent. The pure product was dried at 60 °C in vacuum and then stored in glove box. Yields range from 60% to 70% according to the synthesized compound.

2.1.2. Synthesis of 4-ethylphosphate-bis(biphenyl), 4EPbisBP

This product was prepared starting from 4-phenylphenol (2.5 g, 14.69 mmol), NaH (352 mg, 14.69 mmol, 1 equiv.) in THF (150 mL) and ethyldichlorophosphate (0.72 mL, 6.12 mmol, 0.41 equiv.) using the general procedure.

¹H NMR δ : 1.42 (dt, 3H, $J = 7.2$ Hz, $J = 1.0$ Hz, CH₂CH₃); 4.39 (dq, 2H, $J = 8.4$ Hz, $J = 7.2$ Hz, CH₂CH₃); 7.28–7.38 (m, 6H, H_{ar}); 7.43 (dt, 4H, $J = 7.2$ Hz, $J = 1.8$ Hz, H_{ar}); 7.52–7.60 (m, 8H, H_{ar}).

2.1.3. Synthesis of 4-diethylphosphate biphenyl, 4DEPBP

The title product was prepared from 4-phenylphenol (2 g, 11.75 mmol), NaH (282 mg, 11.75 mmol, 1 equiv.) in THF (150 mL) and diethylchlorophosphate (2.54 mL, 17.58 mmol, 1.5 equiv.) using the general procedure.

¹H NMR δ : 1.37 (t, 4H, $J = 7.2$ Hz, CH₂CH₃); 1.38 (t, 4H, $J = 6.9$ Hz, CH₂CH₃); 4.23 (dq, 2H, $J = 7.2$ Hz, $J = 1.3$ Hz, CH₂CH₃); 4.26 (dq, 2H, $J = 6.9$ Hz, $J = 1.3$ Hz, CH₂CH₃); 7.26–7.32 (m, 2H, H_{ar}); 7.32–7.38 (m, 1H, H_{ar}); 7.40–7.47 (m, 2H, H_{ar}); 7.52–7.61 (m, 4H, H_{ar}).

2.1.4. Synthesis of 4,4'-diethylphosphate biphenyl, 4,4'DEPBP

The title product was prepared from 4,4'-dihydroxybiphenyl (2 g, 10.74 mmol), NaH (564 mg, 23.50 mmol, 2.2 equiv.) in THF (150 mL) and diethylchlorophosphate (5 mL, 34.60 mmol, 3.2 equiv.) using the general procedure.

¹H NMR δ : 1.37 (t, 6H, $J = 7.2$ Hz, CH₂CH₃); 1.38 (t, 6H, $J = 6.9$ Hz, CH₂CH₃); 4.22 (dq, 4H, $J = 7.2$ Hz, $J = 1.3$ Hz, CH₂CH₃); 4.26 (dq, 4H, $J = 6.9$ Hz, $J = 1.3$ Hz, CH₂CH₃); 7.28 (ddt, 4H, $J = 9.0$ Hz, $J = 2.8$ Hz, $J = 1.0$ Hz, H_{ar}); 7.50 (ddt, 4H, $J = 9.0$ Hz, $J = 2.8$ Hz, $J = 1.0$ Hz, H_{ar}).

2.1.5. Synthesis of 2,2'-diethylphosphate biphenyl, 2,2'DEPBP

The title product was prepared from 2,2'-dihydroxybiphenyl (2 g, 10.74 mmol), NaH (564 mg, 23.50 mmol, 2.2 equiv.) in THF (150 mL) and diethylchlorophosphate (5 mL, 34.60 mmol, 3.2 equiv.) using the general procedure.

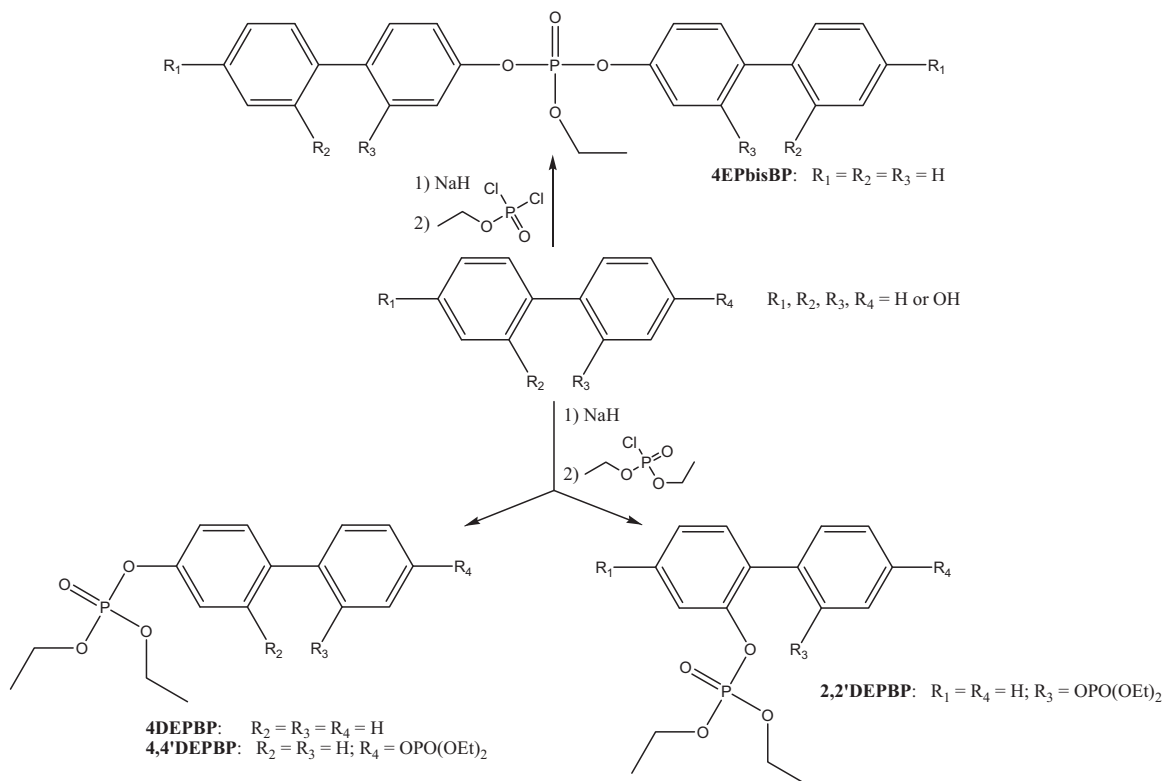
¹H NMR δ : 1.14 (dt, 12H, $J = 7.0$ Hz, $J = 0.7$ Hz, CH₂CH₃); 3.87 (ds^t, 8H, $J = 7.2$ Hz, $J = 2.9$ Hz, CH₂CH₃); 7.19 (tt, 2H, $J = 7.5$ Hz, $J = 0.9$ Hz, H_{ar}); 7.29–7.35 (m, 4H, H_{ar}); 7.41 (dt, 2H, $J = 8.7$ Hz, $J = 1.2$ Hz, H_{ar}).

2.2. Electrolyte

Acetonitrile (Rathburn) + 1 M tetraethylammonium tetrafluoroborate (TEABF₄, Aldrich) was used for the electrochemical investigations performed on platinum electrode. Ethylene carbonate/propylene carbonate/dimethyl carbonate (1/1/3 by vol) + 1 M LiPF₆, Purolite[®] purchased by Ferro was used as electrolyte with active material as working electrode and during cycling tests.

2.3. Electrochemical investigation

Cyclic voltammetry (CV) was performed at ambient temperature in glove box. The counter electrode was a Pt wire, and the working electrode was a Pt disk (diameter: 3 mm). The reference electrode was an Ag wire in AgNO₃ 10 mM in acetonitrile + 0.1 M



Scheme 1. Synthesis of the phosphate biphenyl derivatives.

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