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Short communication

New covalent salts of the 4+ V class for Li batteries

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ABSTRACT

There is urgent action required for replacing $LiPF_6$ as a solute for Li-ion batteries electrolytes. This salt, prone to highly Lewis acidic PF_5 release and hydrolysis to HF is responsible for deleterious reaction on carbonate solvents, corrosion of electrode materials leading to safety problems then release to toxic chemicals. A major advantage of $LiPF_6$ is that it passivates aluminium. Most attempts to replace $LiPF_6$ with hydrolytically-stable salts have been unsuccessful because of Al corrosion.

We present here two "Hückel" type salts, namely lithium (2-fluoroalkyl-4,5-dicyano-imidazolate); fluoroalkyle = CF_3 (TDI), C_2F_5 (PDI) with high charge delocalization. These thermally stable salts give both appreciably conductive solutions in EC/DMC (>6 mS cm^{-1} at 20 °C) with a lower decrease with temperature than $LiPF_6$. Non fluorinated lithium (4,5-dicyano-1,2,3-triazolate) is comparatively less than half as conductive. The lithium transference number T_+ measured by PFG-NMR is also higher. Voltammetry scans with either platinum or aluminium electrodes show an oxidation wall at 4.6 V versus Li^+:Li°. These two salts are thus the first examples of strictly covalent, non-corroding salts allowing 4+ V electrode material operation. This is demonstrated with experimental $Li/LiMn_2O_4$ cells as beyond the third cycles, the fade of the three electrolytes were quasi-identical, though $LiPF_6$ had a sharper initial decrease.

1. Introduction

The electrolyte is arguably the most critical component in batteries, as it should maintain its functions in contact with both the reducing negative electrode and oxidizing positive. This is especially true for lithium batteries where a 4+ V voltage span inevitably depends on the metastability of the electrolyte versus at least one electrode. Great hopes now rest on these batteries, beyond their undeniable success in portable electronic, with scale-up to a progressive electrification of transportation modes to EVs, HEVs and plug-in HEVs. Most of the research effort came after the first practical "Lithium-ion" (LIB) technology in 1991, where Li^+ is shuttled between two intercalation compounds, now established mainly as graphite (−) and cobalt-based layered oxides (+), manifestly the most extreme voltages that can be operated "safely", though the list of incidents due to runaway reactions becomes longer with @ 10^9 batteries in operation. The miracle(s) taking place within batteries 10–100 g is unlikely to scale-up for the 200 Kg of an EV. Mixture of carbonates, and $LiPF_6$ as solute are used in the quasi-totality of LIBs because of their high conductivity, but the determining factor is the absence of corrosion of aluminium current collectors at high anodic voltages (>4.5 V *vs.* Li^+:Li°), i.e. well beyond the thermodynamic potential (1.3 V), and no other metal can offer a substitute in terms of cost, weight and malleability. The drawbacks of $LiPF_6$ are severe: (i) the high conductivity is relative as the transport number is low [1]; (ii) the tendency to dissociate into LiF and PF_5 with the latter inducing cationic chemistry deleterious to electrolyte; (iii) the facile hydrolysis to HF, inducing corrosion of the cathode materials, for instance Mn dissolution in $LiMn_2O_4$. The leached-out species after diffusing to negative electrode modify the SEI, raising its impedance, with resulting overheating and dramatic safety issues; (iv) combustion releases copious amount of HF; (v) less spectacular than a fire, smouldering, i.e. the reaction at high temperature with ethylene carbonate yields a derivative of fluoroethanol, a family of exceedingly toxic (LD 50 = 0.5 mg kg^{-1} in mice) chemicals [2].

Of the possible substitutes for $LiPF_6$, none of the classical $LiAsF_6$, $LiSbF_6$, $LiClO_4$ are close to meeting safety or innocuousness requirement. The "designer" anion $[(CF_3SO_2)_2N]^-$ developed for polymer electrolytes (now also successful as ionic liquid component) would be ideal, except its crippling lack of aluminium protection. Conversely, the coordination anion, (bisoxalato)boron (BOB) ion, does passivate aluminium, but oxidises with gas evolution (CO_2) specially above room temperature. Besides, the high rigidity/bulk of the molecule induces unfavourable phase diagrams at low

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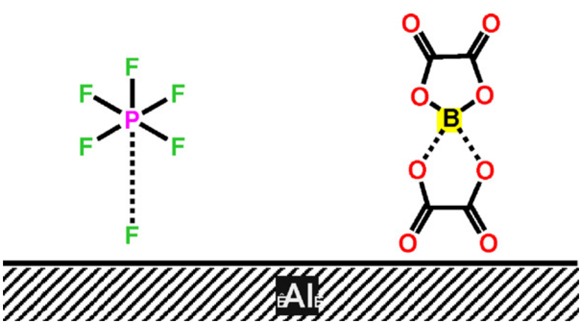

Fig. 1. Scheme of Al passivation with labile coordination salts.

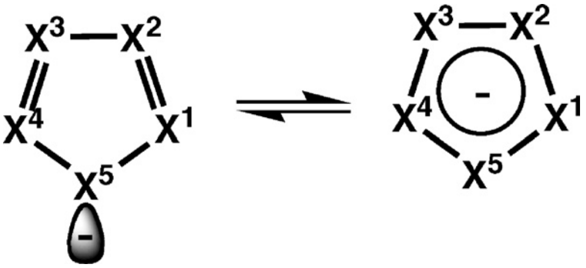

Fig. 2. The structure of "Hückel" anions: X = N, CCN, CCR_F, etc.

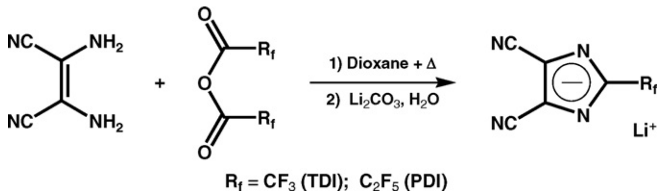

Fig. 3. Synthesis scheme for LiTDI and LiPDI.

temperature. Conventional wisdom suggests that the lability of F^- and $C_2O_4{}^{2-}$ from $PF_6{}^-$ resp. BOB^- is the reason for passive film formation (Fig. 1). A promising substitute for $LiPF_6$ is $Li[FSO_2NSO_2F]$ (LiFSI) which does not corrode aluminium up to at least 4 V. The cleavage of the S–F bond, (though more covalent than P–F) suggests that the passivating layer on Al is AlF_3, a compound with high lattice energy, and used in microelectronics to protect Si for F-plasma etching. In similarity, the oxalate anion whose chelate "pincer" gap is more adapted to Al than B radii, would adsorb also (Fig. 1).

The question thus is the existence of a truly covalent anion, not prone to hydrolysis and irreversible HF, yet able to form a passivating layer on Al°, or at least preserve the native Al_2O_3 layer. Several years ago, we have introduced the concept of "Hückel anions" [3] (Fig. 2), i.e. the delocalization of 6 "π" electrons on an aromatic 5-membered ring. A wealth of compounds with ring nitrogen a and/or CN in the periphery [4,5] have been modelled and show very weak Li^+–anion interactions, especially as the CN substitution increases. The simple representative, 4,5-dicyano-1,2,3-triazole (DCTA) has favourable conductivities in PEO electrolytes [6]. To further increase the resistance to oxidation and lessen the ion-pair formation, replacement of central N by C–CF_3 or C_2F_5 to 4,5-dicyano-2-trifluoromethyl-imidazole and 4,5-dicyano-2-pentafuoroethyl-imidazole (TDI and PDI respectively) has, also in PEO electrolytes, showed excellent conductivities and favourable phase diagram. No oxidation was seen before the polyether own limit (4 V) [6]. We inferred that these salts deserved further investigation in classical liquid electrolytes, as a covalent salt is of considerable technological advantage, without the release of a strong Lewis acid like PF_5 able to induce a series of deleterious reactions with solvent and avoid the formation of fluoroethanol derivatives, unacceptable for general application of EVs. These salts will be compared with the non-fluorinated LiDCTA and $LiPF_6$.

2. Experimental

TDI and PDI are made in a one-pot reaction from commercial chemicals (Fig. 3) in respectively 55 and 50% yield [7,8]. The two white powders were dried at 150 °C for12 h in a Büchi TO-50 oven prior to being used and kept in a dry box. LiDCTA was made from the reaction of diamino-maleonitrile with *tert*-butyl nitrite in diethyl ether à 0 °C for 48 h. The turbid yellow suspension was centrifuged and stripped from solvent. Crude 4,5 dicyanotriazole was sublimed in vacuum (80 °C) to obtain the pure acid. The Li salt was made in ethanol by reaction on 10% excess of Li_2CO_3, filtration and drying. $LiPF_6$ 1 M in EC/DMC (50/50, w/w) was obtained from Merck (LP30®).

Coupled thermogravimetric and DSC traces between RT and 300 °C under a constant flow of argon (50 ml min^{-1}) were acquired with a Netzsch Jupiter STA 449 C thermal analyser at a heating/cooling rate of 10 °C min^{-1}. The isothermal drift and sensitivity values are 0.6 μg h^{-1} and 0.1 μg, respectively. Aluminium crucibles were loaded with 25 mg of the salts and sealed in the dry box. A small hole was punched in the lid just prior to loading in the apparatus.

Conductivity measurements were performed using a CDC749 (Radiometer Analytical) cell. All the electrochemical experiments were conducted at 20 °C using a VMP3 system (Biologic S.A., Claix, France) with a 1 M lithium salt dissolved in EC/DMC (50/50, w/w) solvents mixture.

PFG-NMR diffusion measurements were carried out on 9.4 T Bruker Avance 400 NMR spectrometre equipped with a Bruker 5 mm broadband probe with a *z*-axis gradient and a temperature controller (stability and accuracy 0.2 °C). NMR resonance frequencies are 400.1 MHz, 376.50 MHz and 155.51 MHz respectively for 1H, 19F and 7Li nuclei. The self-diffusion measurements were performed with the pulsed field gradient stimulated echo and LED sequence using 2 spoil gradients (PFG NMR) [9]. The magnitude of the pulsed field gradient was varied between 0 and 40 G cm–1, the diffusion time Δ between two pulses was fixed at 100 ms and the gradient pulse duration δ was set between 3 and 10 ms depending on the diffusion coefficient of mobile species. This allowed us to observe the attenuation of spin echo amplitude over a range of at least 2 decades leading to a good accuracy (<5%) of the self-diffusion coefficient values. They were determined from the classic relationship $A/A0 = \exp[-Dg^2\gamma^2\delta^2(\Delta - \delta/3)]$ where g is the magnitude of the two gradient pulses, γ is the gyromagnetic ratio of the nucleus under study and A and $A0$ are respectively the area of the signal obtained with or without gradient pulses.

Cyclic voltammetry measurements were acquired at a scan rate of 30 mV s^{-1}, in the 0.5–6 V or 0.01–6 V potential ranges (*vs.* Li^+:Li°). An Al or Pt wire was used as working electrode, a Pt wire as counter electrode and metallic Li as reference electrode.

Galvanostatic tests were performed in Swagelok® cells using a plastic positive electrode on an Al disk containing 64 wt% $LiMn_2O_4$, 8 wt% SP carbon, and 28 wt% poly(vinylidene fluoride)-co-hexafluoropropylene (PVdF-HFP) copolymer binder (the electrode films were cast and processed using a procedure previously reported) [10], a 1 cm disk of Li foil as the negative electrode, and a Whatman GF/D borosilicate glass fibre mat separator. The electrode rate capability was determined via the collection of a signature curve as the function of the salt. After a low rate charging, the cell was successively discharged at decreasing rates (5 C, 2.5 C, 1 C, 0.5 C, C/5, C/10 and C/20) with a relaxation time of 30 min between each step.