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Boron Esters as Tunable Anion Carriers for Non-Aqueous Batteries Electrochemistry

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Abstract: Compounds like LiF, Li_2O, and Li_2O_2 have considerable importance in batteries; the first two are ubiquitous in the protective SEI at the negative electrode, or the result of conversion reactions with fluorides and oxides. The latter, Li_2O_2, forms from oxygen reduction in the much vaunted Li/air batteries. Mastering their solubility in Li-based electrolytes is viewed as essential for further progress in battery safety, lifetime, or capacity. Aprotic solvents cannot provide the H-bonds necessary to their dissolution, and simple practical solutions have yet to materialize. Here we disclose a novel and large family of boron esters of general formula $Y-C((CH_2O)(Z_1O)(Z_2O))B$ whose Lewis acidity stems from geometrical constraint and can be tuned via electron affinity either by $Y = CH_3 \Rightarrow Y = NO_2$ or $Z_{1,2} = CH_2 \Rightarrow Z_{1,2} = CO$ so as to partially or fully dissolve the above compounds both in battery solvent EC/DMC and in DMF. The extreme simplicity of synthesis and variability of these boron-based anion carriers, where the exchange rate is fast, are not only a valuable addition to coordination science but also a step forward to improve present battery systems.

1. Introduction

Electrochemistry has been mainly confined to aqueous systems where all the dissociation and complexation constants have been established. In comparison, either molten salts or nonaqueous solvents represent a much smaller fraction of data. Nonprotogenic solvents (customarily “aprotic”) allow the extension of the potential window beyond that of water but have received little industrial use due to lower conductivities, and ionic liquids may prove more adequate for metal electrowining. The main application of organic solvents is as electrolytes for lithium batteries where metastability and the formation of a friendly passivation layer (SEI) allow spanning up to 4.8 V in lithium-ion batteries. Beyond portable electronics, the latter are now considered for much wider applications in the transportation sector with EVs, HEVs, and Plug-in HEVs, all more or less contributing to urgent CO_2 abatement.

The organic carbonates used in battery electrochemistry, as typical aprotic solvents, have little ability to solvate small negative charges due to the lack of hydrogen bonding. Yet, anions like F^-, OH^-, O^{2-}, and O_2^{2-} have considerable importance in lithium battery operation. The SEI on the negative electrode contains ubiquitously Li_2O and LiOH from the reduction of the solvents or adventitious water, while LiF is also found resulting either from reductive elimination on the anion or from nucleophilic attack of PF_5 by CH_3O^-, in turn a result of $O{=}C(OCH_3)_2$ reduction.[1] Controlling the SEI is of uttermost importance for safety and cycle-life of the cells, while its excessive thickness results in irreversible capacity loss and increased impedances.

Considering the intrinsic limitations of intercalation (i.e., 0.5−1 e^-/transition metal or LiC_6), the so-called “conversion” reactions have been proposed. In particular, for negative electrodes, the *in situ* reduction of, for example, $MO + 2\,Li^+ + 2e^- \Leftrightarrow M° + Li_2O$ (M = Co, Ni, Mn...) becomes partially reversible due to the nano sizes of the phases formed.[2] The large specific capacities obtained are appealing, but the charge and recharge processes are separated by almost a volt, reducing the energy efficiency. It is conjectured here that partial solubilization of Li_2O could bypass the rate-limiting diffusion path in the solid state, thus reduce this polarization.

The staggering capacity of lithium-air batteries justifies intensive research on the subject. O_2 reduction in aprotic solvents results in the transient formation of $O_2^{\bullet-}$ radical anion, further reduced (or disproportionating) in the presence of Li^+ to Li_2O_2 at ≈ 2.8 V vs Li°.[3,4] This insoluble salt progressively clogs the pores of the air electrode, mechanically limiting the capacity. Besides, the reoxidation to dioxygen occurs only at much more positive potentials (3.5−4 V), presumably a corollary of the insolubility of Li_2O_2, justifying a mean to improve its solubility. Also for positive electrode materials, graphite fluoride CF_x shows excellent electroactivity, but only in primary cells.[5] The possibility to adapt this high capacity electrode to secondary

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(1) Gachot, G.; Grugeon, S.; Armand, M.; Pilard, S.; Guenot, P.; Tarascon, J.-M.; Laruelle, S. *J. Power Sources* **2008**, *178*, 409–421.

(2) Poizot, P.; Laruelle, S.; Grugeon, S.; Dupont, L.; Tarascon, J.-M. *Nature (London)* **2000**, *407*, 496–499.

(3) Abraham, K. M.; Jiang, Z. *J. Electrochem. Soc.* **1996**, *143*, 1–5.

(4) Ogasawara, T.; Debart, A.; Holzapfel, M.; Novák, P.; Bruce, P. G. *J. Am. Chem. Soc.* **2006**, *128*, 1390–1393.

(5) Fukuda, M.; Iijima, T. *Lithium Batteries*; Academic Press: New York, 1983; pp 211−239.

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batteries and rebuild C−F bonds is a dream scenario that could depend on the solubilization of the LiF formed upon reduction.[6]

Protonated aza-crowns can act as anion traps,[7] but the resulting entities remain multiply charged cations with the limitations of hydrogen bonds in terms of electrochemical stability. Cleverly, the similar use of aza-crowns but in which the NH proton has been replaced by the strongly electron-withdrawing group CF_3SO_2, inducing a partial positive charge on nitrogen, have also been proposed, but they are exceedingly complex to make and heavy.[8] Calixarenes can solvate anions, but of larger sizes (I^-, $CF_3SO_3^-$...) and again rely on hydrogen bonds.[9]

The simplest strategy to increase the solubility of small anion salts in the absence of hydrogen bonds is to resort to Lewis acids able to bind to the anions strongly enough to overcome the large lattice energy of, for example, LiF and Li_2O. Boron, with its valence of 3 and tendency to sp^3 4-fold coordination leaving an empty "p" orbital, is the candidate of choice for building Lewis acids. BF_3 is the archetype of such strong acids. On the other hand, boron esters are only weakly acidic because of extensive participation of the oxygen "p" orbitals, resulting in a planar configuration of $B(OR)_3$ compounds. Back-bonding also occurs partially in BF_3 but cannot counter the large electronegativity of fluorine. When BF_3 complexes F^-, the resulting stable BF_4^- is a well-known non-nucleophilic anion. Yet, BF_4^- cannot be considered as a fluoride ion carrier since the exchange of solvation shell around the boron nucleus is slow, and thus it cannot release F^- other than under forcing conditions (high temperature, reaction with highly electrophilic phenyl cations in the Balz-Schiemann reaction...). Organic moieties attached to boron do not possess electron pairs, are thus immune to back-bonding. While $B(CH_3)_3$ is too easily oxidized, the aromatic $B(C_6H_5)_3$ is somewhat more stable and able to dissolve CsF but not LiF, though the complex with CH_3^- has been tentatively proposed as battery electrolyte[10] despite an anodic limitation at 3.5 V. The perfluorinated analogue $B(C_6F_5)_3$ (TPFPB) has recently been enjoying a spate of interest due to its strength as Lewis acid, expressed by the dissolution and conductivity enhancement of LiF, Li_2O and Li_2O_2 by several orders of magnitude.[11,12] In fact, a wealth of organo-boron Lewis acids have been either synthesized or computed to evaluate their strength,[13] and TPFPB appears the strongest, and this parallels the degree of fluorination of the molecules. Very recently TPFPB had been shown to form adducts with already weakly coordinating anions like $C(CN)_3^-$ forming $C(CN{\Rightarrow}TPFPB)_3^-$.[14] Such behemoths with $M_w \gg 1000$ are not likely to play a role in battery electrochemistry. TPFPB itself is a very difficult molecule to prepare and, thus, expensive and not predictably suitable for large-scale use. The aromatic C−F bonds may be prone to facile reduction and cleavage due to the ease of electron injection in the depleted "π" system. The large steric hindrance of the three phenyl rings likely prevents coordination by multi B centers (e.g., $\equiv B \Leftarrow O \Rightarrow B\equiv$) in the ≈109° sp^3 conformation, desirable to further spread the charge of divalent anions.

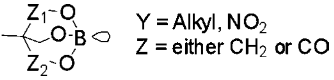

Figure 1. General formula of the borate compounds.

In this context, we have embarked on the design of tunable strength Lewis acids, simple to make and with robust chemical bonds to encompass a wide voltage stability range. Figure 1 represents the general formula of the family of compounds that have been retained for study.

It was expected that the forced positioning of the oxygens from the boron ester group in three of the four sp^3 positions would prevent the overlap of oxygen "p" electrons with the B empty orbital, raising considerably the Lewis acid strength of the latter. Further, the electron withdrawing ability of the molecule could be adjusted by substituting the Y = alkyl by electronegative NO_2, or replacing sequentially CH_2 groups by C=O, turning the moieties into carboxylic acids.

We report here an electrochemical assessment of this family of molecules, based mainly on conductivity studies to conclude on the pertinence of the design.

2. Experimental Methods

2.1. Synthesis. The Lewis acids were all prepared from a simple transesterification step by reacting $B(OR)_3$ on $Y{-}C(ZOH)_2CH_2OH$ with $Y = CH_3$ and $Z = CH_2$ or CO or $Y = NO_2$ and $Z = CH_2$ in the presence or absence of the salt to form adducts.

The starting compounds with $Z^1 = Z^2 = CH_2$ are commercial with $Y = CH_3$, C_2H_5, NO_2. Only $Y = CH_3$ and NO_2 are reported here, (1,1,1-tri(hydroxymethyl) ethane (97%), tris(hydroxymethyl) nitromethane (98%). Similarly, the compound $Z^1 = CO$, $Z^2 = CH_2$ (2,2-Bis(hydroxymethyl) propionic acid (DMPA, 98%) is available from commercial suppliers Aldrich, Fluka, or Alfa and used as received.

Methyl(hydroxymethyl)malonic acid was prepared as follows: to 3.72 g (20 mmol) commercial diethyl(methylmalonate) were added under stirring 21 mols of 37% formaldehyde in water, 10 mL of ethanol and a drop of catalytic DBU (1,8-diazabicyclo[5.4.0]undec-ene). Warming ensued and the mixture became homogeneous after a few minutes. Twenty milliliters of water were added with 1.49 g (23 mmol) of $Ca(OH)_2$ and the slurry was kept at 35 °C for 48 h under stirring for saponification. The white precipitate of $(CH_3)C(CH_2OCH)(CO_2)_2Ca$ was centrifuged and washed 3 times with 20 mL 5% acetic acid to remove excess $Ca(OH)_2$, then with ethanol and dried. Thermo gravimetric analysis showed the produce to be anhydrous. The free acid was obtained in ethanol by reaction between 1.05 equivalent of the Ca salt and 1 equivalent of anhydrous oxalic acid in methanol, centrifugation, and solvent evaporation to yield crystalline $CH_3C(CH_2OH)(CO_2H)_2$. All solvents were handled in a drybox under Ar ($H_2O < 0.1$ ppm, $O_2 < 0.6$ ppm) and were anhydrous grade.

2.2. ESI-HRMS Measurements. ESI-HRMS experiments were performed on a Q-TOF Ultima Global instrument (Waters-Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ion source (Z-spray) and an additional sprayer for the reference compound (LockSpray). The samples, dissolved in CH_3CN, were directly introduced (5 $\mu L min^{-1}$) via an integrated syringe pump in the electrospray source. The source and desolvation

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(6) West, W. C.; Whitacre, J. F.; Leifer, N.; Greenbaum, S.; Smart, M.; Bugga, R.; Blanco, M.; Narayanan, S. R. *J. Electrochem. Soc.* **2007**, *154* (10), A929−A936.

(7) Dietrich, B.; Guilhem, J.; Lehn, J.-M.; Pascard, Sonveaux, C. E. *Helv. Chim. Acta* **1984**, *67* (1), 91–104.

(8) Yang, X. Q.; Lee, H. S.; Xiang, C.; McBreen, J.; Choi, L. S.; Okamoto, Y. *Proc. Electrochem. Soc., 96−17(Lithium Polymer Batteries)* **1997**, 146–153.

(9) Kalita, M.; Solgala, A.; Siekierski, M.; Pawlowska, M.; Rokicki, G.; Wieczorek, W. *J. Power Sources* **2007**, *173* (2), 765–773.

(10) Horowïtz, H. H.; Habermann, J. I.; Kleemann, L. P.; Newman, G. H.; Stogryn, E. L.; Whitney, T. A. *Proc. Electrochem. Soc. 81−4 (Lithium Batteries)* **1981**, 131–143.

(11) Xie, B.; Lee, H. S.; Li, H.; Yang, X. Q.; McBreen, J.; Chen, L. Q. *Electrochem. Commun.* **2008**, *10*, 1195–1197.

(12) Li, L. F.; Xie, B.; Lee, H. S.; Li, H.; Yang, X. Q.; McBreen, J.; Huang, X. J. *J. Power Souces* **2009**, *189*, 539–542.

(13) Chen, Z.; Amine, K. *J. Electrochem. Soc.* **2009**, *156* (8), A672−A676.

(14) Bernsdorf, A.; Brand, H.; Hellmann, R.; Köckerling, M.; Schulz, A.; Villinger, A.; Voss, K. *J. Am. Chem. Soc.* **2009**, *131*, 8958–8970.

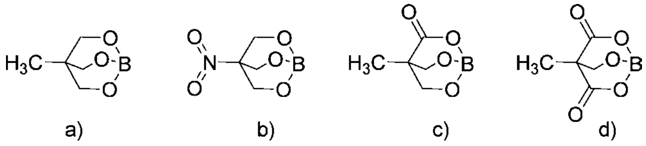


Figure 2. Four following compounds called herein (a) triol borate, (b) nitro-triol borate, (c) diol-monoacid borate, and (d) monoalcohol-diacid borate.

temperatures were kept at 80 and 120 °C, respectively. Nitrogen was used as a drying and nebulizing gas at flow rates of 350 and 50 Lh^{1-}, respectively. Calibration of the instrument was performed using the ions produced by a phosphoric acid solution (0.2% in H_2O/CH_3CN 50/50 v/v). For accurate mass measurements a lock mass correction, using appropriate cluster ions of phosphoric acid $[(H_3PO_4)_n + H]^+$ in the positive ion mode, and $[(H_3PO_4)_n - H]^-$ in the negative ion mode, was applied. The mass range was 50−1000 Da and spectra were recorded at 1s scan^{-1} in the profile mode at a resolution of 10 000 full-width at half-maximum (FWHM). Data acquisition and processing were performed with MassLynx v4.0 software.

2.3. NMR Studies. All NMR experiments were performed at 300.13 MHz using Bruker AVANCE 300 SB and WB spectrometers equipped respectively with a 5 mm QNP ($^1H/^{13}C/^{19}F/^{31}P$) probe with z-gradient for recording ^1H and ^{19}F spectra and a 8 mm BBO probe for ^{11}B. Measurements were performed at 300 K with careful temperature regulation. Samples were prepared after compound dissolution in appropriate deuterated solvents. Details concerning experimental conditions are given in the figure captions. Data acquisition and processing were carried out with XWIN-NMR 3.5 software.

2.4. Conductivity and Atomic Absorption Measurements. Conductivity and atomic absorption tests were made with LiF, NaF, or KF as potential sources of F^- or Li_2O, Li_2O_2 as sources of O^{2-} and O_2^{2-}, taken in excess (equivalent to 0.12M), added in DMF, EC-DMC 50/50 (w/w) in the presence or absence of 0.1 M of the boron complex, equilibrated for 24 h then centrifuged in the drybox.

Conductivity measurements were performed using a CDC749 (Radiometer Analytical) cell connected to a VMP (Biologic, Claix, France) electrochemical workstation. The reported values are average of 3 measurements with a relative standard error of less than 5%.

Li atomic absorption measurements were carried out using a AAnalyst 300 spectrometer (Perking Elmer). The instrument was first calibrated with Li (1, 2, 3 ppm), Na (0.5, 1 ppm), and K (1, 2 ppm) working standards made from their respective stock solution (1 g/L). Manually diluted samples were then aspirated into the air/acetylene flame where the Li, Na, and K atoms absorb light emitted from their respective hollow cathode lamp at 670.8, 589.0, and 766.5 nm.

2.5. Cyclic Voltammetry Measurements. CV scans were acquired on the same VMP workstation with a scan rate of 15 mV.s^{-1} in the 0.05−6 V potential range (versus $Li^+/Li°$). A Pt wire was used as Working and Counter Electrode and metallic Li as reference electrode. All tests were made with 0.1 M of the boron complexes dissolved in EC/DMC 50/50 (w/w) solvents mixture, and with 1 equiv of KF for diol-monoacid borate.

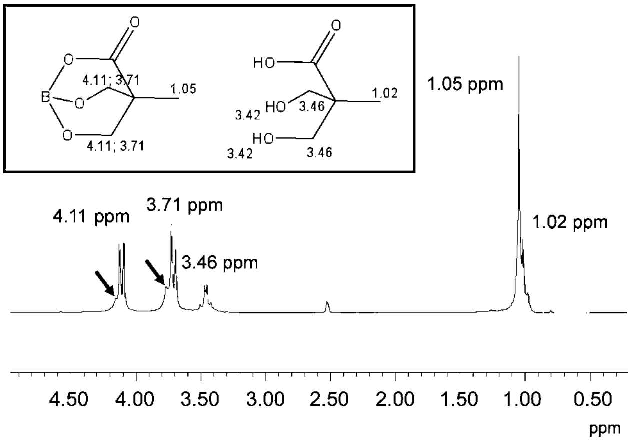


Figure 3. Partial 300 MHz ^1H NMR spectrum of diol-monoacid borate with residual DMPA recorded in DMSO-d_6 at 300 K.

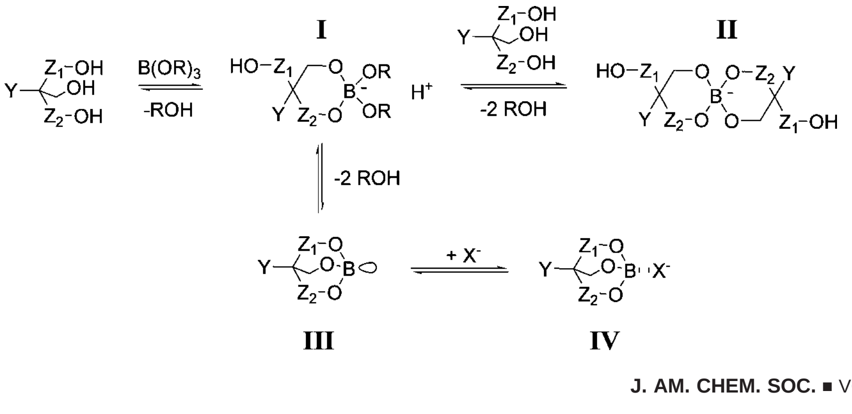
3. Results and Discussion

The four compounds are represented as closed shells in Figure 2. The tendency for boron to form spontaneously simple 5- and 6-member cycles with 1−2, 1−3 glycols and hydroxyacids in water is well-known and leads to mono cycles (**I**) or spiro compounds (**II**) with increased acidity. Scheme 1 is proposed according to the greater affinity of boron for alcohols than acids. This is corroborated by the facile hydrolysis of boron diacids complexes like BOB^- and $[B(C_2O_4)_2]^-$.

These various esters are expected to form easily in many solvents due to the ring closure, in the extreme case to three fused 6-membered rings in a stable 1,8 bicyclooctane configuration. Noticeably, the cooling observed upon esterification reflects the reduction of configurational entropy of the system, and addition of KF, sparingly soluble in ethanol, results rapidly in a clear liquid. In one case, the diol-monoacid acid ($Y = CH_3$, $Z^1 = CO$, $Z^2 = CH_2$) was tested in water. To 0.1 M of this compound in water (pH = 2.0) was added 1 equiv of boric acid and the pH dropped to 1.58. Addition of a second acid equivalent resulted in a pH of 1.45, hinting at the formation of at least the two successive complexes **I** and **II** (Scheme 1).

^1H NMR spectrometry (Figure 3) on the reaction product of equimolecular mixture of diol-monoacid acid and $B(OH)_3$ in methanol shows the formation of the expected diol-monoacid borate (**III**) (1.05 (s,3H); 3.71 (d,2H); 4.11(d,2H)), with small amount of the starting acid (14% in mole) (1.02 (s,3H); 3.46

Scheme 1. Formation Mechanism of Compounds **I**−**IV**



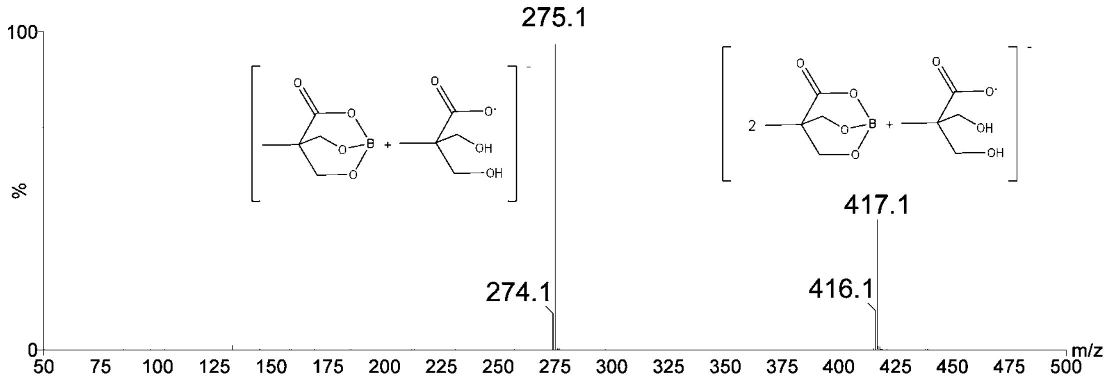


Figure 4. ESI-HRMS spectrum of the formation of diol-monoacid borate with trace of DMPA.

(d,4H)), suggesting an equilibrium between **I**, **III** and the initial reagents. However, the CH_2 prepeaks (Figure 3, arrows) are likely telltales for the presence of small amount of complex **II**.

The ESI-HRMS spectrum confirms the formation of the fully ring closed diol-monoacid borate (Figure 4). Indeed, in negative ionization, the formation of monocharged cluster [diol-monoacid borate, A]$^-$, (calcd for $C_{10}H_{16}O_8B = 275.0940$, found 275.0941 (0.4 ppm)) and [2 diol-monoacid borate, A]$^-$ (calcd for $C_{15}H_{23}O_{12}B_2 = 417.1382$, found 417.1373 (2.1 ppm)) can be observed (A^- being the starting acid, deprotonated within the ionization source). The first cluster 275.0940 *m*/*z* cannot be confused with compound **II** (Scheme 1) could not be the parent of the 417.1382 cluster.

For conductivity measurements, in addition to the workhorse in Li batteries that are the carbonate ester mixtures (ethylene carbonate + dimethyl carbonate 50:50 w/w), DMF was chosen as another solvent for this study though it is not one of the classical components of battery electrolytes. The reason for this choice was its high donicity (DN $\approx$ 28), reflecting its strong ability to solvate cations and its stability toward strong bases (F^-, O^{2-}, $O_2{}^{2-}$), in contrast with EC-DMC (DN $\approx$ 15), less solvating and where the C$-$O bonds are more fragile, which was one of our concerns.[1]

Figure 5 displays the conductivity variations for various salts in the presence of EC-DMC and DMF and 0.1 M anion carrier. As expected, the simplest triol borate behaves as a weak acid. There is no improvement of the conductivity in EC-DMC for LiF and NaF but a ~5-fold enhancement for KF, following the order of lattice energies LiF $>$ NaF $\gg$ KF that cannot be countered by the higher solvation enthalpy of Li^+. For the oxide species, neither Li_2O_2 nor Li_2O is affected, reflecting the double charge of the anions.

In DMF, however, only the very high lattice energy LiF and NaF are unaffected, KF, Li_2O, and Li_2O_2 approaching now 0.1 mS cm^{-1}. For this compound and all of the following ones, the relatively high values of the blank containing only the borate reflects probably the presence of protons from the **I** $\Rightarrow$ **II** and **I** $\Rightarrow$ **III** equilibria. These protons are then consumed for the formation of ROH (Scheme 1) as soon as an excess salt is added and the borate anion adduct **IV** is formed.

With Y = CH_3 ($\rho = -0.07$) replaced by strong electron-withdrawing NO_2 ($\rho = +0.71$), we observe an appreciable increase in conductivity in both solvents for all salts, more than 1 order of magnitude for KF, Li_2O, and Li_2O_2, and a 2-fold jump for LiF and NaF in DMF. A similar order in conductivity jump is also observed in EC-DMC with lower values due to the donicity of the cosolvents.

The first compound of the other family of borates, where the electron-withdrawing group (carboxylic) acid is directly attached to the boron center, is the diol-monoacid borate. The conductivity plots for the same salts now show further enhancement in conductivity. KF shows 2 orders of magnitude in both solvents and almost the same jump with Li_2O and Li_2O_2 whereas NaF gains almost 1 order of magnitude.

The last of this family, the monoalcohol-diacid borate, with two electron-withdrawing groups directly linked to the boron atom is the strongest Lewis acid borate of the series. Two CO_2H groups are the maximum possible in this configuration, the triacid undergoing decarboxylation spontaneously. Even methyl(hydroxymethyl)malonic acid used here is stable only up to 100 °C, before losing CO_2, as ascertained by DSC and TGA scans under argon (not shown). The adducts with different salts show, as expected, the most marked improvements in conductivity. KF, Li_2O, and Li_2O_2 at 2$-$3 mS cm^{-1} are strong electrolytes in DMF, comparable with the best lithium salts with highly delocalized anions at 0.1 M, the maximum authorized by the borate concentration. In less donating carbonates, only KF shows a seemingly total dissociation, in agreement with the lesser requirement for solvation of the large potassium ions. On the other hand, LiF and NaF conductivities do not change appreciably between the two solvents.

To confirm the gains in conductivity as correlated with concentration enhancements of the alkali metal cations initially absent from the electrolytes, atomic absorption measurements were conducted on supernatant electrolytes with different salts that have been equilibrated in the absence (blank) or presence of borate for 24 h, then centrifuged. The results for the diol-monoacid borate are shown in Table 1. In all cases, an increase in the solubility of the salts is observed, KF again showing the most spectacular increase.

An interesting question following the observation of the increase in solubility of these salts is their remaining basicity/nucleophilicity. F^-, $O_2{}^-$, and $O_2{}^{2-}$ when rendered soluble in aprotic solvents with the aid of large cations (cryptates, tetra alkyl ammonium/phosphonium...) show very powerful nucleophilic properties. Besides, the very toxic monofluoroethanol is formed in good yields when KF is heated in the presence of ethylene carbonate.[15] While the boron complexes forming an adduct with anions with high charge density are likely to reduce their basicity/nucleophilicity, is this effect counterbalanced by the large increase in solubility that may promote reactivity? If so, Li_2O and Li_2O_2 would react with carbonates with scission

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(15) Bergmann, E. D.; Shahak, I. *J. Chem. Soc. Section C: Organic* **1966**, *9*, 899–900.

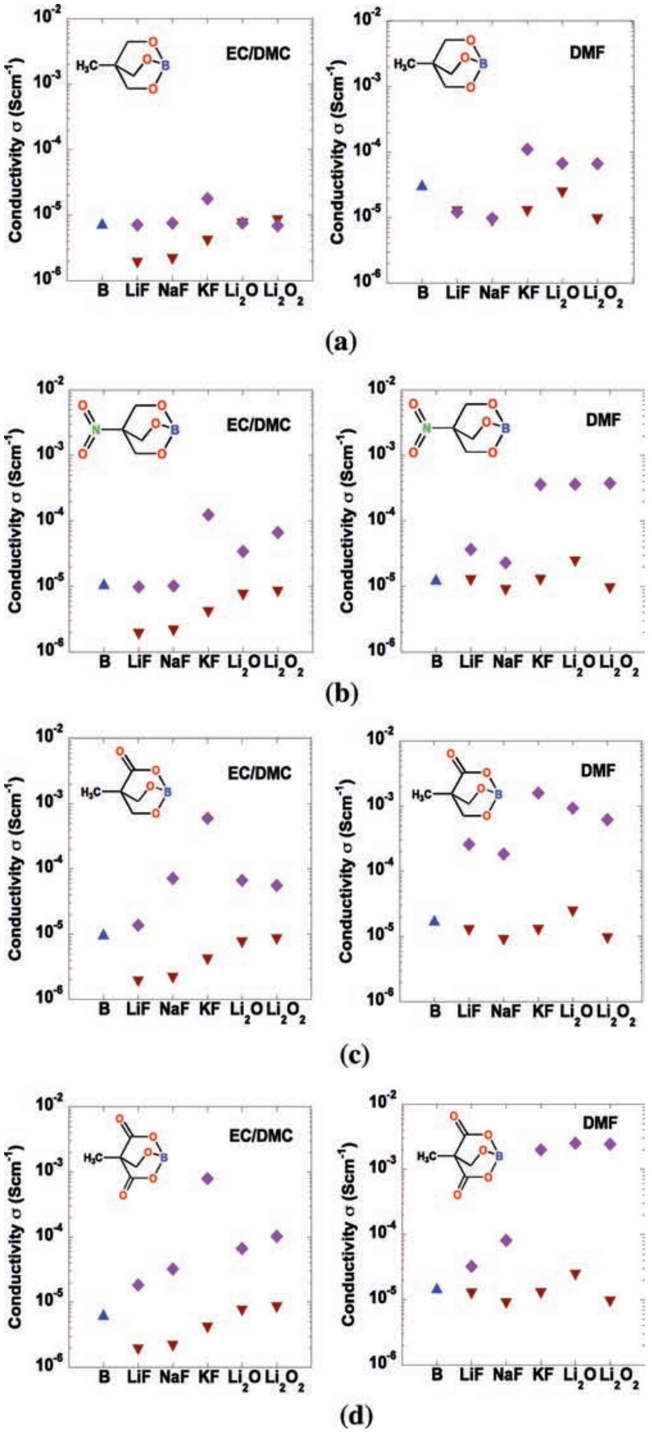

Figure 5. Conductivity variations of all the synthesized borates with LiF, NaF, KF, Li_2O, and Li_2O_2 in EC/DMC and DMF where (a) $CH_3C(CH_2O)_3B$; (b) $NO_2C(CH_2O)_3B$; (c) $CH_3C(CH_2O)_2CO_2B$; (d) $CH_3C(CH_2OH)(CO_2)_2$ and (blue) conductivity of 0.1 M borate, (red) conductivity of the salts in EC/DMC or DMF, and (purple) conductivity of 0.1 M salt with 0.1 M borate.

at the C−O single bond. To check this point, electrolytes resulting from steeping excess of lithium oxide or peroxide in EC-DMC mixture at 55 °C for 11 days in the absence or presence of diol-monoacid borate was analyzed. No evolution was visible to the naked eye, and this observation was confirmed by the MS analysis of the supernatant. Indeed, no peaks of significant amplitude signal the degradation of the electrolyte solvent. This result is of importance for the design of electrolytes both for the proper functioning of displacement reaction and for lithium/air batteries where the borates may prevent premature clogging of the electrode by Li_2O_2. $LiPF_6$, also somewhat sensitive to nucleophilic attack, is to be further tested and reported.

Table 1. Li_2O, Li_2O_2, LiF, NaF, and KF Salts Concentration Measurements by Li Atomic Absorption in the Absence or Presence of Diol-Monoacid-Borate (C = 100 mmol L-1) in EC/DMC or DMF Solvents

salt/diol-monoacid borate	salt concentration (mmol L-Salt or 1) EC/DMC	DMF
Li_2O	1.53 (±0.20)	0.29 (±0.20)
Li_2O/ borate	4.87 (±0.20)	28.82 (±1.50)
Li_2O_2	0.29 (±0.20)	0.29 (±0.20)
Li_2O_2/ borate	3.20 (±0.10)	7.28 (±0.20)
LiF	0.58 (±0.50)	0.29 (±0.50)
LiF/ borate	0.43 (±0.50)	9.60 (±0.40)
NaF	0.11 (±0.04)	0.07 (±0.05)
NaF/ borate	4.92 (±0.05)	5.36 (±0.25)
KF	0.41 (±0.10)	0.13 (±0.09)
KF/ borate	48.02 (±1.00)	81.83 (±4.00)

Another important property expected for an anion carrier is the ability to exchange rapidly the latter with either the liquid phase, or solid crystals containing it, to serve as a catalytic shuttle for the different uses under consideration. To show this, we decided to pursue our experiments on diol-monoacid (DMPA) borate with CsF or KF as a source of "free" (i.e., only H-bond solvated) F^-.

The coordination of fluoride to this borate could lead to the formation of four different fluoride adducts namely B_3F, B_2F, BF, and BF_2 (Figure 6). Indeed, the low steric hindrance of the borate allows to consider one, two or three borates linked to the same fluoride,[16,17] whereas BF_2 formation might be possible[18,19] due to the stronger B−F than B−O bond.

^{11}B NMR, ^{19}F NMR, and ESI-HRMS techniques were used to confirm the formation of these complexes. The complex formed from DMPA and $B(OCH_3)_3$ in DMSO-d_6 was analyzed by ^{11}B NMR. A very broad signal was observed at 21.62 ppm as shown in Figure 7. After the addition of KF, the spectrum shows the appearance of two fine lines at 4.26 and 5.35 ppm along with a broad signal at 5.50 ppm (arrow in Figure 7).

The change in peak aspect indicates a change in the boron electronic density environment. The sharp peaks could be attributed to the formation of BF and BF_2 compounds where the negative charge of the fluorine is shared by a single boron, while the broad signal could be attributed to B_3F and B_2F where, at least two borons share the negative charge of a fluoride.

Besides, owing to boron electronic density and signals multiplicity, B−F could be assigned to the sharpest line (doublet) at 5.35 ppm and BF_2 to the most shielded and largest line (triplet) at 4.26 ppm (Inset Figure 7).

In Figure 8a−e, the chemical shifts of ^{19}F for pure CsF and CsF:DMPA borate ratio of 1:4, 1:2, 1:1 and 1.5:1 in CD_3OD

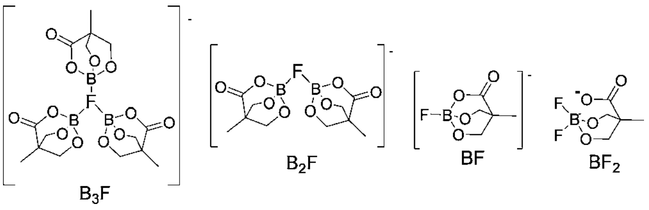

Figure 6. Four different fluoride adducts obtained from coordination of fluoride to diolmonoacid borate.

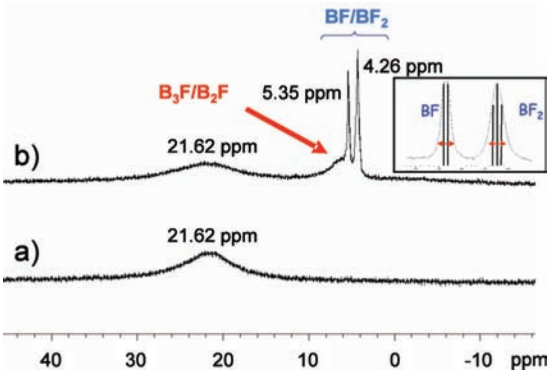

Figure 7. Partial ^{11}B NMR spectrum of (a) diol-monoacid borate (b) mixture of diol-monoacid borate and one equivalent of KF recorded in DMSO-d_6 at 300 K. (Inset) Zoom of the 5.35 and 4.26 ppm lines with extrapolation of the multiplicity of the peaks as deduced from their attribution to BF (doublet) and BF_2 (triplet).

are compared. Figure 8b shows four peaks at −48.9, −51.9, −53.8, and −55.9 ppm, which could be attributed to B_3F, B_2F, BF, and BF_2 compounds (in terms of increasing electron density on the fluoride atom, $B_3F < B_2F < BF < BF_2$), respectively. More specifically, the attribution of the BF and BF_2 peaks is strengthened by the fact that they do not present the classical aspect of a quadruplet but show four lines of approximately the same intensity (1:1:1:1) accordingly to the literature.[20]

With increase in the fluorine concentration, the signal of the most fluorinated compounds increases while that of B_3F compound begins to decrease, and then disappears, as observed in Figure 8e. Furthermore, the increase in fluorine concentration is also accompanied by a shift in the peaks, thus evidencing an exchange rate faster than the NMR typical frequency ($>10^7$ s^{-1}). In the case of a very low concentration of fluorine, a shift is no longer observed (Figure 8b and e), which might be due to a slow exchange rate within the B:F > 1 species.

ESI-HRMS analysis of a mixture of CsF/diol-DMPA borate ratio of 1:1 in methanol (Figure 9) lead us to the confirmation that the most prominent peak observed in ^{19}F NMR corresponds to compound BF, the diol-monoacid borate fluoride adduct (calcd for $C_5H_7O_4FB$ 161.0422, found 161.0416 (3.7 ppm)).

Finally, the voltage stability window of the borates, that is, the product resulting from 1:1 addition of the trifunctional ligand to $B(OCH_3)_3$ followed by vacuum drying, was measured on a Pt electrode in EC/DMC (Figure 10). The simple triol, with CH_3 as Y group (Figure 10a), presents the narrowest stability with a voltage window of 1−5 V vs $Li^+/Li°$. The Y = NO_2 is expected to undergo reduction, and this is apparent by the faint but broad signal at around 2 V (Figure 10 b), synonymous of a passivation process. In contrast, the diol-monoacid borate (Figure 10c) shows broad reduction peaks starting at 2.5 V in reduction and is seen as the consequence of the **I**, **II**, **III** equilibria with the release of reducible protons. These peaks are no longer visible when the diol-monoacid borate fluoride adduct is used instead (Figure 10d). The fully ring-closed borate fluoride adduct does not introduce any acidic proton and K^+ has a voltage stability limit on reduction beyond that of lithium. The C═O carbonyl of the acid group bears a partial negative charge and is thus quite resistant to reduction.

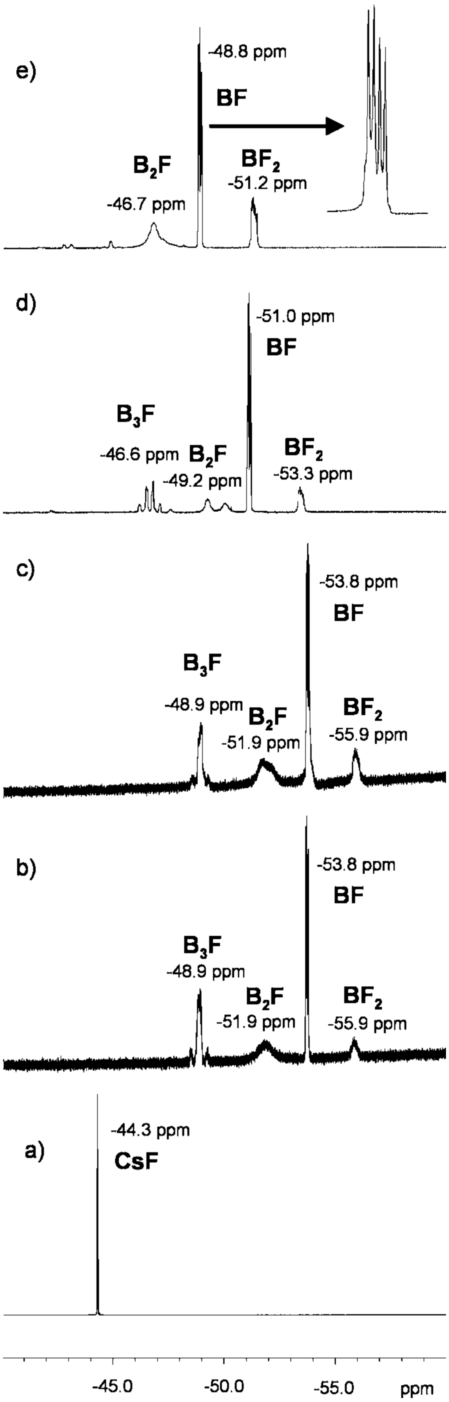

Figure 8. Partial ^{19}F NMR spectra recorded in CD_3OD at 300 K of (a) pure CsF, CsF:diolmonoacid borate ratio of (b) 1:4, (c) 1:2, (d) 1:1 and (e) 1.5:1 with zoom of the peaks at −48.8 ppm.

4. Conclusion

We have shown that a new family of borates based on a very simple concept of preventing spatially the overlap of the oxygen doublets with the empty orbital of boron ester gives the latter

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(16) Melaïmi, M.; Solé, S.; Chiu, C.; Wang, H.; Babbai, F. P. *Inorg. Chem.* **2006**, *45*, 8136–8143.

(17) Aldridge, S.; Fallis, I. A.; Howard, S. T. *Chem. Commun.* **2001**, 231–232.

(18) Cooper, C.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, *13*, 1365–1366.

(19) Xu, Z.; Kim, S. K.; Han, S. J.; Lee, C.; Kociok-Kohn, G.; James, T. D.; Yoon, J. *Eur. J. Org. Chem.* **2009**, *18*, 3058–3065.

(20) Oliveira, R.-A.; Silva, R.-O.; Molander, G.-A.; Menezes, P.-H. *Magn. Reson. Chem.* **2009**, *47*, 873–878.

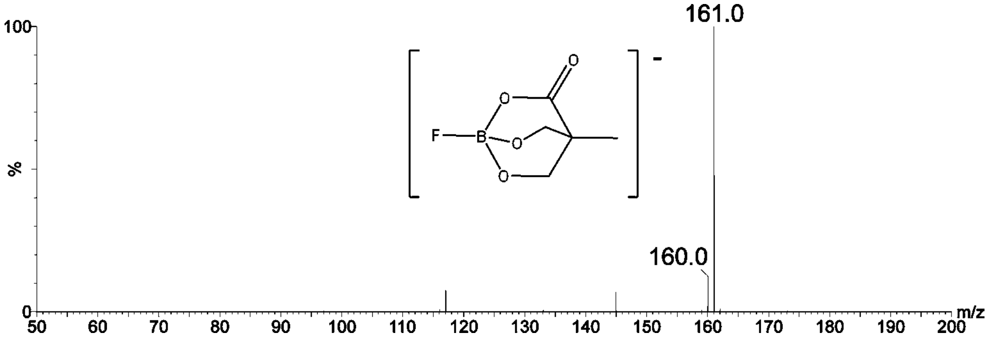

Figure 9. ESI-HRMS of the spectrum of the formation of diol-monoacid borate fluoride adduct.

a quite strong affinity for adding to small anions. These borates allow extention of the electrochemistry of small anions well beyond the voltage stability window of H-bonds which are often the prerequisite for solubility of the corresponding metallic salts.

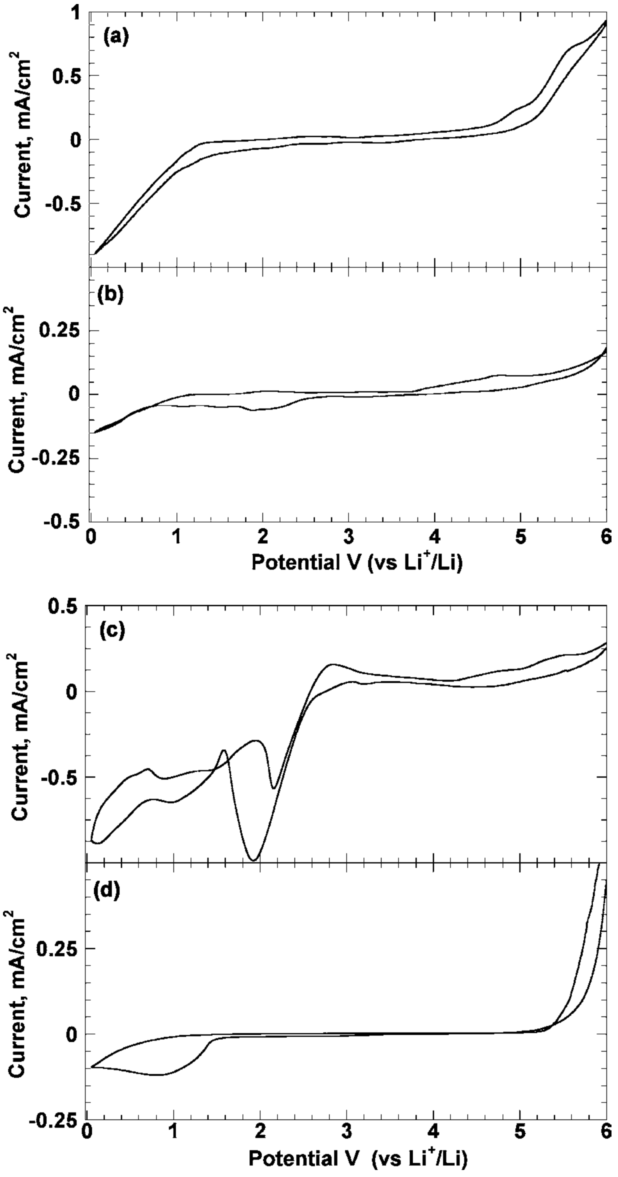

Figure 10. Cyclic voltammograms of (a) triol borate, (b) nitro-triol borate, (c) diol-monoacid borate, and (d) mixture of diol-monoacid borate and 1 equiv of KF between 0.05 and 6 V at a scan rate of 15 mV s^{-1} in EC/DMC solvents.

The present ligands are simple C, H, O, and N derivatives with an easily accessible chemistry. Moreover, the strength of the Lewis acidity can be tuned to a great extent, and in the extreme case presented (two carbonyls) was able to change notoriously insoluble salts into quasi-strong electrolytes. We have shown that the anions that form adducts are, at least in the case of fluorine, bound in a dynamic manner and exchange easily with the same species in a different environment. We acknowledge that proof is yet to be given for the oxygen species O^2 and O_2^{2-} but this will require ^{17}O NMR, which is a study in itself and beyond the scope of this paper. As a good surprise, it was also found that the complexed anions O^{2-} and O_2^{2-}, which could be feared to react on fragile solvents like EC or DMC when made soluble, lose in fact enough of their basicity/nucleophilicity to leave these molecules intact even at 55 °C, the lithium-ion critical temperature. However, it should be remembered that the primary step in oxygen reduction is the superoxide ion radical $O_2^{\bullet -}$,[21] which is an extremely powerful soft nucleophile that may destroy the organic solvent (or coordination anions like $LiPF_6$) before further reduction or disproportionation reaction results in O_2^{2-}, more basic but shown to form strong B−O interactions transforming it into tamer species. Yet, complexed F^- retains still enough reactivity to be an interesting catalyst for the simple Halex reaction Cl $\Longrightarrow$ F, especially in inorganic chemistry, and this will be demonstrated in a subsequent paper.

We are aware that this study cannot, within the allotted space, arrogate a complete survey of this wide family. Each of the four compounds studied deserves more in-depth studies. In particular, the equilibrium of the tricyclic species formation may differ from species to species, also as a function of the solvent. The formation of multiboron complexes around a monatomic anion suggested here is by NMR and is new, as the steric hindrance of these "pony-tail" molecules is minimal, in contrast with triphenyl boron derivatives. In our first examples given, the species are still hard (Pearson's sense) anions, with charges dispersed on atoms with little capacity for polarization. Introduction of soft centers like N in amides or imides would certainly increase the solubility, or of equal importance, reduce the difference in conductivity observed between highly donor DMF and solvents with a lesser tendency to share electron doublets, like carbonates, but in which cation (Li^+) desolvation, required at electrode processes in lithium batteries, is faster (e.g., at graphite interface). It should be remembered that such fine adjustment will also be needed for SEI control, conversion reaction reversibility, and oxygen electrode, as a subtle trade-

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(21) Bruce, P. G.; Paterson, A. J.; Débart, A.; Bao, J.; Peng, Z.; Shaju, K. M.; IMLB 2008, Abstract No. 4.

off between solubility and deleterious cross-talk between electrodes is a necessity (e.g., transport of O_2^{2-} to the negative electrode, resulting in self-discharge).

It should be questioned why such simple combinations of well-known polyols/acid alcohols have not been identified before as precursors of the versatile Lewis acids they allow to build. Most probably, the elusive nature of the “pristine” B complex, with several equilibria, likely solvent-dependent control ring closure is the answer. BH_3 or $B[N(CH_3)_2]_3$ as precursors are expected to release nonreactive species. Quite obviously, this large family just unveiled deserves further investigations, with boron but also with aluminum, where the involvement of “d” orbitals may even enrich the coordination possibilities, as well on new molecules spanning even broader Lewis acid strength range. Preliminary tests on oxides conversion electrodes, both the SEI species formed and on the cycle efficiencies, show a marked effect with traces of diol-monoacid borate (<0.4%). Though the efficiencies are presently negatively affected, the pertinence of this small anion electrochemistry approach seems to be justified.

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