



Benzimidazole and imidazole lithium salts for battery electrolytes

Johan Scheers^{a,*}, Patrik Johansson^a, Przemysław Szczeciński^b, Władysław Wiczorek^b, Michel Armand^c, Per Jacobsson^a

^a Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

^b Polymer Ionics Research Group, Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, PL-00664 Warsaw, Poland

^c Laboratoire de Réactivité et de Chimie des Solides, Université de Picardie Jules Verne, 33 rue St. Leu, 80089 Amiens, France

ARTICLE INFO

Article history:

Received 19 September 2009

Received in revised form

11 December 2009

Accepted 14 December 2009

Available online 22 December 2009

Keywords:

Lithium batteries

Salts

Ion pairs

Dissociation

Anion oxidation potentials

B3LYP

ABSTRACT

The intrinsic anion oxidation potential (ΔE_v) and lithium ion pair dissociation energy (ΔE_d) are two important properties for predicting the potential use of new lithium salts for battery electrolytes. In this work several cyano substituted fluoroalkylated benzimidazole and imidazole anions have been investigated computationally to obtain ΔE_v and ΔE_d . Varying the number and position of cyano substituents results in large effects on the electrochemical stability of the anion and on the possible lithium ion pair configurations. The lengthening of the fluoroalkyl group introduces several new stable ion pair configurations and a small increase in anion oxidation stability. The most promising fluoroalkylated anions in the present work are the 4,5,6,7-tetracyano-2-fluoroalkylated benzimidazolides (TTB and PTB), with oxidation potentials suitable for high voltage Li-ion battery applications (<4.2 V) and much improved ΔE_d compared to PF_6^- —a benchmark for commercially available anions. Further improvements in ΔE_d , with maintained stability towards oxidation, are obtainable by replacing the fluoroalkyl group by an additional cyano group, but possibly demanding increased synthesis efforts.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

An ideal lithium salt for battery application is cheap, easy to prepare, and environmentally benign. In the battery electrolyte the ideal salt dissociates completely into electrochemically active cations and into passive, charge-balancing “ghost” anions. These anions should be thermally and electrochemically stable or, if necessary, contribute to a passivating, yet conducting layer, at either electrode. Unfortunately, all these conditions are not met in a real system where the behaviour of the anion, the only degree of freedom of the salt, is of paramount importance for the overall cell performance. To approach the ideal design of new lithium salts involves the tailoring of anions to find the best compromise of properties.

The PF_6^- anion is the commercial standard of lithium batteries today and has together with the related BF_4^- anion for long worked as a role model for constructing new anions. Synthesis efforts have focused on new anions with either improved thermal properties compared to PF_6^- or higher conductivities with respect to BF_4^- [1]. Relatively modest alterations have resulted in the construction of anions such as $\text{PF}_3(\text{C}_2\text{F}_5)_3^-$ (FAP) [2] and $\text{BF}_3(\text{C}_2\text{F}_5)^-$ [3], while larger structural modifications have resulted in the centre

atoms appearing in completely new dresses. An example of the latter is the bis(oxalato)borate $\text{B}(\text{C}_2\text{O}_4)_2^-$ (BOB) [4], which initially seemed to be a very promising alternative to PF_6^- , but suffer from limited salt solubility and poor conductivity in carbonate based solvents—problems recently approached by resorting to alternative solvents [5]. A different route to new anions has focused on modifications of CF_3SO_3^- (triflate) or rather its successor $\text{N}(\text{SO}_2\text{CF}_3)_2^-$ (TFSI). However, the inherent inability of the triflate and the TFSI anions to passivate the aluminium current collector at the cathode, seems to be hard to overcome also for newer relatives, such as $\text{N}(\text{SO}_2\text{F})_2^-$ (FSI) [6].

A different approach to new lithium battery anions is the design of substituted heterocycles. Two anions based on this concept was introduced in 2003, with the dicyanotriazolide C_5N_4^- (TADC¹) [7,8] and the bis(trifluoroborane)imidazolide $\text{C}_3\text{N}_2(\text{BF}_3)_2^-$ (Id) [9]. The latter of these anions was intended for Li-ion batteries and presented the highest conductive alternative of several synthesized lithium salts, based on the same concept [10]. Tested in a Li-ion cell, the Iid salt showed results comparable to LiPF_6 , with a high ambient temperature conductivity, good solubility, and good electrochemical stability (>4.8 V vs. $\text{Li}^+/\text{Li}^\ominus$) [9]. Highlighting the favourable synthesis aspects of this salt, Iid was advocated as a low-cost alternative to LiPF_6 . However, the B–F bond poses a poten-

* Corresponding author. Tel.: +46 31 772 3177; fax: +46 31 772 2090.
E-mail address: johan.scheers@chalmers.se (J. Scheers).

¹ Also referred to as DCTA.

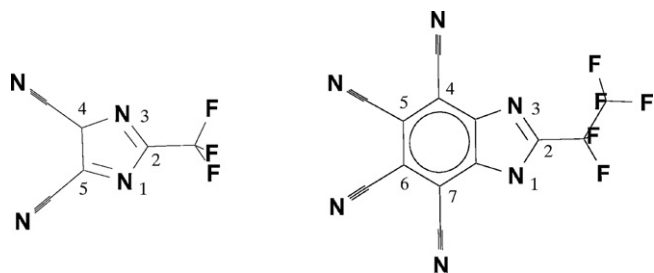


Fig. 1. The investigated families of anions and the numbering conventions used are exemplified by the TDI anion (left) and the PTB anion (right).

tial problem, although not as severe as for the P–F bond in PF_6^- , of possible decomposition or hydrolysis with the resulting formation of LiF or HF [11]. Related to this is the partial disproportionation of the Id anion into BF_4^- at a temperature of 85°C [12], with a negative effect also on the overall conductivity.

LiTADC was originally aimed at polymer electrolytes [8]. Parallel to the experimental work on the LiTADC salt theoretical efforts resulted in several suggestions for synthesis of related azoles, including imidazoles [13]. Although many of these salts were predicted to have improved lithium ion dissociation qualities over TADC, practical difficulties in obtaining the proposed salts have so far hindered experimental explorations of their potencies [14]. Therefore, attention has instead been directed towards other heterocycles with more facile synthesis routes.

Two anions brought to focus very recently are the 4,5-dicyano-2-trifluoromethyl imidazole (TDI) and its 2-pentafluoroethyl analogue (PDI). The lithium salts of these anions have by some of us been characterized in model polymer electrolytes [15] and stressed as “tailor made” salts for lithium battery applications [16]. Of these salts, the synthesis of LiTDI has been shown to be the most facile. The first report of this salt appeared in 2004 [17], when it was prepared in good yield in connection with the finding of a new, improved synthesis route for the protonated (uncharged) form of TDI, known since the mid 70s [18].

In this work we use LiTDI and LiPDI as templates and screen for further synthesis candidates by means of computational *ab initio* methods. New anions are proposed by first extending the heterocyclic imidazole ring to a benzimidazole ring, with two or four cyano groups symmetrically positioned on the ring, and secondly by also looking at alternatives where the fluoroalkyl substituent is replaced by a smaller, less flexible group. Ion pair configurations and dissociation energies, together with anion stabilities towards oxidation are evaluated. Information is obtained about the sensitivity of these properties with respect to ring size (imidazole or benzimidazole), the number and positioning of $-\text{CN}$ groups, and the choice of substituent ($-\text{CF}_3$, $-\text{C}_2\text{F}_5$, or $-\text{CN}$) at position 2 of the heterocyclic ring.

2. Computational details

The structural motifs in common for the fluoroalkylated anions investigated are illustrated in Fig. 1; the cyano groups ($-\text{CN}$) and either the trifluoromethyl ($-\text{CF}_3$), or pentafluoroethyl ($-\text{C}_2\text{F}_5$) group at position 2 of the pentacycle. Considered here are only anions with two or four cyano groups positioned on chemically equivalent sites, with respect to a vertical mirror plane through the ring system and the fluoroalkyl group. Because of the restricted size of the imidazoles only one dicyano imidazolidine is possible, with the $-\text{CN}$ substituents connected to carbons 4 and 5 of the imidazole ring. For the benzimidazolidines, symmetrical substitution ($-\text{CN}$ for $-\text{H}$) at positions 4 and 7, or alternatively at 5 and 6, give two different structures, while substitution at all four positions, 4–7, render a

tetracyano substituted benzimidazolidine. Considering the variation of the fluoroalkyl group, there are in total eight ($2+6$) different fluoroalkylated anions. When replacing the fluoroalkyl group with a third or fifth cyano group, respectively, the grand total number of unique anions becomes twelve.

To be consistent with the previously published work on TDI and PDI all anions have been given three letter acronyms based on the first letter of the group attached to the second ring carbon (Trifluoromethyl, Pentafluoroethyl, or Cyano), the number of cyano substituents (*Di-* or *Tetra-*), and the type of ring structure (Imidazole or Benzimidazole) in the specified order. When conflicts occur subscript numbers have been used to highlight the positions of the cyano groups on the ring. The twelve main anions presented in this work are: 4,5-dicyano-2-trifluoromethylimidazole (TDI), 4,5-dicyano-2-pentafluoroethylimidazole (PDI), 2,4,5-tricyanoimidazole (CDI [13]), 5,6-dicyano-2-trifluoromethylbenzimidazole (TDB₅₆), 5,6-dicyano-2-pentafluoroethylbenzimidazole (PDB₅₆), 2,5,6-tricyanobenzimidazole (CDB₅₆), 4,7-dicyano-2-trifluoromethylbenzimidazole (TDB₄₇), 4,7-dicyano-2-pentafluoroethylbenzimidazole (PDB₄₇), 2,4,7-tricyanobenzimidazole (CDB₄₇), 4,5,6,7-tetracyano-2-trifluoromethylbenzimidazole (TTB), 4,5,6,7-tetracyano-2-pentafluoroethylbenzimidazole (PTB), and 2,4,5,6,7-pentacyanobenzimidazole (CTB).

In the search for lithium ion pair configurations, over thirty starting structures were generated for the largest anions, by positioning the lithium cation at possible mono-, bi-, and tridentate coordination sites, in and out of the plane of the ring system. Care was taken also to include the different potential lithium ion coordination sites generated when rotating the pentafluoroethyl substituent. After an initial, individual screening of ion pair configurations for each anion, a repeated search with different starting coordinates was performed, aimed at probable sites not found at once; for ion pair configurations that were possible for several anions, but not found for all, an existing energy minimum configuration was modified and used as a starting structure for the remaining anions. The computational approaches used; HF/6-31G(d) and B3LYP/6-311+G(d), were chosen to be able to compare the resulting lithium ion pair dissociation energies, $\Delta E_d = (E_{\text{cation}} + E_{\text{anion}}) - E_{\text{ionpair}}$, with existing literature data for a large range of different types of anions [19]. Full B3LYP calculations, including geometry optimizations, were performed on the structures obtained from the HF calculations.

Analyses of vibration frequencies for all of the structures above were made to sort out transition states, with one larger than marginal ($>30\text{ cm}^{-1}$) imaginary frequency, from true energy minima. Reported energies exclude zero point vibration energies (ZPVEs), which otherwise lower the reported energies by $<10\text{ kJ mol}^{-1}$. Basis set superposition errors (BSSEs) were checked for the ion pair configurations of the largest anion (PTB) using counterpoise correction. Computed BSSEs were $<20\text{ kJ mol}^{-1}$ for the smaller basis set (6-31G(d) at HF) and $<5\text{ kJ mol}^{-1}$ for the larger basis set (6-311+G(d) at B3LYP). For ion pair configurations with comparable values of ΔE_d , BSSEs were within only a few kJ mol^{-1} . Thus, the BSSEs are excluded as they will not cause any severe reordering of ion pair configuration stabilities, possibly only for pairs already extremely close in energy. The exclusion of ZPVEs and BSSEs also make comparison with reference data [19,20] straightforward.

For the “free” pentafluoroethyl anions two conformers are possible, in and out of the plane of the ring. The initial screening at the HF level showed a $\sim 2\text{ kJ mol}^{-1}$ preference for the $-\text{C}_2\text{F}_5$ out of plane conformer, while equal conformer energies were predicted by the B3LYP calculations. All relative energies reported have been evaluated with reference to the anions in the out of plane conformation.

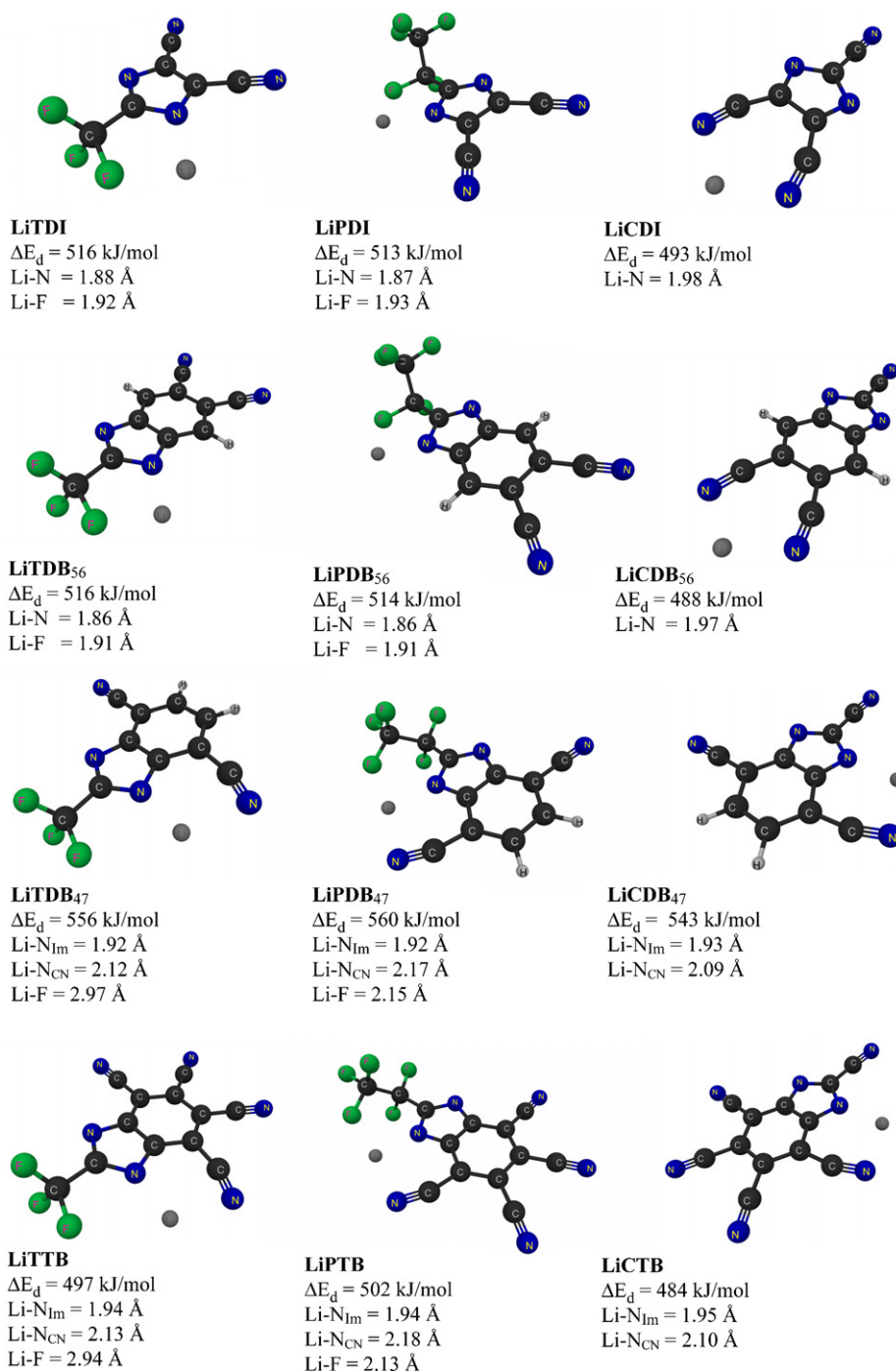


Fig. 2. The most stable lithium ion pair configuration for each anion (B3LYP/6-311+G(d)). The 2-position substituent is changed along each row in the horizontal direction, from $-\text{CF}_3$, $-\text{C}_2\text{F}_5$, to $-\text{CN}$. In the vertical direction the number and position of the remaining cyano groups are varied. Li^+ in each ball and stick representation appear without a stick attached to it.

The intrinsic anion oxidation potentials were obtained by evaluating the vertical transition energy ΔE_v —the energy difference between the minimum energy structure of an anion and the single point energy of its neutral radical, with nuclei coordinates of the optimized anion. ΔE_v is used as an approximation to the free energy change for the anion oxidation, ΔG_{ox} , which is the quantity proportional to the absolute oxidation potential [21]. To convert the absolute potential, in units of eV, to a relative potential in reference to the $\text{Li}^+/\text{Li}^\circ$ redox couple, it is noted that the reference half reaction behind the SHE – the Standard Hydrogen Electrode – has an experimental absolute oxidation potential close to 4.5 eV [21,22].

Since the $\text{Li}^+/\text{Li}^\circ$ reference is approximately -3 V with respect to SHE [23], the calculated oxidation potential can be compared to the $\text{Li}^+/\text{Li}^\circ$ reference by relating it to a $\text{Li}^+/\text{Li}^\circ$ absolute value of 1.5 eV (4.5–3). In practice, a more exact value of 1.46 eV is frequently used [24,25], which was subtracted from the calculated absolute potential in this work. The specific method used to compute ΔE_v was VSXC/6-311+G(2df,p), for information on this approach and the approximation in using ΔE_v instead of the corresponding free energy, see Ref. [20] and references therein.

All starting structures were obtained by assembling the anions and ion pairs in the graphical user interface provided by Spartan'06

[26]. All reported results were computed using the Gaussian 03 program package [27]. The illustrations in Fig. 2 were made using MacMolPlt [28].

3. Results and discussion

3.1. Lithium ion pair configurations—overview

Several potential coordination sites for Li^+ can be imagined for each of the twelve anions; (i) in the plane and along the rim of the anion ring structure, (ii) above each ring, or (iii) in solitaire coordination to the fluoroalkyl group. Our calculations reveal ion pair configurations of all three types and for the largest anion, PTB, as many as nine unique lithium ion pair configurations are identified. Disregarding the very similar configurations where only the orientation of the C_2F_5 group is changed, eight different ion pair configurations remain, each corresponding to an energy minimum state. This “flexibility” of Li^+ pairing with the heterocyclic anions is in sharp contrast to the restricted mono-, bi-, and tridentate sites available with classic, high symmetry anions like PF_6^- [29].

Structuring the many ion pair configurations found, they can be classified as being of “mixed” or “pure” type. The mixed type refers to configurations where Li^+ is coordinated to at least two of the following chemical groups: a fluorine atom (F), an imidazole ring nitrogen atom (N_I), a cyano group nitrogen atom (N_C), or the delocalized electron density of the pentacyclic ring (R_I). The hexacyclic ring of the benzimidazole (R_B) is too isolated to participate in any mixed bonding. Pure coordination on the other hand involves Li^+ coordination to only one type of chemical group (F, N_I , or N_C) or the electron density of one ring (R_I or R_B).

Fig. 2 is an illustration of the most stable of the identified lithium ion pair configurations based on the B3LYP results. Evident from this figure is the clear preference for mixed ion pair configurations among the fluoroalkylated anions of columns 1 and 2. Visible in Fig. 2 is also a shift in coordination point at the pentafluoroethyl group, from $-\text{CF}_2$ to $-\text{CF}_3$, when a cyano group is introduced at position four of the benzimidazole ring (PDB₄₇ and PTB). The two Li^+ coordination possibilities to the pentafluoroethyl group have been found for all but the PDB₅₆ anion and are only separated in energy by 4–7 kJ mol^{-1} . It seems as if the presence or not of a nearby cyano group is crucial for Li^+ coordination to one of the outermost fluorine atoms of the pentafluoroethyl unit; in PDB₄₇ and PTB the 4-cyano group is close to the pentafluoroethyl group, in PDI the 5-cyano group is further away (favouring the $-\text{CF}_2$ coordination instead), and in PDB₅₆ the 5-cyano group is too far away to allow for a $-\text{CF}_3$ coordination at all.

A more extensive illustration of the ion pair energy distributions is presented in Fig. 3 (detailed configurations and energies are provided as supplementary material). The different types of configurations are separated into mixed (+) and pure configurations (capitalized letters). Vertical lines indicate the most stable ion pair energies for two reference phosphates. All the presented anions have computed ion pair dissociation energies lower than LiPF_6 [19], the standard choice in batteries today. However, the dissociation energies are larger than for the, so far only theoretically proposed, hexacyano phosphate, $\text{LiP}(\text{CN})_6$ [30]. The $\text{P}(\text{CN})_6^-$ anion is an interesting reference as it is one of the weakest lithium coordinating anions computed. If the (benz)imidazole anions are instead compared to structurally related cyclic anions, the most dissociative anions covered here are in many cases preferable. Data for a family of pentacyclic anions starting with the all nitrogen pentacycle N_5^- and ending with the pentacyano substituted all carbon pentacycle, C_{10}N_5 (after stepwise substitution of $-\text{C}-\text{CN}$ for N) reveal dissociation energies in the interval [577–466] kJ mol^{-1} [13,19], spanning the entire region between the vertical reference lines of Fig. 3. A more exact comparison with the aforementioned anions Id and

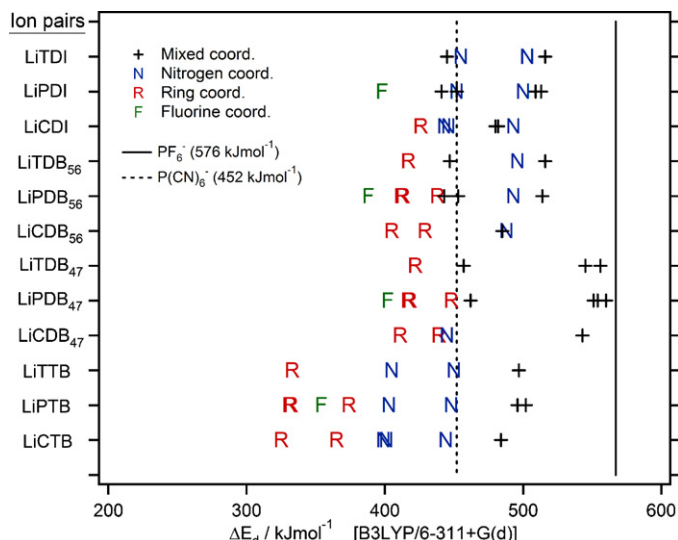


Fig. 3. Lithium ion pair dissociation energies, ΔE_d at the level of B3LYP/6-311 + G(d). On each row the distribution of configurations for a single anion is depicted, with increasing interaction energies to the right. Capitalized letters indicates Li^+ coordination to a single type of group, while + indicates coordination to at least two different types of groups. Reference energies for two phosphate anions are shown as vertical lines [19,30].

TADC ($\Delta E_d = 496$ and 541 kJ mol^{-1} , respectively [19]), reveal that ΔE_d of the tetracyano substituted anions are comparable with that of LiId.

The overall trend in the distribution of configurations of Fig. 3 is that the fluoro involved mixed ion pair configurations are followed in energy by configurations where Li^+ is bidentately coordinated to two cyano groups (not available for the 4,7-cyano substituted anions). Then follows mixed configurations where Li^+ is out of the imidazole ring plane and interacts both with the imidazole ring electron density and a fluoroalkyl group (if possible), or mono cyano coordinated configurations. Pure ring (pentacyclic > hexacyclic) or solitaire fluorine atom coordination by Li^+ form the weakest complexes. Regarding the different ring structures, a mere extension of the ring, going from the imidazole anions to the closely related 5,6-dicyano benzimidazoles, show little effect on the spread of energies and no effect on the energy of the most stable configurations. It is reasonable to assume that any possible effects in performance that may be observed experimentally will depend largely on the difference in size of the imidazolides and 5,6-dicyano benzimidazolides, effects that would be interesting to search for experimentally.

3.2. Lithium ion pair configurations—details

The wealth of information in Fig. 3 includes several important results concerning the relative distribution of ion pair configurations among the anions; one of the most interesting being the differences imposed by a reorganization of the cyano groups of the 5,6-dicyano benzimidazole anions, to obtain the 4,7-dicyano substituted structural isomer. The closer positioning of the cyano groups with respect to the fluoroalkyl chain leads to new ion pair formation possibilities with significant increases in ion pair energies, for example +9% when going from LiPDB₅₆ to LiPDB₄₇. A similar and even larger (+11%) increase in energy is seen comparing the all cyano substituted isomers, CDB₅₆ and CDB₄₇. Indeed, also the Li^+ to ring coordination configurations of the 4,7-benzimidazolides consistently increase in energy, however only slightly (4–10 kJ mol^{-1} or 1–2%), indicating that the predicted performance decreases for these anions are not only related to new configurations becoming

available, but also to a slightly less suitable distribution of electrons across the anions. The strong effect on the highest energy ion pair configurations also leads to a wider spread in energy compared to the 5,6-substituted benzimidazole anions.

The introduction of cyano groups at all four ring positions of the hexacyclic part of the benzimidazole demonstrates the power of cyano substitution for creating weakly lithium coordinating anions. The high energy mixed configurations available for the 4,7-substituted benzimidazoles are also available for TTb and PTb, but now with substantial decreases in energy ($\sim 60 \text{ kJ mol}^{-1}$). With respect to the 5,6-substituted benzimidazoles, the increased delocalization of the negative charge with two added cyano groups on the main ring more than compensates for the added lithium ion coordination possibilities. The most stable ion pair of LiTTb is almost 20 kJ mol^{-1} lower in energy than that of LiTDB₅₆ and for LiPTb the situation is similar with respect to LiPDB₅₆. Observing the local effect on the Li⁺ coordination to the larger of the two rings, the addition of two extra cyano groups shows a very strong effect ($80\text{--}90 \text{ kJ mol}^{-1}$) on this ion pair configuration. This is true also for the non-fluoroalkylated benzimidazoles. In addition, a large effect is expected also for the most stable ion pair configurations, but is partially cancelled by the extra configurations introduced.

Additional configurations made possible by the cyano groups in positions 4 and 7 are not only an issue for the fluoroalkylated anions. Comparing the most stable ion pair configurations of the non-fluoroalkylated anions in the right hand column of Fig. 2, the ion pair energy advantages seen for LiTTb and LiPTb over LiTDB₅₆ and LiPDB₅₆ are not repeated. The energies of LiCTb, LiCDB₅₆, and LiCDI, are very similar and differ only by a few kJ mol^{-1} . The reason is the mixed coordination of Li⁺ to the ring nitrogen and 4-cyano group of CTb, making the most stable ion pair energy of this anion equal to the most stable bidentate cyano group Li⁺ coordinated configurations of LiCDB₅₆ and LiCDI. Two notable results with regard to the ion pairs of these non-fluoroalkylated anions (CDI, CDB₅₆, CDB₄₇, and CTb) are first that the latter two of these anions form only one ion pair configuration higher in energy than the weakly Li⁺ coordinating phosphate $\text{P}(\text{CN})_6^-$, albeit the penalty of this ion pair configuration for CDB₄₇ is extremely large. Secondly, the results for CDI and CDB₅₆ presents one of few conflicts between the HF and B3LYP results; while the B3LYP results predict the pure bidentate $-\text{CN}$ coordinated configurations to be the most stable (where possible), HF results favour mixed ion pair configurations for all anions. However, from HF the configuration energy differences for the two possibilities are negligible for LiCDI, while the B3LYP results favour the most stable configuration by 11 kJ mol^{-1} . For CDB₅₆ the situation is reversed, almost equal configuration energies are obtained from B3LYP, while a 15 kJ mol^{-1} difference is suggested from HF.

A comparison overall of the two methods (supplementary material) reveal that for 71 stable ion pair configurations identified with both HF and B3LYP, the HF results for ΔE_d are on average 1.2% higher in energy, with the maximum differences being +4.5% and -2.7% compared to the B3LYP results. General trends are that configurations where Li⁺ are mono- or bidentately coordinated to cyano groups of the anions give smaller values of ΔE_d for HF, while mixed configurations yield higher energies. The first of these differences sometimes lead to a slight reordering of energies for low ion pair configurations between HF and B3LYP. For Li⁺ coordination to the larger ring of the benzimidazoles the HF results yield slightly higher energies for the dicyano substituted anions, while the situation is reversed for the tetracyano substituted anions. The HF method also suggest a few very closely related configurations that are not found with B3LYP, where the Li⁺ is mixed coordinated to the same groups, but shifted towards different coordination points.

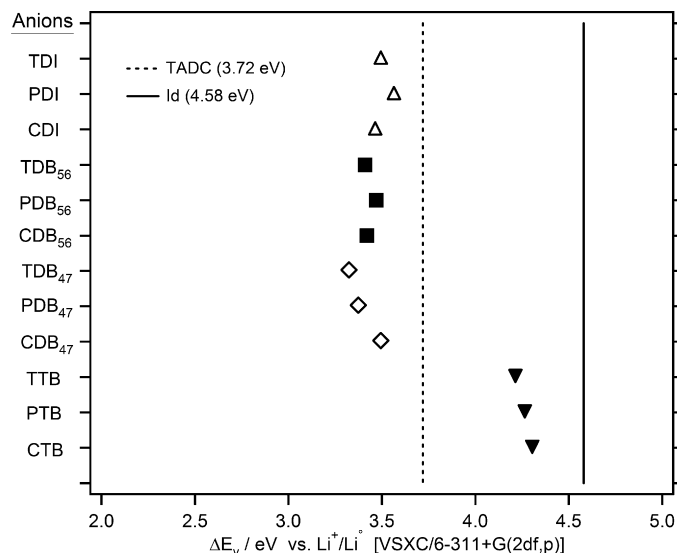


Fig. 4. Intrinsic anion oxidation potentials, ΔE_v at the level of VSXC/6-311+G(2df,p). A single anion is represented on each row, with increasing anion stability to the right. Vertical lines are reference results for the heterocycles TADC and Id [20].

3.3. Anion oxidation potentials

For a comparison of calculated oxidation potentials, ΔE_v (eV vs. $\text{Li}^+/\text{Li}^\circ$), to experimentally measured ones, E_{ox} (V vs. $\text{Li}^+/\text{Li}^\circ$), it should be noted that the computational approach tends to underestimate E_{ox} , in many cases by as much as 1–1.5 V and sometimes even more [20]. The issue is further complicated by variations in experimental results for a given anion, where differences in experimental setups or interpretation of data sometimes lead to widely different reported values of E_{ox} [20]. Based on these considerations and the so far relatively scarce comparison of experimental and computed data (for twelve anions) in Ref. [20], the computed results for ΔE_v should be viewed as a lower limit for E_{ox} rather than an exact measure of this property.

A plot of the ΔE_v results for the twelve benzimidazole and imidazole anions considered in this work are presented in Fig. 4. Compared to the inorganic anions used for reference in Fig. 3, PF_6^- ($\Delta E_v = 5.26 \text{ eV}$ [20]) and $\text{P}(\text{CN})_6^-$ ($\Delta E_v = 6.24 \text{ eV}$ [30]), the oxidation potentials of our “organic” anions are much lower. More suitable comparisons are made with the computed anion oxidation potentials of Id and TADC [20], included as vertical lines in Fig. 4. Although the oxidation potentials for the TTb, PTb, and CTb anions do not reach the theoretical value of Id (4.58 eV [20]), these anions are with $\Delta E_v = 4.2\text{--}4.3 \text{ eV}$ vs. $\text{Li}^+/\text{Li}^\circ$ suggested to be more stable against oxidation compared to TADC (3.72 eV [20]). The large gap in oxidation potential, seen between the tetra- and disubstituted anions, suggests that the lower computed stabilities ($\leq 3.6 \text{ eV}$) for the remaining nine anions may restrict their use to medium or low voltage applications. However, it should be pointed out that the imidazoles, TDI and PDI, recently have been reported to be stable up to 4.6 V vs. metallic lithium, experimentally [16]. In view of the general underestimations of E_{ox} , the tetracyano substituted benzimidazoles ($\Delta E_v = 4.2\text{--}4.3 \text{ eV}$) are predicted to be stable enough, and possibly with some margin, for application in high voltage Li-ion batteries.

3.4. Further anion modifications

Considering the importance of the mixed type lithium ion pair configurations, it would be beneficial to replace either the fluo-

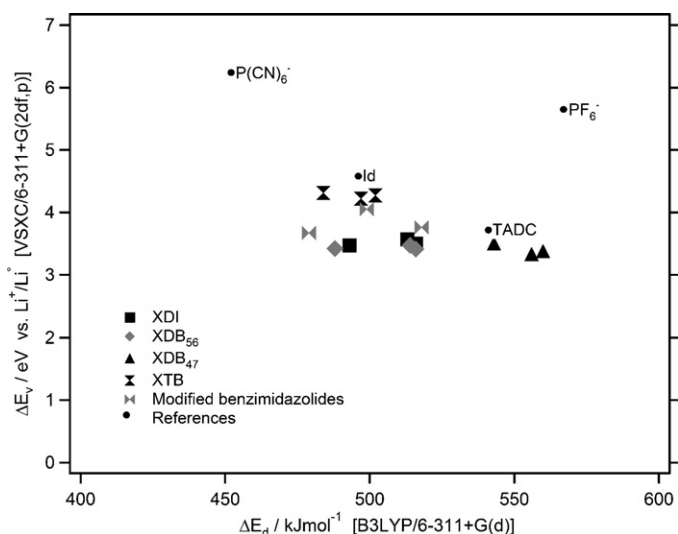


Fig. 5. On the vertical axis: intrinsic anion oxidation potentials, ΔE_v . On the horizontal axis: lithium ion pair dissociation energies, ΔE_d . The three modified benzimidazolides are from left to right; the 4,7-fluoro, 2-fluoro, and 2-methyl substituted versions of XTb (X = F, T, or P), respectively.

roalkyl group or the 4- and 7-cyano groups with other, less lithium ion coordinating substituents, without severely affecting the oxidative stability of the anion. A mere lengthening of the fluoroalkyl group, based on preliminary calculations on XDI and XTb with a heptafluoropropyl ($-C_3F_7$) substituent, seems to have negligible effects on either property, apart from providing further configuration possibilities, which is in line with the observations already made for $-CF_3$ and $-C_2F_5$. From Fig. 3 it can be seen that the exclusion of the most stable mixed configurations for the tetracyano substituted anions has the potential of reducing ΔE_d to dissociation energies in the region of those predicted for $P(CN)_6^-$ [30]. As demonstrated in Section 3.1 and in Figs. 2 and 3, the effect of replacing the fluoroalkyl substituent with another cyano group to give the CDI, CDB, and CTB anions do indeed lead to a lowering of ΔE_d , with maintained electrochemical stability, but with only limited effect on ΔE_v . If instead a smaller fluoro ($-F$) or methyl ($-CH_3$) group is introduced in place of the fluoroalkyl substituent, the smaller electron withdrawing power of these substituents result in a penalty in the form of a lower oxidation potential, which may be affordable for the most stable tetracyano substituted benzimidazole anion. Focusing on this last anion the introduction of a $-F$ substituent leads to a ~ 0.2 V drop in ΔE_v ($\Delta E_v = 4.05$ eV), but without the sought improvement of ΔE_d (499 kJ mol $^{-1}$). For the methyl substituted anion, a decrease in performance is seen for both properties ($\Delta E_v = 3.76$ eV vs. Li^+/Li° , $\Delta E_d = 518$ kJ mol $^{-1}$). A possible explanation is that with the negative charge being less delocalized, the remaining ion pair configurations become more stable, cancelling the effect of reducing the configurations.

An alternative to replacing the 2-position substituent; exchanging the 4- and 7-position cyano groups of CTB with fluoro groups, leads to a slight decrease in ΔE_d (479 kJ mol $^{-1}$), but is accompanied with a large drop in ΔE_v ($\Delta E_v = 3.68$ eV). This is discouraging compared to CTB, but as a modification of CDB₅₆ (where the $-F$ groups have been substituted for the hydrogens) it is an improvement of both properties ($\Delta E_d = 488$ kJ mol $^{-1}$; $\Delta E_v = 3.42$ V).

4. Conclusion

A summary of the results for the anions introduced in this work is presented in Fig. 5, including the results for the reference anions and the modified anions (except the $-C_3F_7$ substituted anions). The

distribution of benzimidazolide and imidazolide anions in Fig. 5 show a typical behaviour of heterocyclic anion alternatives to PF_6^- : if tailored correctly they offer more dissociative lithium ion pairs compared to $LiPF_6^-$, evident from the lower values of ΔE_d along the horizontal axis, but are not as electrochemically stable (ΔE_v , vertical axis). The latter is, however, not crucial as long as the anions exceed the stability window for the intended application, for Li-ion batteries ~ 4.2 V.

The horizontal spread of data points among the benzimidazolides, particularly the difference between the structural isomers XDB₅₆ and XDB₄₇ (X = C, T, or P), indicate that with very small alterations, such as the positioning of $-CN$ substituents on the heterocycle, ion pairing can be changed drastically. With equal predicted properties for analogous imidazolides and benzimidazolides (XDI and XDB₅₆), the difference in anion size is an important variable for choosing an appropriate lithium salt.

Overall the potential of using cyano chemistry to create new lithium salts with excellent electrochemical stabilities and ion pairing properties is evident. The previously recognized improvement of both the electrochemical stability and the lithium ion pair dissociation ability, by increasing the number of cyano groups, is apparent also for the benzimidazole salts and further strengthened by the predictions made for $P(CN)_6^-$. In Fig. 5, $P(CN)_6^-$ occupies a region, which hopefully, will host a larger population of anion alternatives for lithium salts in the near future. However, an increase in the number of $-CN$ groups leads to a larger anion size and require increased synthesis efforts. The tetracyano benzimidazolides, XTb, are the most promising candidates of the explored families of anions, but as of present neither of the benzimidazole lithium salts nor $LiP(CN)_6$ has been reported experimentally.

Acknowledgements

This work was supported by grants from the Swedish Research Council (VR). Computer resources at the National Supercomputer Centre (NSC) in Linköping Sweden was used and granted by the Swedish National Infrastructure for Computing (SNIC). The corresponding author gratefully acknowledges Stiftelsen Futura for a travel grant to the conference to which this special issue is devoted.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jpowsour.2009.12.052.

References

- [1] K. Xu, Chem. Rev. 104 (2004) 4303–4417.
- [2] J.S. Gnanaraj, M.D. Levi, Y. Gofer, D. Aurbach, M. Schmidt, J. Electrochem. Soc. 150 (2003) A445–A454.
- [3] M. Ue, T. Fujii, Z.-B. Zhou, M. Takeda, S. Kinoshita, Solid State Ionics 177 (2006) 323–331.
- [4] W. Xu, C.A. Angell, Electrochem. Solid-State Lett. 4 (2001) E1–E4.
- [5] J.-Y. Huang, X.-J. Liu, X.-L. Kang, Z.-X. Yu, T.-T. Xu, W.-H. Qiu, J. Power Sources 189 (2009) 458–461.
- [6] A. Abouimrane, J. Ding, I.J. Davidson, J. Power Sources 189 (2009) 693–696.
- [7] P. Johansson, S. Béranger, M. Armand, H. Nilsson, P. Jacobsson, Solid State Ionics 156 (2003) 129–139.
- [8] M. Egashira, B. Scrosati, M. Armand, S. Béranger, C. Michot, Electrochem. Solid-State Lett. 6 (2003) A71–A73.
- [9] T.J. Barbarich, P.F. Driscoll, Electrochem. Solid-State Lett. 6 (2003) A113–A116.
- [10] T.J. Barbarich, K.M. Abraham, J. DiCarlo, Proceedings of the 40th Power Sources Conference, IEEE, Cherry Hill, NJ, 2002, pp. 331–334.
- [11] K. Tasaki, K. Kanda, S. Nakamura, M. Ue, J. Electrochem. Soc. 150 (2003) A1628–A1636.
- [12] T.J. Barbarich, P.F. Driscoll, S. Izquierdo, L.N. Zakharov, C.D. Incarvito, A.L. Rheingold, Inorg. Chem. 43 (2004) 7764–7773.
- [13] P. Johansson, H. Nilsson, P. Jacobsson, M. Armand, Phys. Chem. Chem. Phys. 6 (2004) 895–899.
- [14] M. Armand, P. Johansson, J. Power Sources 178 (2008) 821–825.

- [15] L. Niedzicki, M. Kasprzyk, K. Kuziak, G.Z. Żukowska, M. Armand, M. Bukowska, M. Marcinek, P. Szczeciński, W. Wieczorek, *J. Power Sources* 192 (2009) 612–617.
- [16] L. Niedzicki, G.Z. Żukowska, M. Bukowska, P. Szczeciński, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marcinek, W. Wieczorek, *Electrochim. Acta*, accepted.
- [17] M. Bukowska, J. Prejzner, P. Szczeciński, *Polish J. Chem.* 78 (2004) 417–422.
- [18] R.W. Begland, D.R. Hartter, F.N. Jones, D.J. Sam, W.A. Sheppard, O.W. Webster, F.J. Weigert, *J. Org. Chem.* 39 (1974) 2341–2350.
- [19] P. Johansson, *Phys. Chem. Chem. Phys.* 9 (2007) 1493–1498.
- [20] P. Johansson, *J. Phys. Chem. A* 110 (2006) 12077–12080;
P. Johansson, *J. Phys. Chem. A* 111 (2007) 1378–1379.
- [21] P. Winget, C.J. Cramer, D.G. Truhlar, *Theor. Chem. Acc.* 112 (2004) 217–227.
- [22] M. Namazian, H.R. Zare, M.L. Coote, *Biophys. Chem.* 132 (2008) 64–68.
- [23] M. Winter, J.O. Besenhard, M.E. Spahr, P. Novák, *Adv. Mater.* 10 (1998) 725–763.
- [24] J.M. Vollmer, L.A. Curtiss, D.R. Vissers, K. Amine, *J. Electrochem. Soc.* 151 (2004) A178–A183.
- [25] R.L. Wang, C. Buhrmester, J.R. Dahn, *J. Electrochem. Soc.* 153 (2006) A445–A449.
- [26] Spartan'06, Wavefunction Inc., Irvine, CA, USA.
- [27] M.J. Frisch, et al., GAUSSIAN 03, Revision C. 02, Gaussian Inc., Pittsburgh, PA, 2003.
- [28] B.M. Bode, M.S. Gordon, *J. Mol. Graphics Model.* 16 (1998) 133–138.
- [29] P. Johansson, P. Jacobsson, *J. Phys. Chem. A* 105 (2001) 8504–8509.
- [30] J. Scheers, P. Johansson, P. Jacobsson, *J. Electrochem. Soc.* 155 (2008) A628–A634.