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Electrolytes for Li-Ion Batteries

Superhalogens as Building Blocks of Halogen-Free Electrolytes in Lithium-Ion Batteries**

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Abstract: *Most electrolytes currently used in Li-ion batteries contain halogens, which are toxic. In the search for halogen-free electrolytes, we studied the electronic structure of the current electrolytes using first-principles theory. The results showed that all current electrolytes are based on superhalogens, i.e., the vertical electron detachment energies of the moieties that make up the negative ions are larger than those of any halogen atom. Realizing that several superhalogens exist that do not contain a single halogen atom, we studied their potential as effective electrolytes by calculating not only the energy needed to remove a* Li^+ *ion but also their affinity towards* H_2O*. Several halogen-free electrolytes are identified among which* $Li(CB_{11}H_{12})$ *is shown to have the greatest potential.*

Li-ion batteries play an important role in modern portable electronics, due to their light weight and high energy density.[1–3] The three primary components of a Li-ion battery are the anode, cathode, and electrolyte. Whereas graphite is used as the most popular commercial anode, the cathode is generally composed of metal oxides, layered oxides (such as lithium cobalt oxide), polyanions (such as lithium iron phosphate), or a spinel (such as lithium manganese oxide).[4–7] The Li^+ ions that move from anode to cathode when discharging and reverse when charging are supplied by the electrolytes. Considerable research is under way to improve the cost, efficiency, durability, and safety of Li-ion batteries by improving the materials of the anodes, cathodes, and electrolytes.[8–15]

Here we focus on the electrolytes that act as ion carrier between the anode and cathode when current flows through an external circuit. The current electrolytes consist of lithium salts such as $LiAsF_6$, $LiBF_4$, $LiPF_6$, $LiFePO_4$, $LiClO_4$, $LiN(SO_2F)_2$, and $LiN(SO_2CF_3)_2$, combined with organic solvents like ethylene carbonate and dimethyl carbonate.[16–19] Although these electrolytes are commercially available and popularly used in Li-ion batteries, they have certain disadvantages. With the exception of $LiFePO_4$, the above electrolytes contain halogens, which are toxic. $LiAsF_6$ is poisonous, whereas $LiClO_4$ is explosive. $LiBF_4$ has inferior ability in forming solid electrolyte interphases at the graphite electrode,[20–22] whereas $LiN(SO_2CF_3)_2$ corrodes the cathode.[23] $LiPF_6$ decomposes to PF_5 and LiF, the former readily hydrolyzing to form HF and PF_3O. These two products are very reactive on both the cathode and anode surfaces and impact negatively on the electrode's performance.[24] Recently it has been shown that $LiFePO_4$ suffers from the same memory effect that has plagued nickel–cadmium and nickel–metal hydride batteries, which gradually lose usable capacity if recharged repeatedly after being only partially discharged.[25] Furthermore, Li-ion batteries have limited performance at elevated temperatures and due to surface phenomena on both electrodes, their life cycle is also limited.[26] The safety features of commercially prepared Li-ion batteries are also insufficient for large size applications.[27,28] To tackle these problems, several attempts have been made by either introducing new solvents or using different salts and additives.[29,30]

There are three characteristics of electrolytes that need improvement. First, they should be halogen-free to improve safety. Second, since the binding energy between Li^+ and the anionic part of the salt plays an important role in ion conduction, it should be small so that ions can move easily from one electrode to the other. Third, the affinity of the electrolyte to water should also be low so as to increase battery life. Here we show that an in-depth understanding of the electronic structure and stability of current electrolytes allows us to address the above-mentioned three challenges.

We begin by analyzing the electronic structure of the negative ions of the Li salts. These are BF_4^-, PF_6^- AsF_6^-, $FePO_4^-$, ClO_4^-, $N(SO_2F)_2^-$, and $N(SO_2CF_3)_2^-$, as discussed above. We note that the oxidation state of B is +3, whereas it is +5 for P and As. Fluorine, on the other hand is electronegative and needs only one electron to satisfy its electronic shell closure. Consequently, BF_4, PF_6, and AsF_6 need one extra electron for shell closing. With the electronic configuration of Fe^{2+}, P^{5+}, and O^{2-}, $FePO_4$ also needs one extra electron for electron shell closing. In the case of ClO_4^-, four oxygen atoms need eight electrons to close their electronic shells, but Cl can contribute a maximum of seven electrons. Thus, one extra electron is needed to fulfill the electronic shell closure. Electron counting in $N(SO_2F)_2$ and $N(SO_2CF_3)_2$ is slightly more complicated as the oxidation state of N can vary from −3 to +5 and that of S from −2 to +6, depending on the nature of the ligand. For example, in N_2O, N is in the +1 state, whereas it is in the −3 state in NH_3. In $N(SO_2F)_2$, N, S, O, and F have oxidation states of +1, +4, −2, and −1, respectively. In $N(SO_2CF_3)_2$, on the other hand, the oxidation state of N is

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-3. Thus, whereas SO_2F needs one electron to have electronic shell closure, SO_2CF_3 has one more electron than necessary for electronic shell closure. Consequently, SO_2F behaves like a halogen atom whereas SO_2CF_3 behaves like an alkali atom. However, both $N(SO_2F)_2$ and $N(SO_2CF_3)_2$ need an extra electron to close their electronic shells, and hence they serve as negative ions in the Li salt. Since the extra electron in all the above moieties is distributed over a large phase space, the reduction in electron–electron repulsion makes these molecules very stable as anions. In the 1980s, Gutsev and Boldyrev[31] had shown that, when a core metal atom M is surrounded by halogen atoms X such that their number exceeds the maximal valence, k of M by one, the resulting molecule MX_{k+1} will have electron affinities larger than that of any halogen atom. This is because the added electron would be delocalized over $(k+1)$ halogen atoms, thus reducing electron–electron repulsion, and hence increasing their stability. To confirm that the moieties that make up the anions of current electrolytes are indeed superhalogens, we optimized the structure of the anions and calculated their vertical detachment energies (VDE), i.e., the energy needed to remove an electron. The VDEs are determined from the difference between the ground state energies of the anions and their corresponding neutrals at the anion geometry. First-principles calculations based on density functional theory with hybrid functional for exchange–correlation potential were carried out to first find the ground state geometries and total energies of anionic BF_4, PF_6, AsF_6, $FePO_4$, ClO_4, $N(SO_2F)_2$, and $N(SO_2CF_3)_2$ species. All the anions and their Li salts were optimized at the wB97XD level of theory[32] using the 6-311+G(d) basis set. Although from our past studies[33–35] we found that the B3LYP level of theory can provide reasonably good results, the wB97XD level of theory is used to include the dispersion and long-range interaction in our calculation. Frequency analysis was performed at the same level of theory to ensure that there are no imaginary frequencies and the structures belong to a minimum in the potential energy surface. All optimizations were performed using the Gaussian 09 program[36] and the structures were modeled using the Gauss view program[36].

The optimized geometries of the BF_4^-, PF_6^-, AsF_6^-, $FePO_4^-$, ClO_4^-, $N(SO_2F)_2^-$, and $N(SO_2CF_3)_2^-$ anions are given in Figure 1 and their corresponding VDEs are presented in Table 1. Note that in all cases, the VDEs are larger than the electron affinity of chlorine. Thus, all these species are superhalogens. Of particular note is $N(SO_2F)_2$. The calculated VDE of SO_2F is 4.74 eV which already makes it a superhalogen. Since $N(SO_2F)_2$ is composed of SO_2F superhalogens and its VDE is larger than that of SO_2F, it can be considered as a hyperhalogen.[37] Unlike conventional superhalogens, in which metal atoms serve as the core and halogens as ligands, in $N(SO_2CF_3)_2^-$, SO_2CF_3 serves as the cationic core and N, with an oxidation state of -3, serves as the electronegative ligand.

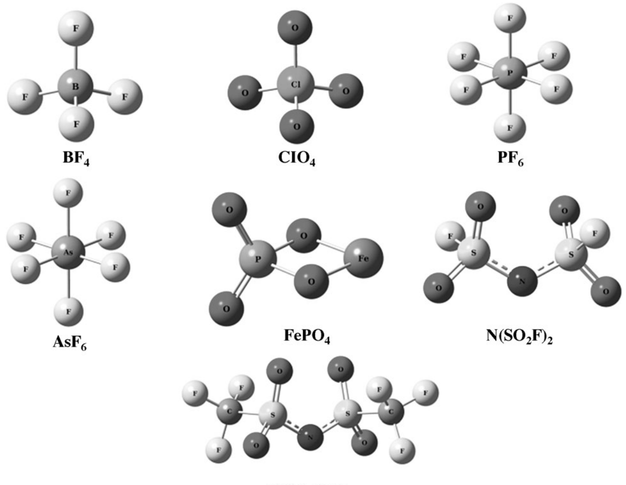

Figure 1. Optimized geometries of different anions in currently used electrolytes in Li-ion batteries.

Table 1: Calculated vertical detachment energy (VDE), Li^+ binding energy (ΔE_{Li^+}), binding energy of H_2O (ΔE_{H_2O}), and molar volume at the wB97XD/6-311+G(d) level for currently used electrolytes in Li-ion battery.

Anions	VDE [eV]	ΔE_{Li^+} [eV]	ΔE_{H_2O} [eV]	Volume [cm^3 mol^{-1}]
$FePO_4$	4.32	7.38	1.04	57.24
ClO_4	5.83	5.96	1.02	50.63
$N(SO_2F)_2$	6.89	5.82	1.02	80.14
$N(SO_2CF_3)_2$	7.01	6.01	0.99	126.01
BF_4	7.66	6.08	1.41	46.62
PF_6	8.55	5.73	1.07	63.27
AsF_6	8.91	5.65	1.09	58.17

Having established that all the negative ions of current electrolytes are superhalogens, we note that this field has been developing for more than 30 years. Although the superhalogens studied in the 1980s and 1990s mostly consisted of a simple metal atom at the core surrounded by halogen ligands, extensive research over the past decade has greatly expanded the pool of superhalogens. These include transition metal atoms at the core[38] as well as non-halogens such as O as ligands.[39] Superhalogens that contain neither a metal nor a halogen atom have also been identified.[40–43] Examples of these superhalogens are: NO_3, CN, BH_4, BO_2, MnO_4, and $CB_{11}H_{12}$. This knowledge prompted us to examine, if some of these superhalogens may also be good candidates for electrolytes in Li-ion batteries.

To be competitive with current electrolytes, the halogen-free electrolytes must satisfy two important criteria outlined earlier. First, the energy to remove Li^+ from the salt should be the same or lower than that in currently used electrolytes. Second, the affinity of halogen-free electrolytes toward water must not be larger than that of currently used electrolytes. These quantities are evaluated using the equations,

$$\Delta E_{Li^+} = (E_{anion} + E_{Li^+}) - E_{Salt} \tag{1}$$

$$\Delta E_{H_2O} = (E_{salt} + E_{H_2O}) - E_{Salt+H_2O} \tag{2}$$

These energies are given in Table 1 for the current commercially used electrolytes. We have also calculated the molar volumes of these anions to see whether they have any effect on the binding energy. The geometries of Li-salts and their H_2O complexes are given in the Supporting Information (SI-I and II).

From Table 1 one can see that the VDEs range from 4.32 eV to 8.91 eV, whereas ΔE_{Li^+} ranges from 5.73 eV to 7.38 eV. The molar volumes of $N(SO_2F)_2$ and $N(SO_2CF_3)_2$ are larger than those of any other anions. One would expect ΔE_{Li^+} to decrease with increasing VDE and molar volume. While we observe this trend in some of the negative ions in Table 1, the dependence of ΔE_{Li^+} on the VDE and molar volume is more complicated and cannot be predicted a priori. $FePO_4$ has the smallest VDE and the largest ΔE_{Li^+}, whereas the reverse is true for PF_6. The VDEs of ClO_4 and $N(SO_2F)_2$ are higher than that of $FePO_4$, but their Li^+ binding energies are lower. As far as the Li^+ binding energy is concerned, PF_6 should be the preferred anion in the Li-salt. With the exception of BF_4, all the salts in Table 1 have nearly equal affinity toward water.

To see if other superhalogens that have been identified would be better candidates for Li-salts, we have examined six such moieties. Four of these, NO_3, BH_4, B_3H_8, and $CB_{11}H_{12}$, are halogen-free, whereas two others, BeF_3 and AuF_6, do contain halogen atoms. The optimized geometries of these anions are given in Figure 2.

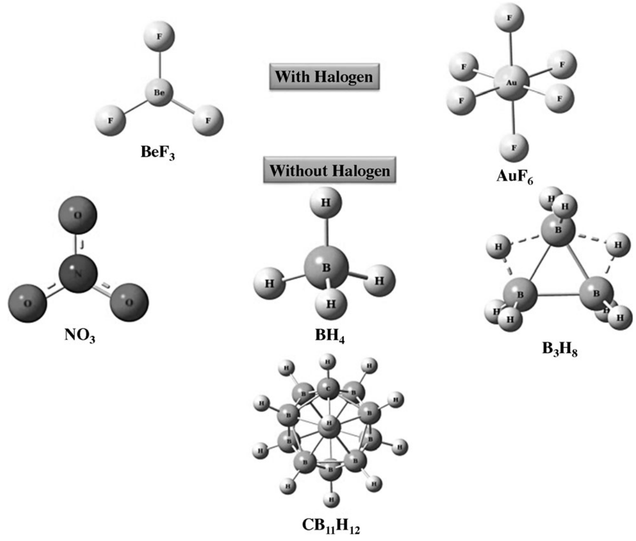

Figure 2. Optimized geometries of anions of four potential candidates for halogen-free electrolytes. Also given for comparison are two other halogen-containing anions that are not currently used in commercial applications.

Table 2: Calculated VDE, Li^+ binding energy (ΔE_{Li^+}, eV), binding energy of H_2O (ΔE_{H_2O}, eV), and molar volume (cm**3/mol) of four potential new electrolytes for Li-ion battery. Also given for comparison are results for BeF_3 and AuF_6.

Anions	VDE [eV]	ΔE_{Li^+} [eV]	ΔE_{H_2O} [eV]	Volume [$cm^3 mol^{-1}$]
NO_3	4.22	6.53	0.96	39.22
BH_4	4.50	6.62	0.92	41.62
B_3H_8	4.72	6.25	0.93	72.53
$CB_{11}H_{12}$	5.99	5.08	1.08	126.78
BeF_3	6.99	6.50	0.98	39.88
AuF_6	8.86	5.50	1.06	64.98

The geometries of the corresponding Li-salts and those of their interaction with H_2O are given in the SI (SI-III and IV). Since AuF_6 is structurally similar to PF_6 and AsF_6, which are the anionic parts of commercially used $LiPF_6$ and $LiAsF_6$ electrolytes, one could assume that $LiAuF_6$ may have similar characteristics. Unlike As, Au is not toxic. The calculated VDEs and Li^+ and H_2O binding energies as well as molar volumes are given in Table 2. Among these anions, BH_4 has the highest Li^+ binding energy in $LiBH_4$ and the lowest in $LiCB_{11}H_{12}$. The binding energies of the salts to water are about the same for all the electrolytes in Table 2, but less than those of the current electrolytes given in Table 1. Considering the binding energy of Li^+ in the electrolyte and its affinity toward water as two of the most relevant parameters, we see that $LiCB_{11}H_{12}$ has the most desirable characteristics for an electrolyte in a Li-ion battery. Furthermore, it is halogen-free. These properties are associated with the large molar volume of $LiCB_{11}H_{12}$. Other metal borohydrides such as $LiBH_4$ and LiB_3H_8 can also be a good choice for electrolytes (see Table 2) as they too are halogen-free.

We have also explored the potential of $Li_2B_{12}H_{12}$ as another halogen-free electrolyte. Here, the advantage is that there are two Li ions per each $B_{12}H_{12}{}^{2-}$ moiety. To study its potential, we calculated the energy needed to remove Li^+ ions from $Li_2B_{12}H_{12}$. It takes 5.94 eV to remove the first Li^+, compared to 6.62 eV from $LiBH_4$. However, removal of the second Li^+ would require much higher energy, namely, 9.00 eV. Thus, $Li_2B_{12}H_{12}$ may not offer significant advantage over $LiBH_4$ for use in Li-ion battery. We note that recently the potential of Li metal borohydrides for electrochemical storage[44,45] has been experimentally demonstrated.

In summary, we show that the building blocks of all current halogen-containing electrolytes are superhalogens. Since many halogen-free superhalogens are known, we studied their potential as building blocks of new electrolytes by calculating the binding energies of Li^+ and H_2O. These results are summarized in Tables 1 and 2 and Figure SI-V in the SI. Among all halogen-free electrolytes, $LiCB_{11}H_{12}$ has the greatest potential. Other metal borohydrides such as $LiBH_4$, LiB_3H_8, and $Li_2B_{12}H_{12}$ are also potential candidates. For practical applications, the electrolytes need to be soluble. A literature search shows that Li salts composed of halogen-free superhalogens such as $LiNO_3$ and $LiBH_4$ are soluble in ethanol and ether, respectively. We expect that all other halogen-free salts may be soluble in some organic solvents. We hope that our study will stimulate researchers to synthesize new electrolytes based on halogen-free superhalogens.

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