

Designing new electrolytic salts for Lithium Ion Batteries using superhalogen anions



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ABSTRACT

The electrolytes used in Lithium Ion Batteries (LIBs) such as LiBF_4 , LiPF_6 , etc. are Li-salts of some complex anions, BF_4^- , PF_6^- , etc. The investigation shows the vertical detachment energy (VDE) of these anions exceeds to that of halogen, and therefore they behave as superhalogen anions. Consequently, it might be possible to design new electrolytic salts using other superhalogen anions. We have explored this possibility using Li-salts of various superhalogen anions such as BO_2^- , AlH_4^- , TiH_5^- and VH_6^- as well as hyperhalogen anions, $\text{BH}_{4-y}(\text{BH}_4)_y^-$ ($y = 1-4$). Our density functional calculations show that Li-salts of these complex anions possess similar characteristics as those of electrolytic salts in LIBs. Note that they all are halogen free and hence, less-toxic and safer than LiBF_4 , LiPF_6 , etc. In particular, $\text{LiB}_4\text{H}_{13}$ and $\text{LiB}_5\text{H}_{16}$ are two potential candidates for electrolytic salt due to their smaller Li-dissociation energy (ΔE) than those of LiBF_4 , LiPF_6 , etc. We have also noticed that ΔE of $\text{LiBH}_{4-y}(\text{BH}_4)_y$ varies inversely with the VDE of $\text{BH}_{4-y}(\text{BH}_4)_y^-$ anions, which increases with the increase in y . These findings may guide experimentalists and future researchers to design and synthesize new electrolytic salts for LIBs.

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1. Introduction

Lithium-Ion Batteries (LIBs) have become the main power source of modern electronic devices due to their high density of energy storage [1,2]. The multifunctional cellular phones and expanding applications of LIBs in other power storage systems demand a persistent increase in its energy storage capacity. This necessitates the development of potentially active materials, the task which has been attracting attention of experimentalists as well as theoreticians [3,4]. A typical LIB consists of a graphite anode and transition metal oxide complex of Li (such as LiCoO_2 , LiMn_2O_2 , etc.) as cathode. These two electrodes are separated by a non-aqueous organic electrolyte that acts as an ionic medium. The electrolytes are made up of non-coordinating anionic complexes of Li, such as LiBF_4 , LiPF_6 , LiClO_4 and LiFePO_4 , etc. dissolved in a polar aprotic solvent. It is generally accepted that organic electrolytes are decomposed during the first lithium intercalation into graphite to form a solid electrolyte interface (SEI) film between the graphite anode surface and the electrolyte, and it is the SEI film that largely determines the performance of graphite as anode in rechargeable batteries [1]. For instance, the higher the film passivating ability, the better capacity and longer life cycle of the

lithium-intercalated graphite anodes. A number of efforts have been made on the investigations of various organic solvents in order to increase the reversibility and capacity of LIBs [5,6]. Most common organic solvents include esters or ethers or their mixtures. In this line, ethylene carbonate and propylene carbonates have extensively been studied by Wang et al. [7,8]. They have theoretically suggested a variety of additives to these solvents, which are beautifully reviewed by Zhang [9]. Most of the currently used electrolytic salts such as LiBF_4 , LiPF_6 , LiClO_4 , etc. contain halogen and hence, they cannot be considered as safe from environmental perspectives. Therefore, it is desirable to quest for new electrolytic salts, which are less toxic and at the same time, as efficient (conducting) as existing salts in LIBs.

A recent investigation [10] has indicated the superhalogen as building block of electrolytes in LIBs. The word ‘superhalogen’ refers to the species, whose electron affinity exceed to that of halogen atoms. Being proposed by Gutsev and Bolyrev [11,12] for the first time during 1980s, these species have attracted continuous attentions [13–20]. Such species possess strong oxidizing property [21] and form ionic complexes with appropriate metal atoms [18,19]. A general formula of MX_{k+1} has been proposed [11] for typical superhalogen species, where M is a core atom with formal valence of k and X is electronegative ligands such as F, Cl, O, CN, OF, etc. The electrolytic salts in LIBs are lithium complexes of superhalogen anions. For instance, LiBF_4 and LiPF_6 can be thought

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of as Li^+BF_4^- and Li^+PF_6^- , respectively, where BF_4^- and PF_6^- are superhalogens satisfying MX_{k+1} formula. A recent study [22] has demonstrated that the electronic properties of LiBeF_3 closely resemble those of LiBF_4 and LiPF_6 . Therefore, it is expected that the concept of superhalogen might be useful in designing new electrolytic salts in LIBs, as noticed in previous investigation [10], which proposed Li-salts of BeF_3^- , AuF_6^- , NO_3^- , BH_4^- , B_3H_8^- and $\text{CB}_{11}\text{H}_{12}^-$ superhalogen anions as a possible candidate for electrolytes in LIBs. Note that LiBeF_3 and LiAuF_6 do contain fluorine and hence, are relatively more toxic. Furthermore, LiNO_3 is not sufficiently conducting to be used as electrolytic salt. This prompted us to design new electrolytes using the concept of superhalogen, which might be more efficient than proposed salts in the previous study [10].

2. Computational details

All lithium salts (Li-X) and corresponding anions (X^-) considered in this study were fully optimized at ωB97xD method [23] using 6-311+G(d) basis set [24] using Gaussian 09 program [25]. The functional ωB97xD includes empirical dispersion, which has been found appropriate for the systems with long range interactions [26]. Furthermore, the present computational scheme, $\omega\text{B97xD}/6-311+G(d)$, has already been used in the previous study on Li-salts [10]. Moreover, $\omega\text{B97xD}/6-311+G(d)$ calculated VDE of NaCl_2^- superhalogen 5.53 eV agrees well with experimental VDE of 5.60 ± 0.10 eV measured by photoelectron spectroscopy [15]. The geometry optimization was performed without any symmetry constraints and followed by frequency calculations to ensure that the optimized structures correspond to true minima in the potential energy surface. The vertical detachment energy (VDE) of anions has been calculated by difference of total energy of optimized structure of anions and corresponding neutral structure, i.e.,

$$\text{VDE} = E[\text{X}]_{\text{single point}} - E[\text{X}^-]_{\text{optimized}}$$

where $E[\text{X}^-]_{\text{optimized}}$ is the total energy of optimized structure of X^- and $E[\text{X}]_{\text{single point}}$ is the single point energy of neutral structure (X) at optimized geometry of X^- .

3. Results and discussion

We start our discussion with typical electrolytic salts in LIBs, which include LiBF_4 , LiPF_6 , LiClO_4 , LiFePO_4 and LiAsF_6 , etc. The VDE of corresponding anions are listed in Table 1. One can note that all VDE values exceed the electron affinity of halogen atom, which is limited to 3.62 eV for Cl [27]. Therefore, these anions belong to the class of superhalogen. The optimized structure of BF_4^- , PF_6^- and their Li-salts are displayed in Fig. 1. Since these anions consist of fluorine atoms, which are relatively more toxic and therefore environmental safety remains a grave issue. As an attempt to overcome this issue, Li-salts of BeF_3^- , AuF_6^- , NO_3^- , BH_4^- , B_3H_8^- and $\text{CB}_{11}\text{H}_{12}^-$ have been considered [10]. The VDE of these

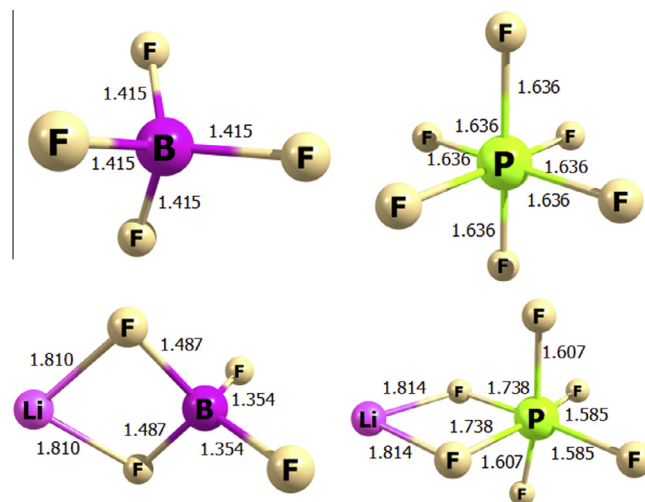


Fig. 1. Equilibrium structures of BF_4^- , PF_6^- superhalogen anions and their Li-salts, which are currently used as electrolytic salts in LIBs. The bond lengths in Å are calculated at $\omega\text{B97xD}/6-311+G(d)$ level.

anions are also listed in Table 1, which establish their superhalogen behavior. Note that BeF_3^- and their compounds are poisonous due to toxicity of beryllium content and AuF_6^- does contain halogen. In fact, many transition metal hexafluorides have been reported to possess higher electron affinity than halogen, excluding WF_6 [28]. Therefore, they all possess more or less similar properties and form almost similar Li-salts, like LiAuF_6 , LiAsF_6 and LiPF_6 . However, they all suffer with certain level of toxicity due to presence of halogen. The salt of $\text{CB}_{11}\text{H}_{12}^-$ has been found to possess more favourable properties [10] and hence, $\text{LiCB}_{11}\text{H}_{12}$ has been advocated as a possible candidate for electrolytes in future LIBs. However, it contains carbon unlike most of the electrolytic salts, which are purely inorganic compounds. Therefore, a rigorous search for superhalogen anions, whose Li-salts could be employed as electrolytes in LIBs, is needed.

In Fig. 2, we have displayed the structures of some anions such as BO_2^- , AlH_4^- , TiH_5^- and VH_6^- . The VDEs of these anions are also listed in Table 1, which suggest that these species also belong to the superhalogen series. One of the advantages of these species is that they all are halogen free and hence, less toxic. The equilibrium structures of Li-salts of these anions are also displayed in Fig. 2. We have also designed some borohydride $\text{BH}_{4-y}(\text{BH}_4)_y^-$ ($y = 1-4$) anions by successive replacement of H atoms by BH_4^- moieties in BH_4^- superhalogen. These are a special class of superhalogens, referred to as hyperhalogens [29,30], in which the role of ligands is played by a superhalogen itself. The equilibrium structures of resulting B_2H_7^- , $\text{B}_3\text{H}_{10}^-$, $\text{B}_4\text{H}_{13}^-$ and $\text{B}_5\text{H}_{16}^-$ hyperhalogens are displayed in Fig. 3 along with their Li-salts. The VDE of these hyperhalogens increases successively with the increase in BH_4^- ligands and reaches to as high as 7.28 eV for $\text{B}_5\text{H}_{16}^-$.

In order to behave as electrolytes, Li-salts should add to the conductivity of electrolytic medium. It is known that electrolytic salt contributes a lithium ion by dissociating into ionic fragments. Therefore, we have considered the dissociation of Li-X complexes into Li^+ and X^- . The corresponding dissociation energy ($\Delta E[\text{Li}^+]$) is calculated as follows:

$$\Delta E[\text{Li}^+] = E[\text{Li}^+] + E[\text{X}^-] - E[\text{Li-X}]$$

where $E[\cdot]$ represent total electronic energy of respective species including zero point correction. For an efficient electrolyte, $\Delta E[\text{Li}^+]$ should be comparable to or smaller than those for commercial electrolytes. The calculated $\Delta E[\text{Li}^+]$ values for various Li-salts are listed

Table 1
The VDE of complex anions for electrolytic salts at $\omega\text{B97xD}/6-311+G(d)$ level.

Currently used	VDE (eV)	Proposed ^a	VDE (eV)	Proposed ^b	VDE (eV)
FePO_4	4.32	NO_3^-	4.22	VH_6^-	4.23
ClO_4^-	5.83	BH_4^-	4.50	BO_2^-	4.44
$\text{N}(\text{SO}_2\text{F}_2)$	6.89	B_3H_8^-	4.72	AlH_4^-	4.69
$\text{N}(\text{SO}_2\text{CF}_3)_2$	7.01	$\text{CB}_{11}\text{H}_{12}^-$	5.99	TiH_5^-	4.72
BF_4^-	7.66	BeF_3^-	6.99	B_2H_7^-	5.52
PF_6^-	8.55	AuF_6^-	8.66	$\text{B}_3\text{H}_{10}^-$	6.25
AsF_6^-	8.91			$\text{B}_4\text{H}_{13}^-$	6.64
				$\text{B}_5\text{H}_{16}^-$	7.28

^a Ref. [10].

^b This work.

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