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Electrochemical oxidation stability of anions for modern battery electrolytes: a CBS and DFT study†

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The electrochemical stability vs. oxidation is a crucial property of anions in order to be suitable as components in lithium-ion batteries. Here the applicability of a number of computational approaches and methods to assess this property, employing a wide selection of DFT functionals, has been studied using the CCSD(T)/CBS method as the reference. In all, the vertical anion oxidation potential, ΔE_v , is a fair way to calculate the stability vs. oxidation, however, a functional of at least hybrid quality is recommended. In addition, the chemical hardness, η , is identified as a novel approach to calculate the stability vs. oxidation.

1 Introduction

Electrolytes are a key component of batteries and their electrochemical stability windows (ESWs); the potential range wherein none of its components breaks down due to oxidation or reduction, currently limit the capabilities of Li-ion batteries (LIBs).¹ This is due to the high voltages possible for LIBs, often above 4 V. As there is a strong desire to produce even higher voltage cathodes,² to allow for even higher energy density LIBs – a very high oxidation stability (preferably >5 V vs. Li^+/Li) is aimed at for future electrolytes. For the complementary/competing sodium-ion battery technology,³ currently seeing a rapid increase in attention, the overall development is foreseen to take the same direction. In order to reduce trial-and-error efforts, tools to predict electrochemical stability from chemical structure alone are of large interest. Generally, one way is by *in silico* screening, which allows for rapid evaluation of candidates for future synthesis.

Indeed, the ESWs of electrolyte solvents has been tackled computationally previously.^{4–6} This is in part due to the large importance of the solid electrolyte interphase (SEI) passivation layer on the LIB anode, formed by (controlled) electrolyte degradation.⁷ As the solvent tends to be reduced, the reduction limit of the ESW has had focus on the solvent, with extensive studies to understand the SEI formation.^{8–11} While the reduction limit of the anions has been studied in special solvents such as ionic liquids,^{12–14} the anions are not in general reduced in LIB (or SIB) electrolytes. The creation of a SEI,

partially by anion reduction, is a vast subject outside the scope of this paper.

In contrast, it is the (lithium) salt anion that often sets the oxidation limit, *e.g.* for ClO_4^- it is 6.1 V vs. Li^+/Li , while it is 6.8 V for PF_6^- in the same solvent.¹⁵ In contrast, the solvents used are known to have a fair stability vs. oxidation, *e.g.* the standard blend of ethylene and dimethyl carbonate (EC/DMC) was found to have a limit of 6.7 V vs. Li^+/Li .⁴ The stability of the anions *versus* oxidation are therefore often reported whenever novel salts for LIBs or SIBs are reported, either as experimental¹⁶ or computed¹⁷ values.

The experimentally measured ESWs have some variance due to the large number of factors affecting the final value, such as the sweep rate, solvent(s), and electrode(s) used.^{4,15,18,19} Thus reference values for the ESWs, *e.g.* the intrinsic anion redox potentials, properties solely of the anions and independent of the electrode/solvent chemistry and physics, are highly warranted.

For the anion oxidation stability, a common approach is to calculate the HOMO energy,²⁰ E_{HOMO} , due to the correlation between E_{HOMO} and the oxidation stability (based on the Koopmans theorem²¹). This approach can for example utilize Hartree–Fock (HF) methods with a small to medium sized basis set (*e.g.* 6-31G* or 6-311+G*) and is applicable to a vast number of compounds as it is computationally inexpensive.

To increase the accuracy, electron correlation must be taken into account, such as with density functional theory (DFT). Unfortunately, the Koopmans theorem is often not valid within the DFT formalism, due to the poor quality of the orbitals,²² despite their physical relevance.^{23–25} Thus an alternative approach, using the energy difference from a vertical excitation, is often used, either within the Frank–Condon approximation^{26,27} (ΔE_v) or allowing also for geometry relaxation of the excited state²⁸ to obtain the ionization potential (IP). Both approaches are illustrated in Fig. 1.

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† Electronic supplementary information (ESI) available: A table showing the extrapolation details of the CBS approach, the ΔE_v and η values for a number of additional anions and functionals. See DOI: 10.1039/c4cp04592k



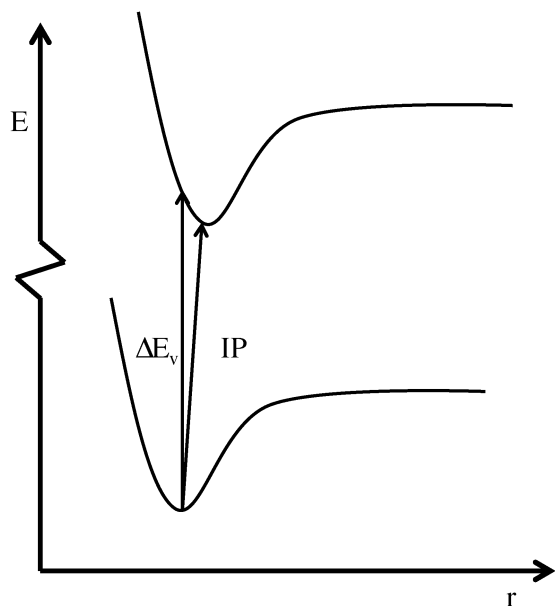


Fig. 1 Illustration of the different approaches used to calculate the anion oxidation potential using DFT: the vertical excitation energy (ΔE_v) and the ionization potential (IP).

As hybrid (or better) functionals are recommended for anions,²² the computational cost for such calculations is higher than for a pure HF calculation, as this approach at least involves an extra single-point calculation and significantly higher if geometry optimization of the excited state is performed. Allowing for geometry relaxation, however, also allows for a thermodynamic approach.^{28,29} If double-hybrid functionals are used, the computational cost increases even more.

Yet another approach is to study the chemical hardness, η – a concept that arises naturally from conceptual DFT:³⁰

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} \quad (1)$$

which is the resistance of the electronic chemical potential, μ , to the changing of the number of electrons. To our knowledge, this is only the second attempt to utilize this concept for the anion ESW.³¹

Here the first systematic study involving CCSD(T), MP2, and DFT calculations with a series of basis sets is presented – employed to obtain reference values for the intrinsic anion oxidation potentials at the complete basis set (CBS) limit. This enables a thorough assessment of the applicability and performance of the various methods available to calculate intrinsic oxidation potentials of anions.^{26–28}

2 Computational methodology

A number of anions that all at some point have been considered for LIB electrolytes were selected to be studied in detail (a subset of those previously studied by us³²); BF_4^- , PF_6^- , ClO_4^- , TFSI ($[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$), BOB ($[\text{B}(\text{C}_2\text{O}_4)_2]^-$), TDI ($\text{C}_5\text{N}_4\text{CF}_3^-$), Tf (CF_3SO_3^-), N_5^- , N_5C_2^- , N_5C_4^- (two isomers), N_5C_6^- (two isomers),

$\text{Im}(\text{BF}_3)_2^-$ and $\text{N}_5\text{C}_{10}^-$. A number of small anions were also added, as a control set. Additionally, some anions were found to be too large for the CBS method, and only partial results are therefore listed in the ESI.[†]

Single point energies were calculated with each of the following DFT functionals (with the 6-311+G* basis set): B3LYP,^{33–35} BMK,³⁶ PBE0,³⁷ TPSS,³⁸ TPSSH,³⁹ the M06 suite (M06, M06-2X, M06-L),⁴⁰ VSXC,^{41,42} B2PLYP,⁴³ and mPW2PLYP.⁴⁴ The B3LYP/6-311+G* equilibrium geometry was used for the anions and for the oxidized and reduced species.

The CCSD(T) calculations with the aug-cc-pVXZ (X = T, Q, 5) basis sets used an extrapolation to the CBS limit:⁴⁵

$$E(n) = E^{\text{CBS}} + An^{-3} \quad (2)$$

where n is the cardinality of the basis set used, *i.e.* $n = 3$ for aug-cc-pVTZ. This formula, chosen for its simplicity and performance,⁴⁶ was used to extrapolate the HF, MP2 and CCSD(T) energies. A separate extrapolation for the correlated part of the energy and the HF energy proved to have no significant effect on the results.

Due to the $O(N^7)$ scaling of CCSD(T), the rise in computational cost and time is staggering[‡] – making the full CCSD(T)/CBS treatment not feasible at present for all of the anions. Therefore, a mixed CBS method was employed, wherein a correction term is added to a MP2/CBS value (also extrapolated using eqn (2)). The correction term, $\Delta\text{CCSD(T)}$, was calculated with MP2/6-31G* and CCSD(T)/6-31G* (a small but reasonable basis set for our purpose⁴⁷):

$$\Delta\text{CCSD(T)} = E_{\text{CCSD(T)}}^{6-31\text{G}^*} - E_{\text{MP2}}^{6-31\text{G}^*} \quad (3)$$

The CCSD(T)/CBS values are then:

$$E_{\text{CCSD(T)}}^{\text{CBS}} = E_{\text{MP2}}^{\text{CBS}} + \Delta\text{CCSD(T)} \quad (4)$$

Values obtained with this method are forthcoming designated as ΔCBS .

A finite difference scheme was used for the calculation of the chemical hardness:

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} = \frac{1}{2} \times (E_{N+1} - 2E_N + E_{N-1}) \quad (5)$$

where E_N is the energy of the anion, and E_{N+1} and E_{N-1} are the energies of the reduced and oxidized anion species, respectively. The reduced anion species, E_{N+1} , could be considered an unphysical approximation, however, this is countered by the experimental observation of such species.¹²

E_{HOMO} values were extracted from the HF/6-311+G* calculations.

The vertical anion oxidation potentials, ΔE_v , were calculated using single point energies ($\Delta E_v = E_{N-1} - E_N$). As the experimental results in general are given *vs.* Li^+/Li , the computed ΔE_v are all shifted by 1.46 V.⁸ The Gaussian 09⁴⁸ program was used for all calculations and the Int = ExactBasisTransform keyword was used for the CBS calculations in order to ensure that no basis functions that contribute to the energy were pruned away during basis transformations.

[‡] Illustrating this, moving from TZ (230 basis functions) to 5Z (635 basis functions) for BF_4^- , increases the CPU time needed by a factor 100.



3 Results & discussion

The analysis of the results starts with a comparison between the CBS and the Δ CBS methods for small anions, followed by a further analysis of Δ CBS values of larger anions. Thereafter, we compare the performance of different functionals. Each section treats and discusses the HOMO, ΔE_v , and η approaches.

3.1 CBS vs. Δ CBS

Only a portion of the anions were small enough to allow CCSD(T) calculations with the aug-cc-pV5Z basis sets. Therefore, most anions had to resort to the Δ CBS measure rather than CBS. As MP2 energies are included in the results of the CCSD(T) calculations, the anions in Table 1 can also function as an internal benchmark for the Δ CBS method. In general, the values obtained from the Δ CBS method are close to the values from the CCSD(T)/CBS method. This holds for both the ΔE_v and η approaches, showing the general validity of the Δ CBS method. For BF_4^- , however, the Δ CBS values are 10% and 6% lower than the CBS values, giving a possible upper bound for possible errors. The BF_4^- values are close to revised experimental value of 6.2 V vs. Li^+/Li .

Surprisingly, neither the CBS nor the Δ CBS ΔE_v values for the halides are in the expected order of $\text{F}^- > \text{Cl}^- > \text{Br}^-$, instead $\text{Cl}^- > \text{Br}^- > \text{F}^-$ is observed. Comparing the E_{ox} values with the ΔE_v values for the halides, shows that the ΔE_v value is drastically lower. Similarly, the experimental E_{ox} value of ClO_4^- of 6.0 V vs. Li^+/Li is far higher than expected from the CBS calculations, with a ΔE_v value of 4.34 V vs. Li^+/Li . It seems as if the atomic anions have a problem with a proper radical description affecting this measure.

The hardness, η , has the expected ordering for the halides, furthermore, the hardness values are on average closer to the E_{ox} than the ΔE_v values. For example, BF_4^- has a hardness that is well within the range of the E_{ox} values, despite having the highest difference between η values calculated by CBS and Δ CBS. BF_4^- is also the only anion with a higher ΔE_v than η . ClO_4^- is the only anion for which all E_{ox} values are larger than the hardness.

Table 1 Anions with full CCSD(T)/CBS results. All values are given in V vs. Li^+/Li , except η and E_{HOMO} (eV). E_{ox} is experimental values

Anion	ΔE_v CCSD(T)/ CBS	ΔE_v Δ CBS	η CCSD(T)/ CBS	η Δ CBS	E_{HOMO} HF/6- 311+G*	E_{ox} Experimental
Br^-	2.12	2.10	4.37	4.36	-3.79	4.1 ⁴⁹
F^-	1.96	1.99	6.02	6.07	-4.08	5.9 ⁴⁹
Cl^-	2.21	2.25	4.89	4.89	-4.83	4.4 ⁴⁹
HS^-	0.89	0.93	2.93	2.92	-2.56	—
HF_2^-	4.93	4.97	5.40	5.44	-7.73	—
NO_3^-	2.72	2.74	4.40	4.30	-6.33	—
OCN^-	2.33	2.35	4.06	4.07	-4.35	—
SCN^-	2.16	2.22	3.64	3.66	-3.84	—
BF_4^-	7.03	6.35	6.42	6.06	-10.45	6.2; ²⁸ 6.6, 8.3 ¹⁵
BrO_3^-	3.44	3.54	4.48	4.55	-6.04	—
ClO_4^-	4.34	4.36	5.06	5.06	-7.89	6.0; ²⁸ 6.1, 7.0 ¹⁵
HCO_2^-	2.80	2.85	3.80	3.81	-5.11	—
BH_4^-	3.21	3.23	3.90	3.85	-5.19	—

The E_{HOMO} values have the same issues for the halides as the ΔE_v values, *i.e.* wrong ordering. Unfortunately, it is not the same ordering, *i.e.* $\text{Cl}^- > \text{F}^- > \text{Br}^-$. Looking at the E_{ox} values, the E_{HOMO} value for BF_4^- is very large, -10.45 eV, far larger than expected. It is not clear what causes BF_4^- to stand out for all measures.

3.2 Δ CBS

In Table 2 we show the Δ CBS values only for the larger anions for which CBS was not viable. A comparison vs. experimental data show that the ΔE_v approach tends to overestimate the oxidation potentials. This includes the BOB (by 1.63 V) and MOB (by 1.09 V) anions – with BOB correctly described to be more stable. Furthermore, some values are very close to the measured E_{ox} with $\text{Im}(\text{BF}_3)_2^-$ as the stellar example (only 0.07 V difference). For some other anions, a definite comparison is not possible, due to the large variations in E_{ox} values. These include TFSI, where the ΔE_v value is close to some of the E_{ox} values. Both AsF_6^- and PF_6^- have ΔE_v values close to the E_{ox} maximum values.

Overall, the hardness has qualitatively similar predictive power, as the ΔE_v values. In general, the η values are close to the E_{ox} values. Starting with the anions with single E_{ox} values, the η values are slightly higher, however, the difference is not as large as for the ΔE_v values. BOB and MOB have the largest differences, both 0.8 V, between E_{ox} and η . The η values of TFSI, Tf, PF_6^- and AsF_6^- are all within the range of reported E_{ox} values. Looking at the relative stability of BOB and MOB, we note that the difference between the ΔE_v values (0.6 V) is far higher than the η values (0.1 eV), the latter being closer to the E_{ox} difference.

The E_{HOMO} values show an unexpected ordering of oxidative stability; the third most stable anion, is the BOB anion (-8.81 eV), more stable than TFSI (-8.60 eV) and TDI (-5.54 eV), despite both having higher E_{ox} values than BOB. It is also notable that

Table 2 Anions with Δ CBS results for ΔE_v and η . All values are given in V vs. Li^+/Li , except η and E_{HOMO} which are in eV

Anion	ΔE_v	η	E_{HOMO}	E_{ox} Experimental
N_5^-	4.54	5.80	-6.10	—
NCN_2^-	2.86	4.44	-4.82	—
AsF_6^-	8.38	7.02	-12.13	6.5; ²⁸ 6.8, 8.6 ¹⁵
PF_6^-	8.57	7.21	-11.67	6.3; ²⁸ 6.8, 8.4 ¹⁵
$\text{C}(\text{CN})_3^-$	2.78	3.81	-4.60	—
CH_3COO^-	1.48	2.99	-5.10	—
N_5C_2^-	4.27	4.62	-5.70	—
Tf	5.31	5.04	-7.50	5.0, 5.9; ²⁸ 6.0, 7.0 ¹⁵
FSI	5.34	5.24	-8.66	> 4.5 ⁵⁰
$\text{N}_5\text{C}_4\text{a}^-$	4.32	5.51	-5.78	> 4.0 ^{51,52}
$\text{N}_5\text{C}_4\text{b}^-$	4.05	5.01	-5.55	—
$\text{N}_5\text{C}_6\text{a}^-$	4.45	5.02	-6.04	—
$\text{N}_5\text{C}_6\text{b}^-$	4.08	5.37	-5.49	—
BOB	6.13	5.30	-8.81	4.5 ⁵³
N_5C_8^-	4.20	4.47	-5.80	—
TDI	4.02	5.21	-5.54	4.80 ⁵⁴
TFSI	6.12	5.62	-8.60	5.3, 6.1; ²⁸ 6.3, 7.1; ¹⁵ 5.40 ⁵⁵
$\text{Im}(\text{BF}_3)_2^-$	4.92	4.53	-6.32	4.85 ¹⁶
MOB	5.49	5.23	-8.72	4.4 ⁵⁶
$\text{N}_5\text{C}_{10}^-$	4.59	—	-6.24	—
$\text{B}(\text{CH}_3)_4^-$	3.01	3.57	-5.34	2.9 ¹⁵



E_{HOMO} is the only measure that indicates AsF_6^- to be more stable than PF_6^- , as obtained by the maximum E_{ox} values.

3.3 Functional dependency

The analysis of the DFT functional performance is discussed first for ΔE_v and subsequently for η and grouped by functional type.

The ΔE_v values from DFT and HF in Table 3 in general underestimate ΔE_v – using ΔCBS as reference – with an average deviation negative for HF and all functionals (except M06-2X, +0.01 V), as seen in Fig. 2.

Starting with HF, one notable issue is the values for F^- and HS^- , both negative (vs. Li^+/Li). In practice this means that HF predicts that these anions would reduce Li^+ . HF also has the highest average and standard deviations. Notably, the Hückel anions ($\text{N}_5\text{C}_{2n}^-$, excluding N_5^-) have far lower values than the ΔCBS reference, with the difference ranging from 1.47 V to 2.09 V. The highly symmetric and quite special anion N_5^- is, however, slightly higher in energy than the reference, by 0.18 V. Other notable anions are AsF_6^- and PF_6^- , higher by 0.78 V and 0.38 V, respectively.

Each of the functionals used have different issues, a few observations, grouped by functional complexity, are here highlighted.

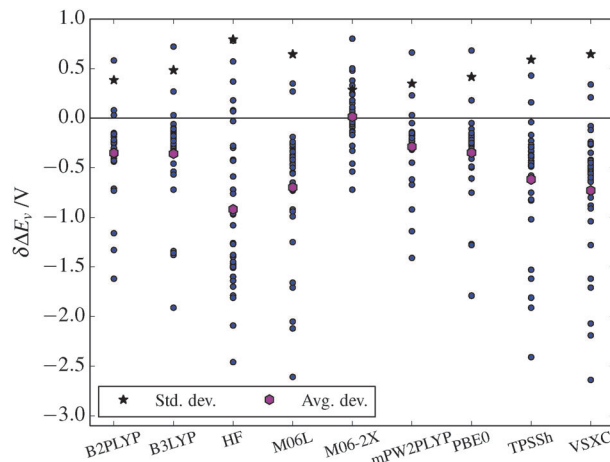


Fig. 2 The deviation, $\delta\Delta E_v$, of the ΔE_v value from the ΔCBS reference value for each of the methods. Average and standard deviations are also shown.

Starting with the non-hybrid functionals, VSXC has the largest average deviation (−0.73 V) of the DFT functionals. It underestimates the ΔE_v of a few anions by more than 2 V: PF_6^- is underestimated by 2.65 V, AsF_6^- by 2.19 V, and BOB by 2.07 V.

Table 3 Vertical oxidation potential (ΔE_v) of anions from selected DFT functionals and HF. ΔCBS values given for comparison. All values in V vs. Li^+/Li . The average and standard deviations are comparative to the ΔCBS values

Anion	ΔCBS	B2PLYP	B3LYP	HF	M06-L	M06-2X	mPW2PLYP	PBE0	TPSSH	VSXC
Br^-	2.10	1.91	2.13	1.02	1.85	2.03	1.93	2.05	2.06	2.02
Cl^-	1.99	2.02	2.26	1.02	2.26	2.23	2.02	2.17	2.15	2.20
F^-	2.25	1.84	2.03	−0.21	1.70	1.71	1.80	1.76	1.78	2.01
HS^-	0.93	0.62	0.87	−0.33	0.74	0.84	0.63	0.77	0.76	0.81
HF_2^-	4.97	4.72	4.60	4.94	4.05	5.12	4.81	4.56	4.22	4.09
NO_3^-	2.74	2.30	2.64	3.31	2.19	3.22	2.45	2.63	2.31	2.11
OCN^-	2.35	2.20	2.23	0.95	2.05	2.37	2.21	2.16	2.05	2.00
SCN^-	2.22	1.96	2.08	0.95	1.95	2.19	1.98	2.05	1.99	1.95
BF_4^-	6.35	6.43	5.98	6.05	5.36	6.85	6.58	6.03	5.52	5.31
BrO_3^-	3.54	3.19	3.31	2.95	2.89	3.61	3.27	3.28	3.05	2.97
ClO_4^-	4.36	4.20	4.20	4.08	3.80	4.74	4.31	4.21	3.88	3.72
HCO_2^-	2.85	2.14	2.31	2.13	1.91	2.57	2.23	2.24	2.03	1.94
BH_4^-	3.23	3.00	3.11	2.27	2.80	3.10	3.02	3.01	2.96	2.70
N_5^-	4.54	4.15	4.26	4.72	3.81	4.72	4.25	4.26	3.95	3.74
$\text{N}(\text{CN})_2^-$	2.86	2.67	2.65	1.37	2.49	2.88	2.68	2.62	2.47	2.38
AsF_6^-	8.38	7.22	7.00	9.16	6.26	8.24	7.46	7.11	6.47	6.19
PF_6^-	8.57	6.95	6.66	8.94	5.96	7.85	7.16	6.78	6.16	5.93
$\text{C}(\text{CN})_3^-$	2.78	2.53	2.60	1.27	2.45	2.80	2.55	2.58	2.44	2.34
CH_3COO^-	1.48	2.06	2.20	0.72	1.83	2.28	2.14	2.16	1.91	1.82
N_5C_2^-	4.27	4.10	4.08	2.48	3.94	4.28	4.11	4.06	3.93	3.85
Tf	5.31	4.90	3.97	5.39	3.60	5.41	5.02	4.96	3.69	3.60
FSI	5.34	5.10	5.08	4.92	4.65	5.67	5.20	5.11	4.76	4.59
$\text{N}_5\text{C}_4\text{a}^-$	4.32	4.10	4.02	2.23	3.86	4.26	4.11	4.01	3.87	3.78
$\text{N}_5\text{C}_4\text{b}^-$	4.05	3.86	3.87	2.58	3.71	4.10	3.88	3.86	3.72	3.62
$\text{N}_5\text{C}_6\text{a}^-$	4.45	4.19	4.19	2.85	4.04	4.44	4.21	4.19	4.05	3.94
$\text{N}_5\text{C}_6\text{b}^-$	4.08	3.78	3.77	2.27	3.61	4.02	3.80	3.77	3.63	3.52
BOB	6.13	4.80	4.77	5.70	4.08	5.67	4.99	4.85	4.32	4.06
N_5C_8^-	4.20	3.95	3.97	2.70	3.81	4.23	3.97	3.98	3.83	3.71
TDI	4.02	3.80	3.79	2.32	3.60	4.05	3.82	3.77	3.64	3.57
TFSI	6.12	5.39	5.40	4.74	4.46	5.79	5.45	5.37	4.59	4.50
$\text{Im}(\text{BF}_3)_2^-$	4.92	4.76	4.81	3.47	4.68	4.99	4.77	4.77	4.63	4.66
MOB	5.49	5.06	4.92	5.56	4.24	5.60	5.18	4.99	4.47	4.21
$\text{N}_5\text{C}_{10}^-$	4.59	4.26	4.26	2.95	4.09	4.55	4.28	4.28	4.11	3.99
$\text{B}(\text{CH}_3)_4^-$	3.01	2.65	2.55	2.08	2.36	2.84	2.69	2.52	2.39	2.21
Avg. dev.		−0.35	−0.36	−0.92	−0.70	0.01	−0.29	−0.35	−0.62	−0.73
Std. dev.		0.39	0.49	0.81	0.65	0.29	0.36	0.42	0.60	0.65



A few other anions are underestimated by more than 1 V: Tf, TFSI, MOB and BF_4^- . Two anions have their ΔE_v overestimated compared to the reference; Cl^- (by 0.22 V) and CH_3COO^- (by 0.33 V). M06-L has the second highest average deviation (−0.70 V) of the DFT functionals. The problematic anions are the same as for VSXC with only slightly different values.

The hybrid functionals have better performance characteristics, however, B3LYP has the same problematic cases as VSXC and M06-L. Though, as the average deviation implies, the errors are smaller in magnitude; PF_6^- is underestimated by 1.91 V and AsF_6^- by 1.38 V and most others anions are below 1 V in difference. However, the overestimates of CH_3COO^- and Cl^- are somewhat large, 0.72 V and 0.28 V, respectively. PBE0 has similar performance characteristics as B3LYP – including the same problems with PF_6^- , underestimated by 1.79 V, BOB by 1.28 V, and AsF_6^- by 1.27 V.

TPSSH performs somewhat worse than B3LYP. It is also the only hybrid functional that has any value that is underestimated by more than 2 V: PF_6^- by 2.41 V. The deviations for AsF_6^- and BOB are also large: 1.91 V and 1.81 V, respectively.

M06-2X has the distinction of having the lowest deviation of all of the functionals. However, it has a number of overestimates

such as CH_3COO^- by 0.80 V, BF_4^- by 0.50 V, and NO_3^- by 0.48 V. Furthermore, the underestimates are low; PF_6^- 0.72 V, F^- 0.53 V, and BOB 0.46 V. It is also notable that AsF_6^- is underestimated by only 0.14 V. Interestingly, the BF_4^- value of 6.85 V is closer to the CBS value (7.03 V), than the ΔCBS value (6.35 V).

The two double hybrid functionals have very small deviations, as mPW2PLYP has the second lowest average deviation (−0.29 V) and only has two values that differ by more than 1 V: PF_6^- and BOB are underestimated by 1.41 V and 1.14 V, respectively. B2PLYP is similar to mPW2PLYP, however, it has a slightly higher deviation; −0.35 V. It also has three anions that differ by more than 1 V from the reference: PF_6^- is underestimated by 1.62 V, AsF_6^- by 1.16 V, and BOB by 1.33 V.

When the results from all the DFT functionals are taken together, a few points become apparent. First, a larger number of electronegative groups present in the anion structure, tends to cause worse results. Thus heavily fluorinated molecules in general have ΔE_v values underestimated by 1–2 V. This is readily apparent for the PF_6^- and AsF_6^- anions. This is also an issue for BOB, but to a less extent for the MOB variant, which has the less electronegative malonate moiety. This could be an issue for

Table 4 Hardness (η) of anions from selected DFT functionals and HF. ΔCBS values given for comparison. All values in eV. The average and standard deviations are comparative to ΔCBS values

Anion	ΔCBS	B2PLYP	B3LYP	HF	M06-L	M06-2X	mPW2PLYP	PBE0	TPSSH	VSXC
Br^-	4.36	4.92	4.93	4.69	4.86	4.88	4.94	4.90	4.94	5.06
Cl^-	4.89	5.75	5.75	5.50	5.83	5.74	5.76	5.71	5.73	5.43
F^-	6.07	8.47	8.42	7.83	8.33	8.30	8.46	8.30	8.31	8.58
HS^-	2.92	4.17	4.16	3.87	4.14	4.12	4.18	4.10	4.10	4.14
HF_2^-	5.44	8.13	7.89	8.69	7.85	8.25	8.19	7.94	7.78	7.78
NO_3^-	4.30	5.47	5.50	5.88	5.58	5.80	5.51	5.55	5.34	5.37
OCN^-	4.07	4.73	4.66	4.26	4.80	4.73	4.73	4.63	4.59	4.44
SCN^-	3.66	4.23	4.20	3.91	4.33	4.27	4.24	4.19	4.18	4.02
BF_4^-	6.06	6.76	6.43	6.74	6.29	6.94	6.82	6.48	6.25	6.00
BrO_3^-	4.55	4.87	4.86	4.83	4.85	5.08	4.91	4.84	4.76	4.65
ClO_4^-	5.06	5.81	5.72	6.07	5.97	6.08	5.86	5.78	5.65	5.43
HCO_2^-	3.81	5.10	4.77	4.86	4.74	4.95	5.14	4.73	4.64	4.52
BH_4^-	3.85	5.10	5.07	4.88	5.04	4.96	5.11	5.01	5.01	4.75
N_5^-	5.80	6.61	6.49	7.09	6.48	6.86	6.64	6.57	6.39	6.39
$\text{N}(\text{CN})_2^-$	4.44	4.51	4.43	4.05	4.65	4.56	4.52	4.43	4.39	4.11
AsF_6^-	7.02	6.54	6.29	7.86	6.27	7.16	6.64	6.42	6.11	5.83
PF_6^-	7.21	6.91	6.65	8.15	6.32	7.36	7.00	6.75	6.32	6.10
$\text{C}(\text{CN})_3^-$	3.81	4.19	4.16	3.75	4.39	4.28	4.20	4.17	4.12	3.81
CH_3COO^-	2.99	4.29	4.28	3.71	4.31	4.35	4.33	4.26	4.16	4.04
N_5C_2^-	4.62	5.07	4.99	5.00	5.45	5.14	5.08	4.98	4.94	4.75
Tf	5.04	5.67	5.11	6.05	5.19	5.97	5.72	5.62	5.01	4.85
TFSI	5.24	5.56	5.44	5.80	5.61	5.89	5.60	5.52	5.35	5.12
$\text{N}_5\text{C}_4\text{a}^-$	5.51	5.02	4.78	4.33	4.79	4.99	5.00	4.80	4.75	4.74
$\text{N}_5\text{C}_4\text{b}^-$	5.01	5.06	4.85	4.74	4.86	5.09	5.05	4.88	4.82	4.37
$\text{N}_5\text{C}_6\text{a}^-$	5.02	4.68	4.48	4.31	4.47	4.69	4.68	4.50	4.45	4.43
$\text{N}_5\text{C}_6\text{b}^-$	5.37	4.65	4.44	4.14	4.44	4.65	4.64	4.46	4.41	4.39
BOB	5.30	5.05	4.87	5.76	4.69	5.37	5.12	4.94	4.69	4.48
N_5C_8^-	4.47	4.32	4.11	3.95	4.09	4.33	4.31	4.13	4.08	4.05
TDI	5.21	4.74	4.54	4.26	4.54	4.74	4.73	4.55	4.51	4.49
TFSI	5.62	5.53	5.38	5.51	5.15	5.78	5.55	5.41	5.01	4.83
$\text{Im}(\text{BF}_3)_2^-$	4.53	5.06	4.99	4.57	5.39	5.17	5.05	4.98	4.94	5.02
MOB	5.23	5.23	4.98	5.75	4.78	5.39	5.27	5.06	4.81	4.58
$\text{N}_5\text{C}_{10}^-$	— ^a	4.30	4.08	3.87	4.05	4.30	4.29	4.10	4.04	4.01
$\text{B}(\text{CH}_3)_4^-$	3.57	4.21	4.07	4.15	4.32	4.27	4.23	4.08	4.04	3.77
Avg. dev.		0.49	0.35	0.45	0.39	0.61	0.52	0.38	0.26	0.13
Std. dev.		0.78	0.82	0.89	0.86	0.74	0.78	0.79	0.83	0.90

^a $\text{N}_5\text{C}_{10}^-$ has no reference value and is thus neglected in the statistics.



future *ab initio* work on novel electrolyte anions, as they tend to be themed around strongly electronegative groups.

Second, while DFT on the whole results in too low ΔE_v values, the ΔE_v value for CH_3COO^- is in general overestimated from 0.5 V to 0.8 V. The ΔE_v for Cl^- is also often overestimated.

Third, in general the performance of the DFT functionals follows the Jacob's ladder of DFT.⁵⁷ The hybrid functionals perform better than the local functionals, VSXC and M06-L, while the double-hybrid functionals, mPW2PLYP and B2PLYP, perform even better. There is one functional that performs far better, M06-2X, though that may be a fortunate cancellation of errors, as this functional is heavily parameterized.

Moving on to the chemical hardness measure, on average the DFT functionals overestimate the hardness (Table 4 and Fig. 3), as all average deviations are positive. Furthermore, with the large standard deviations, there will be outliers for each functional. Each functional must be inspected, following the same analysis layout as above. Starting with VSXC and M06-L, these have the same outliers, albeit differing slightly in magnitude. Both overestimate the F^- and HF_2^- by over 2 eV, and also have issues with CH_3COO^- and Cl^- . The functionals in general underestimate the hardness of the Hückel anions (N_5C_{2n} , $n = 2 \dots$), and BOB, by 0.5 eV or more. Furthermore, both functionals underestimate PF_6^- and AsF_6^- , M06-L by 0.89 eV and 0.75 eV and VSXC by 1.11 eV and 1.20 eV, respectively. Interestingly, the average deviations for the two functionals are small, 0.13 eV for VSXC and 0.39 eV for M06-L.

Looking at the hybrid functionals; B3LYP, M06-2X, PBE0, and TPSSh, all reveal the same pattern as for the VSXC and M06-L functionals, e.g. an overestimated hardness for F^- and HF_2^- , in each case by ≥ 2 eV. However, the underestimates of the PF_6^- and AsF_6^- anions are much reduced for all the hybrid functionals (except TPSSh). M06-2X has even a slight overestimate of the PF_6^- and AsF_6^- , by 0.16 eV and 0.14 eV, respectively.

The double hybrid functionals, B2PLYP and mPW2PLYP, have some of the largest average deviations of all the functional of Table 4, however, they have some of the smallest standard deviations, implying that they tend to overestimate the hardness.

They also have many of the same outliers as the other functionals, in particular F^- and HF_2^- , which are overestimated by ≥ 2.4 eV. Furthermore, Cl^- and CH_3COO^- continue to have some overestimation (≈ 0.8 eV and 1.3 eV, respectively). The Hückel anions (N_5C_{2n} , $n = 2 \dots$), continue to have some underestimation. However, the magnitude of the underestimate for PF_6^- and AsF_6^- is smaller than for most of the hybrid functionals, with 0.30 eV and 0.38 eV for B2PLYP and 0.21 eV and 0.38 eV for mPW2PLYP, respectively.

Comparing the deviations from the reference values for both approaches, ΔE_v (Fig. 2) and η (Fig. 3), it must be noted that the magnitude of the deviations of η are far larger (note the figure scales). Furthermore, looking at Fig. 1 and 2 of the ESI,[†] show that while DFT can tackle ΔE_v calculations, the same is not clear for η , due to the low correlation with the ΔCBS values.

4 Conclusions

For the calculation of the stability *vs.* oxidation for the present set of anions, using the methodology of ΔE_v , a hybrid (or better yet, double hybrid) functional is recommended. Their resulting ΔE_v values are closer to the benchmark, surpassing the previously recommended VSXC functional of older works.^{26,27} Out of the DFT functionals tested, M06-2X performs the best.

Using the E_{HOMO} measure to predict the stability *vs.* oxidation is debatable, due to the unexpected ordering of the anions' oxidative stability. Furthermore, neither the E_{HOMO} nor the ΔE_v approaches were able to predict the expected ordering of $\text{F}^- > \text{Cl}^- > \text{Br}^-$.

Hardness is another interesting property to study in connection with oxidation potentials, though the origin of its strong correlation with E_{ox} is not clear. Out of the many DFT functionals tested, no strong general recommendation can be made, however, the double hybrids and M06-2X are candidates for the calculation of hardnesses.

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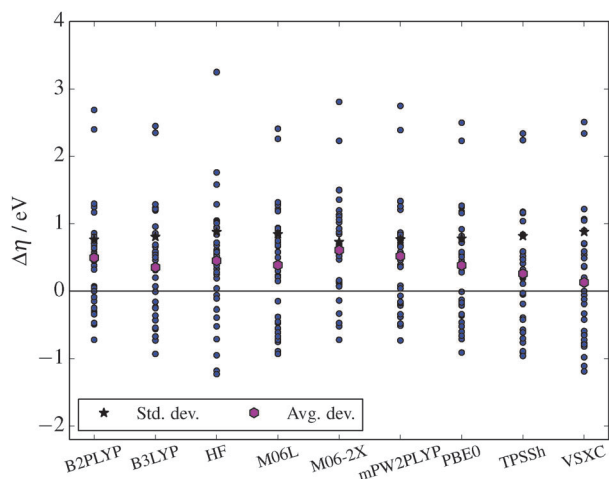


Fig. 3 The deviation of the hardness from the ΔCBS reference value for each of the methods. Average and standard deviations are also shown.



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