# 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, $\Delta E_v$, 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, $\eta$, 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 experimental[16] or computed[17] 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 theorem[21]). 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 in to 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] ($\Delta E_v$) or allowing also for geometry relaxation of the excited state[28] to obtain the ionization potential (IP). Both approaches are illustrated in Fig. 1.

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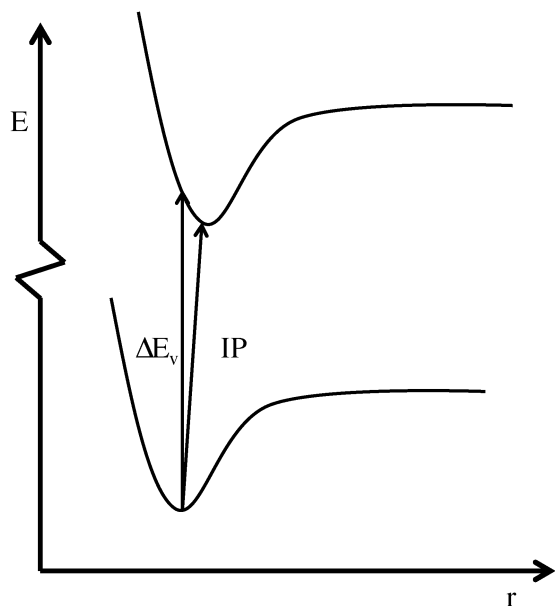
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**Fig. 1** Illustration of the different approaches used to calculate the anion oxidation potential using DFT; the vertical excitation energy ($\Delta E_v$) and the ionization potential (IP).

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, $\eta$ – a concept that arises naturally from conceptual DFT:[30]

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

which is the resistance of the electronic chemical potential, $\mu$, 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 us[32]); $BF_4^-$, $PF_6^-$, $ClO_4^-$, TFSI ($[(CF_3SO_2)_2N]^-$), BOB ($[B(C_2O_4)_2]^-$), TDI ($C_5N_4CF_3^-$), Tf ($CF_3SO_3^-$), $N_5^-$, $N_5C_2^-$, $N_5C_4^-$ (two isomers), $N_5C_6^-$ (two isomers),

$Im(BF_3)_2^-$ and $N_5C_{10}^-$. 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]

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

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, $\Delta$CCSD(T), was calculated with MP2/6-31G* and CCSD(T)/6-31G* (a small but reasonable basis set for our purpose[47]):

$$\Delta CCSD(T) = E^{6\text{-}31G^*}_{CCSD(T)} - E^{6\text{-}31G^*}_{MP2} \qquad (3)$$

The CCSD(T)/CBS values are then:

$$E^{CBS}_{CCSD(T)} = E^{CBS}_{MP2} + \Delta CCSD(T) \qquad (4)$$

Values obtained with this method are forthcoming designated as $\Delta$CBS.

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

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

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, $\Delta E_v$, 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 $\Delta E_v$ are all shifted by 1.46 V.[8] The Gaussian 09[48] 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.

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‡ 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 ΔCBS methods for small anions, followed by a further analysis of ΔCBS values of larger anions. Thereafter, we compare the performance of different functionals. Each section treats and discusses the HOMO, $\Delta E_v$, and $\eta$ approaches.

## 3.1 CBS vs. ΔCBS

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 ΔCBS 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 ΔCBS method. In general, the values obtained from the ΔCBS method are close to the values from the CCSD(T)/CBS method. This holds for both the $\Delta E_v$ and $\eta$ approaches, showing the general validity of the ΔCBS method. For $BF_4^-$, however, the ΔCBS 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 ΔCBS $\Delta E_v$ values for the halides are in the expected order of $F^- > Cl^- > Br^-$, instead $Cl^- > Br^- > F^-$ is observed. Comparing the $E_{ox}$ values with the $\Delta E_v$ values for the halides, shows that the $\Delta E_v$ 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 $\Delta E_v$ 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, $\eta$, has the expected ordering for the halides, furthermore, the hardness values are on average closer to the $E_{ox}$ than the $\Delta E_v$ 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 $\eta$ values calculated by CBS and ΔCBS. $BF_4^-$ is also the only anion with a higher $\Delta E_v$ than $\eta$. $ClO_4^-$ is the only anion for which all $E_{ox}$ values are larger than the hardness.

The $E_{HOMO}$ values have the same issues for the halides as the $\Delta E_v$ values, i.e. wrong ordering. Unfortunately, it is not the same ordering, i.e. $Cl^- > F^- > Br^-$. 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 ΔCBS

In Table 2 we show the ΔCBS values only for the larger anions for which CBS was not viable. A comparison vs. experimental data show that the $\Delta E_v$ 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 $Im(BF_3)_2^-$ 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 $\Delta E_v$ value is close to some of the $E_{ox}$ values. Both $AsF_6^-$ and $PF_6^-$ have $\Delta E_v$ values close to the $E_{ox}$ maximum values.

Overall, the hardness has qualitatively similar predictive power, as the $\Delta E_v$ values. In general, the $\eta$ values are close to the $E_{ox}$ values. Starting with the anions with single $E_{ox}$ values, the $\eta$ values are slightly higher, however, the difference is not as large as for the $\Delta E_v$ values. BOB and MOB have the largest differences, both 0.8 V, between $E_{ox}$ and $\eta$. The $\eta$ 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 $\Delta E_v$ values (0.6 V) is far higher than the $\eta$ 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 1** Anions with full CCSD(T)/CBS results. All values are given in V vs. Li$^+$/Li, except $\eta$ and $E_{HOMO}$ (eV). $E_{ox}$ is experimental values

| Anion | $\Delta E_v$ CCSD(T)/CBS | $\Delta E_v$ ΔCBS | $\eta$ CCSD(T)/CBS | $\eta$ ΔCBS | $E_{HOMO}$ 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 | — |

**Table 2** Anions with ΔCBS results for $\Delta E_v$ and $\eta$. All values are given in V vs. Li$^+$/Li, except $\eta$ and $E_{HOMO}$ which are in eV

| Anion | $\Delta E_v$ | $\eta$ | $E_{HOMO}$ | $E_{ox}$ 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] |
| C(CN)$_3^-$ | 2.78 | 3.81 | −4.60 | — |
| CH$_3$COO$^-$ | 1.48 | 2.99 | −5.10 | — |
| N$_5$C$_2^-$ | 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] |
| N$_5$C$_4$a$^-$ | 4.32 | 5.51 | −5.78 | >4.0[51,52] |
| N$_5$C$_4$b$^-$ | 4.05 | 5.01 | −5.55 | — |
| N$_5$C$_6$a$^-$ | 4.45 | 5.02 | −6.04 | — |
| N$_5$C$_6$b$^-$ | 4.08 | 5.37 | −5.49 | — |
| BOB | 6.13 | 5.30 | −8.81 | 4.5[53] |
| N$_5$C$_8^-$ | 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] |
| Im(BF$_3$)$_2^-$ | 4.92 | 4.53 | −6.32 | 4.85[16] |
| MOB | 5.49 | 5.23 | −8.72 | 4.5[56] |
| N$_5$C$_{10}^-$ | 4.59 | — | −6.24 | — |
| B(CH$_3$)$_4^-$ | 3.01 | 3.57 | −5.34 | 2.9[15] |

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$E_{HOMO}$ 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 $\Delta E_v$ and subsequently for $\eta$ and grouped by functional type.

The $\Delta E_v$ values from DFT and HF in Table 3 in general underestimate $\Delta E_v$ – using $\Delta CBS$ 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 ($N_5C_{2n}^-$, excluding $N_5^-$) have far lower values than the $\Delta CBS$ 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.
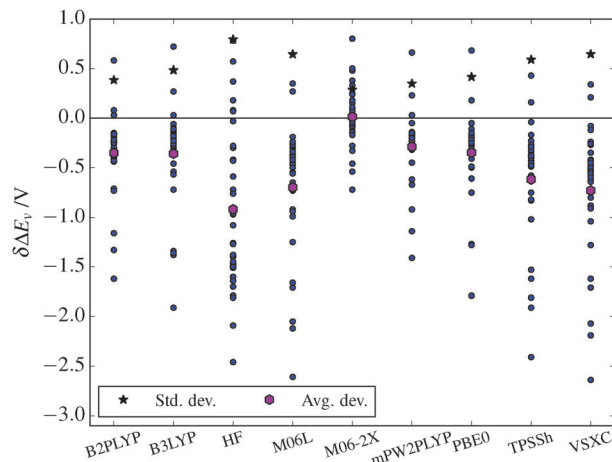


Fig. 2 The deviation, $\delta\Delta E_v$ of the $\Delta E_v$ value from the $\Delta CBS$ reference value for each of the methods. Average and standard deviations are also shown.

Starting with the non-hybrid functionals, VSXC has the largest average deviation (−0.73 V) of the DFT functionals. It underestimates the $\Delta E_v$ 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 ($\Delta E_v$) of anions from selected DFT functionals and HF. $\Delta CBS$ values given for comparison. All values in V *vs.* $Li^+/Li$. The average and standard deviations are comparative to the $\Delta CBS$ values

| Anion | $\Delta CBS$ | 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 |
| $N(CN)_2^-$ | 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 |
| $C(CN)_3^-$ | 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 |
| $N_5C_4a^-$ | 4.32 | 4.10 | 4.02 | 2.23 | 3.86 | 4.26 | 4.11 | 4.01 | 3.87 | 3.78 |
| $N_5C_4b^-$ | 4.05 | 3.86 | 3.87 | 2.58 | 3.71 | 4.10 | 3.88 | 3.86 | 3.72 | 3.62 |
| $N_5C_6a^-$ | 4.45 | 4.19 | 4.19 | 2.85 | 4.04 | 4.44 | 4.21 | 4.19 | 4.05 | 3.94 |
| $N_5C_6b^-$ | 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 |
| $Im(BF_3)_2^-$ | 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 |
| $N_5C_{10}^-$ | 4.59 | 4.26 | 4.26 | 2.95 | 4.09 | 4.55 | 4.28 | 4.28 | 4.11 | 3.99 |
| $B(CH_3)_4^-$ | 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 |

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A few other anions are underestimated by more than 1 V: Tf, TFSI, MOB and $BF_4^-$. Two anions have their $\Delta E_v$ 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 AsF6 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, BF4 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 $\Delta$CBS 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 $\Delta E_v$ 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 malonato moiety. This could be an issue for

**Table 4** Hardness ($\eta$) of anions from selected DFT functionals and HF. $\Delta$CBS values given for comparison. All values in eV. The average and standard deviations are comparative to $\Delta$CBS values

| Anion | $\Delta$CBS | 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 |
| $N(CN)_2^-$ | 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 |
| $C(CN)_3^-$ | 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 |
| FSI | 5.24 | 5.56 | 5.44 | 5.80 | 5.61 | 5.89 | 5.60 | 5.52 | 5.35 | 5.12 |
| $N_5C_4a^-$ | 5.51 | 5.02 | 4.78 | 4.33 | 4.79 | 4.99 | 5.00 | 4.80 | 4.75 | 4.74 |
| $N_5C_4b^-$ | 5.01 | 5.06 | 4.85 | 4.74 | 4.86 | 5.09 | 5.05 | 4.88 | 4.82 | 4.37 |
| $N_5C_6a^-$ | 5.02 | 4.68 | 4.48 | 4.31 | 4.47 | 4.69 | 4.68 | 4.50 | 4.45 | 4.43 |
| $N_5C_6b^-$ | 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 |
| $Im(BF_3)_2^-$ | 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 |
| $N_5C_{10}^-$ | —$^a$ | 4.30 | 4.08 | 3.87 | 4.05 | 4.30 | 4.29 | 4.10 | 4.04 | 4.01 |
| $B(CH_3)_4^-$ | 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 |

$^a$ $N_5C_{10}^-$ 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 $\Delta E_v$ values, the $\Delta E_v$ value for $CH_3COO^-$ is in general overestimated from 0.5 V to 0.8 V. The $\Delta E_v$ 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 ($N_5C_{2n}$, $n = 2...$), 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 $\geq 2$ 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 $\geq 2.4$ eV. Furthermore, $Cl^-$ and $CH_3COO^-$ continue to have some overestimation ($\approx 0.8$ eV and 1.3 eV, respectively). The Hückel anions ($N_5C_{2n}$, $n = 2...$), 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, $\Delta E_v$ (Fig. 2) and $\eta$ (Fig. 3), it must be noted that the magnitude of the deviations of $\eta$ are far larger (note the figure scales). Furthermore, looking at Fig. 1 and 2 of the ESI,† show that while DFT can tackle $\Delta E_v$ calculations, the same is not clear for $\eta$, due to the low correlation with the $\Delta$CBS values.

# 4 Conclusions

For the calculation of the stability *vs.* oxidation for the present set of anions, using the methodology of $\Delta E_v$, a hybrid (or better yet, double hybrid) functional is recommended. Their resulting $\Delta E_v$ 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 $\Delta E_v$ approaches were able to predict the expected ordering of $F^- > Cl^- > Br^-$.

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.

# Acknowledgements

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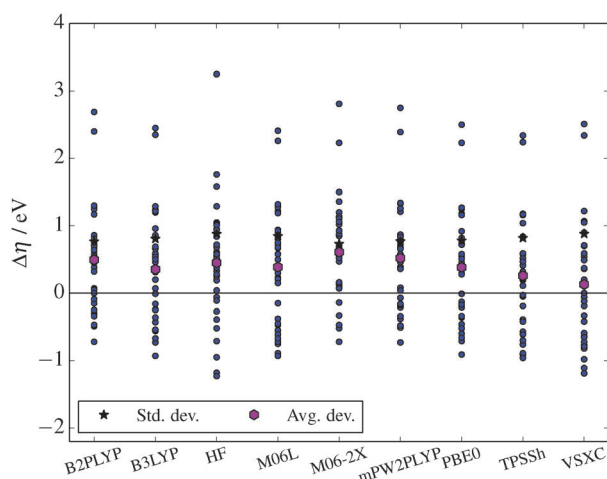5  X. Zhang, J. K. Pugh and P. N. Ross, *J. Electrochem. Soc.*, 2001, **148**, E183–E188.

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

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