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Performances of different DFT functionals to calculate the anodic limit of fluorinated sulphonyl-imide anions for lithium cells.

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Abstract. In this paper we investigated the calculation of the anodic limit of two anions of ionic liquids, largely used as electrolyte of lithium batteries. Starting from a model based on calculations performed on single ions at the MP2 level of theory, we showed that the matching between calculation and experiments decreases while using more expanded basis set with respect to 6-31G**, possibly because of the destabilization of the neutral species when larger basis sets are considered. Additionally, in order to decrease the computational time, the performances for the calculation of the anodic limit obtained by means of a series of DFT functionals with increasing level of complexity (from the Generalized Gradient Approximation to the Range Separated Hybrid meta–Generalized Gradient Approximation) were compared. Overall, the best performing functionals are BMK, ωB97M-V and MN12-SX, while acceptable results can be obtained by M06-2X, M11, M08-HX and M11-L. Some less computationally expensive functionals, like CAM-B3LYP and ωB97X-D, also provide reasonable values of the anodic limit.

1. Introduction

Electrochemical energy storage devices are nowadays ubiquitous [1]. A massive injection of batteries in all-day life occurred with the advent of portable phones and the need for high energy density batteries to power them. In more recent times, the concept of "high energy density" has additionally evolved and the most demanding requirements for electrochemical devices are posed by their use to power transport vehicles [2]. One of the strategies to increase their power density is the increase of the electric potential at which they can operate [3]. This poses serious constraints on the choice of suitable materials, not only on the electrode ones [4], but also on the components of the electrolyte [5] which allows the motion of lithium ions. In fact, electrolyte components should be able to sustain the high voltages and to avoid decomposition also at the highest ones.

In this paper, we investigate from a computational point of view the electrochemical stability of a selected number of anions typically exploited in the formulation of ionic liquids (IL). Ionic liquids are

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presently considered as safe and high performing solvents alternative to liquid carbonates for enhanced aprotic electrolytes in lithium batteries [5]. Over the years, many computational methods for the calculations of the electrochemical stability limits of electrolytes and ionic liquids have been proposed with the goal to mimic the irreversible oxidations or reductions of salts and solvents. In particular for ionic liquids, that are composed of charged species, the irreversible oxidation (removal of one electron) occurs from the anion, while the irreversible reduction (addition of one electron) takes place on the cation. Oxidation and reductions of species (neutral or charged) involve an energy difference between the starting and final states that can be easily put in direct relation to a potential difference compared to a reference electrode, thus mimicking the electrochemical stability.

Despite these concepts can be summarized in such a simple fashion, the ways in which the oxidation and reduction energy and potentials have been calculated are numerous. The simplest models used in the early day, but still used sometimes nowadays, considers a linear correlation between the energy of the highest unoccupied molecular orbital (HOMO) of anions and their oxidation potential [6,7]. This method is not able to provide a quantitative description of the anodic stability of anions. A more elaborate model was proposed considering vertical or adiabatic transitions between the initial ion and the neutral molecule [8,9]. The calculations were performed both in vacuum and in a polarisable medium [8,9]. The inclusion of the medium wants to simulate the presence of a liquid phase [8,9]; however, the derived results overestimate the anodic limit and the electrochemical stability window (ESW, the difference between the anodic and cathodic limit). Moreover, a linear relationship seems to exist between the anodic stability calculated by means of vertical and adiabatic transitions [9]. Various DFT functional were exploited for the calculation of the anodic limits [11-13]. A combination of DFT calculations and molecular dynamics were used in the case for six specific ionic liquids used in lithium batteries [14]. Recently, also the potentiality of ab-initio molecular dynamic has been investigated [15]. Cheng [16] and Kazemiabnavi [17] proposed complex thermochemical cycles to evaluate reduction and oxidation potentials of ILs, following the approach of Winget et al. and Marenich et al. [18,19], also including ion salvation [16,17]. These valuable strategies have been adopted in high throughput screening of hundreds of possible ionic liquids [16,20], using hybrid-DFT calculations and the B3LYP functional.

We recently compared some of these proposed methods for the calculation of the electrochemical stability, having some experimental benchmark data [21]. We showed that calculations performed on the whole ionic couple do not provide accurate results leading to large errors in the estimate of the electrochemical stability window (ESW) of ILs. Calculations based on the investigation of the single ions seem to provide values in better agreement with the experiments [21]. Despite it seems counterintuitive, accurate and precise calculations require vacuum and not a simulated polarisable medium. In fact simulated solvent unphysically stabilize charged species thus leading to unrealistic large ESWs. Overall, the best agreement between computations and experiments is obtained when the oxidation or reduction process are modelled without a structural relaxation (vertical transitions, purely electronic) in vacuum with a MP2 level of theory, whereas the typical B3LYP hybrid-DFT functional is much less accurate [21].

In the present work, we want to tackle two strictly correlated issues in order to deepen the knowledge about the computation of the anodic limit of some common anions of ionic liquids. Starting from the isolated anion model used in Ref. [21] we will investigate: 1) the impact of the size of the basis set on the accuracy of ESW obtained from MP2 calculations, and 2) the effect of the adoption of a large variety of DFT functionals in the accuracy of the computed ESW.

2. Computational

All calculations were performed by means of the Spartan software [22]. In the first part of the study, the structures of the FSI and TFSI anions were optimized at the MP2 level of theory, using various basis sets, starting from 6-31G**, already employed in Ref. [21], and moving to larger basis sets such as 6-31+G**, 6-311G**, 6-311+G*, ccPVDZ and aug-cc-pVDZ. In the second part of the investigation, the structure of the FSI and TFSI anions were optimized by means of various DFT functionals with various level of complexity, ranging from those based on the simplest Generalized Gradient Approximation (GGA) to those relying on the Range Separated Hydrid meta–Generalized Gradient Approximation (RSH-mGGA). To evaluate the influence of the chosen functional on the calculated values of the electrochemical stability, for each of them the 6-31G** basis set was employed.

In general, independently of the particular choice of the functional and basis set, in order to calculate the anodic stability of bis-fluorosulfonyl imide (FSI) and bis-trifluoromethyl sulfonyl imide (TFSI), we followed the procedure previously indicated as that giving the best agreement [21] with the experimental data obtained on five different ionic liquids: EMIFSI, EMITFSI, N1114FSI, N1114TFSI and N122(2O1)TFSI [23, 24]. In this context, we considered a vertical transition between the electronic states of the structurally relaxed anion (initial state) and the neutral state of the same entity (final state), without any structural relaxation in comparison with the initial anion. Calling $E_{tot}(X)$ the electronic energy of the species X, the energy variation during the vertical transition from the anion to the neutral species is:

$$\Delta E_{Anodic} = E_{tot}(A) - E_{tot}(A^-) \tag{1}$$

and the anodic limit of the anion is given by:

$$\textit{Anodic limit (V vs. Li)} = \Delta E_{Anodic}/F - 1.46 \tag{2}$$

where F is the Faraday constant and the factor -1.46 V is due to the necessity of referring these limits to the standard Li^+/Li^0 electrode, as discussed in Ref. [11].

3. Results and discussion

3.1 Impact of the basis set on the accuracy of MP2 predictions

In the first part of this study, we investigated the influence of the basis set extension on the predicted oxidation potential of FSI and TFSI anions, calculated at the MP2 level of theory. Table 1 reports the electronic energy of the anions and of the corresponding neutral species, together with the derived anodic limit.

Table 1. Electronic energy of the FSI and TFSI anions and of the corresponding neutral species and derived anodic stability, calculated at the MP2 level of theory using different basis-sets.

Anion	Basis set	$E(A^-)$ (au)	$E(A)$ (au)	Anodic limit (V)
FSI	6-31G**	-1349.235	-1348.998	4.92
FSI	6-31+G**	-1349.297	-1349.044	5.36
FSI	6-311G*	-1349.556	-1349.308	5.23
FSI	6-311+G**	-1349.597	-1349.342	5.41

FSI	cc-pVDZ	-1349.296	-1349.065	4.78
FSI	aug-cc-pVDZ	-1349.521	-1349.268	5.37
TFSI	6-31G**	-1823.631	-1823.392	4.99
TFSI	6-31+G**	-1823.730	-1823.474	5.45
TFSI	6-311G*	-1824.233	-1823.988	5.12
TFSI	6-311+G**	-1824.301	-1824.048	5.35
TFSI	cc-pVDZ	-1823.783	-1823.549	4.84
TFSI	aug-cc-pVDZ	-1824.117	-1823.863	5.39

A pictorial representation of the accuracy of the calculation results summarized in Table 1 are shown in Figure 1 where we compare the experimental values of the anodic limit of the FSI and TFSI based ionic liquids [23] with the figures obtained by the MP2 modelling.
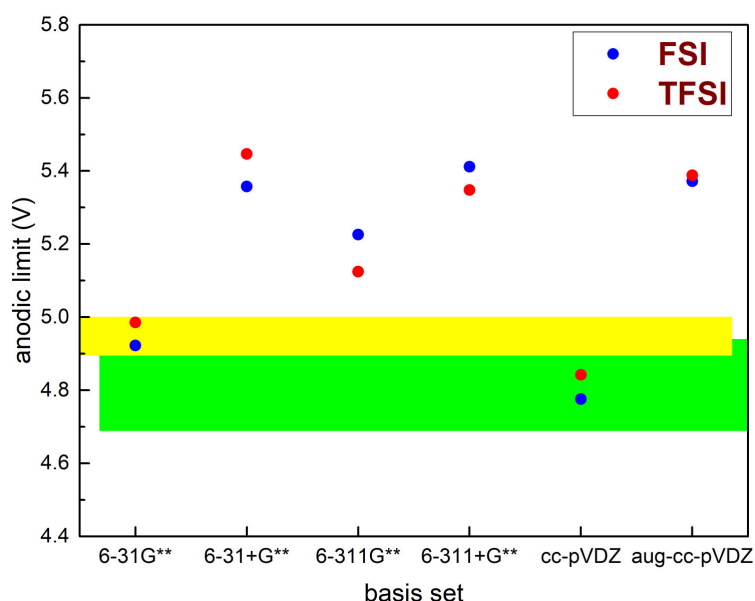

Figure 1. Comparison of the values of the anodic limits of FSI and TFSI calculated at the MP2 level of theory using various basis sets with the range of experimental values reported in Ref. [21, 23] for the FSI- (green rectangle) and TFSI-based (yellow rectangle) ILs.

Experimental oxidation potentials are represented in Figure 1 as coloured regions to take into account the various results reported for different test conditions unrelated to the anion chemical nature itself, e.g. different salt, different electrode, different concentration. The computed anodic limit (AL) ranges between 4.9 and 5.0 V for both anions, when calculated with the 6-31G** basis sets. AL increases up to about 5.4 V considering polarization functions on heavy atoms and hydrogen, as well as diffuse functions on heavy atoms. The Double-zeta cc-pVDZ basis sets provides the lowest values of AL for both FSI and TFSI, while the augmented version of the preceding basis set including diffuse functions provides values comparable to those calculated with 6-311+G** and 6-31+G**. Overall, the

introduction of polarization or diffuse functions can increase the AL by 0.5 V, compared to the benchmark 6-31G**, that is an increase of about 10%.

It is surprising how the matching between calculation and experiments decreases while using more expanded, and thus more accurate, basis sets and that in all cases oxidation potentials are overestimated. Apparently larger and more diffuse basis sets destabilize the neutral oxidized product in respect to the charged reduced reagent molecule. This alteration of the relative stability of reagents and products is unphysical and likely due to a better stabilization of the diffused charge in the reduced state provided by the larger basis set.

3.2 Prediction of the AL of IL by DFT beyond the B3LYP paradigm

In the second section of the present work, we investigated the ability of different DFT functionals to reproduce the values of AL obtained by MP2 calculations, which were shown to well compare with the experimental values [21]. To this aim we performed DFT calculations with a variety of DFT functionals with different level of approximation, all of them using the same 6-31G** basis set. The choice of this basis set is motivated by the excellent performance in MP2 calculations and the remarkable accuracy in the prediction of AL compared to experiments.

Table 2 and 3 report the electronic energy of the FSI and TFSI anion, respectively, and the corresponding neutral species, together with the derived anodic limit calculated by various DFT functionals.

Table 2. Electronic energy of the FSI anion and of the corresponding neutral species and derived anodic stability, calculated by means of different DFT functionals using the 6-31G** basis-sets

name	functional type	$E_{tot}(A^-)$ (au)	$E_{tot}(A)$ (au)	Anodic limit (V)
MP2		-1349.235	-1348.998	4.92
PBE	GGA	-1350.800	-1350.600	3.92
BLYP	GGA	-1351.585	-1351.391	3.76
B97-D2	GGA	-1351.327	-1351.107	4.45
EDF2	GH-GGA	-1351.483	-1351.263	4.49
B3LYP	GH-GGA	-1351.661	-1351.438	4.54
E3PW91	GH-GGA	-1351.364	-1351.137	4.64
omegaB97X-D	RSH-GGA	-1351.473	-1351.239	4.86
CAM-B3LYP	RSH-GGA	-1351.505	-1351.272	4.83
N12-SX	RSH-GGA	-1351.279	-1351.053	4.63
LC-VV10	RSH-GGA	-1350.724	-1350.456	5.76
B97M-V	mGGA	-1351.293	-1351.076	4.39
TPSS-D3	mGGA	-1351.715	-1351.512	4.02
M06-L	mGGA	-1351.615	-1351.397	4.41
M11-L	mGGA	-1351.398	-1351.165	4.80
BMK	mGGA	-1351.225	-1350.984	5.02
M06-2X	GH-mGGA	-1351.404	-1351.159	5.14
M08-HX	GH-mGGA	-1351.329	-1351.080	5.25
MPW1B95	GH-mGGA	-1351.605	-1351.376	4.71
M11	RSH-mGGA	-1351.451	-1351.202	5.25
omegaB97M-V	RSH-mGGA	-1351.492	-1351.258	4.86
MN12-SX	RSH-mGGA	-1351.220	-1350.979	5.03

Functionals were here chosen to test the various levels of approximations with increasing complexity: Generalized Gradient Approximation (GGA), Global Hybrid Generalized Gradient Approximation (GH GGA), Range-Separated Hybrid Generalized Gradient Approximation (RSH GGA), Meta-Generalized Gradient Approximation (mGGA), Global Hybrid Meta-Generalized Gradient

Approximation (GH–mGGA) and finally Range Separated Hydrid meta–Generalized Gradient Approximation (RSH–mGGA).

Table 3. Electronic energy of the TFSI anion and of the corresponding neutral species and derived anodic stability, calculated by means of different DFT functionals using the 6-31G** basis-sets

| name	functional type	$E_{tot}(A^-)$ (au)	$E_{tot}(A)$ (au)	Anodic limit (V)
MP2		-1823.631	-1823.392	4.99
PBE	GGA	-1825.901	-1825.711	3.66
BLYP	GGA	-1827.073	-1826.889	3.50
B97-D2	GGA	-1826.724	-1826.514	4.21
EDF2	GH-GGA	-1826.857	-1826.646	4.21
B3LYP	GH-GGA	-1827.205	-1826.992	4.28
E3PW91	GH-GGA	-1826.738	-1826.522	4.35
omegaB97X-D	RSH-GGA	-1826.900	-1826.674	4.64
CAM-B3LYP	RSH-GGA	-1826.932	-1826.706	4.63
N12-SX	RSH-GGA	-1826.671	-1826.456	4.33
LC-VV10	RSH-GGA	-1825.726	-1825.457	5.79
B97M-V	mGGA	-1826.717	-1826.509	4.16
TPSS-D3	mGGA	-1827.2955	-1827.100	3.80
M06-L	mGGA	-1827.116	-1826.910	4.10
M11L	mGGA	-1826.794	-1826.570	4.57
BMK	mGGA	-1826.608	-1826.377	4.76
M06-2X	GH-mGGA	-1826.805	-1826.566	4.99
M08-HX	GH-mGGA	-1826.686	-1826.443	5.10
MPW1B95	GH-mGGA	-1827.045	-1826.825	4.48
M11	RSH-mGGA	-1826.875	-1826.629	5.17
omegaB97M-V	RSH-mGGA	-1826.944	-1826.714	4.75
MN12-SX	RSH-mGGA	-1826.511	-1826.278	4.80
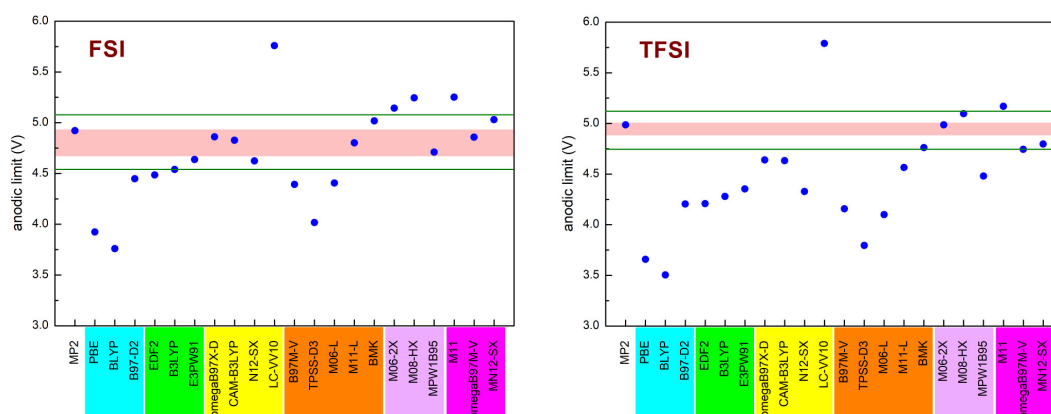
Figure 2. Anodic limit values of FSI (left panel) and TFSI (right panel) calculated by various DFT functional in comparison with the MP2 theory. GGA, GH-GGA, RSH-GGA, mGGA, GH-mGGA and RSH-mGGA functionals are contained in the cyan, green, yellow, orange, violet and magenta rectangles. The rose regions in the figure delimit the range of experimental values reported in Ref. [21, 23] for the ILs, while the horizontal green lines delimit a region with AL within 3% from the experimental figures.

Figure 2 displays a graphical comparison of the anodic limit of FSI and TFSI calculated by various models and the experimental values reported in our previous investigations [21, 23]. In Figure 2 we marked a zone differing by about 3% from the lowest and highest AL of the real ionic liquids, that we will consider as that where functionals give reasonably good results (Reasonably Good Results Zone, RGRZ). Of course, the value of 3% is arbitrary, but it is used to select best performing functional. The GGA DFT functionals greatly underestimate the anodic limit of both anions, except B97-D2 in the case of FSI, that gives a value close to the lowest value of the RGRZ. GH-GGA functionals provide reasonable values of the AL in the case of FSI, but they greatly underestimate the AL in the case of TFSI. RSH-GGA functionals provide values of AL in the RGRZ for FSI, except for LC-VV10 that largely overestimates the AL, also in the case of the TFSI anion. RSH-GGA functionals underestimate the AL of TFSI; however, ωB97X-D and CAM-B3LYP can be close to the lowest limit of the RGRZ. m-GGA functionals B97M-V, TPSS-D3 and M06-L underestimate the AL for both FSI and TFSI, while M11-L and BMK provide values closer to the experimental ones. Concerning the CH-mGGA functional, MPN1B95 gives a reasonable value of AL for FSI, but greatly underestimates the AL of TFSI. On the other hand, M06-2X and M08-HX give reasonable values for TFSI and slightly too high figures for FSI. Finally, within the RSH-mGGA class of functional, M11 slightly overestimates the LA of both anions, while both ωB97M-V and MN12-SX provide values of AL in the RGRZ for both FSI and TFSI.

Overall, the functionals that provide the best results for both anions are BMK (mGGA type), ωB97M-V and MN12-SX (both of type RSH-mGGA). Slightly less performing, but still acceptable for both anions, one finds M06-2X (GH-mGGA), M11 (RSH-mGGA), M08-HX (GH-mGGA) and M11-L (mGGA). Among the less computationally expensive functionals, the best ones seem to be CAM-B3LYP and ωB97X-D (both of type RSH-GGA).

These findings are in good correlation with the screening of a total of 200 density functional on a molecular database of nearly 5000 data points reported by Mardirossian and Head-Gordon [25]. Indeed, those authors pointed out that the most promising functional they considered is ωB97M-V. One of the best hybrid GGAs they could investigate is ωB97X-D [25], that we presently found to give reasonable results, while among the useful hybrid meta-GGAs (besides ωB97M-V) Mardisson and Head-Gordon reported M06-2X-D3 [25], that also is promising in the case of the study of the anodic limit of ionic liquids.

4. Conclusions

In this paper we investigated two aspects of the calculation of the anodic stability of two anions composing experimentally investigated ionic liquids. Starting from a model based on calculations performed on single ions, we considered the impact of the enlargement of the basis set on the values of the anodic limit obtained at the MP2 level of theory. We observed that the matching between calculation and experiments decreases while using more expanded basis sets and that in all cases oxidation potentials are overestimated. A possible explanation for this effect can be found in destabilization of the neutral species when larger basis sets are considered. Moreover, we investigated the performances of a series of DFT functionals with increasing level of complexity (from GGA to RSH-mGGA) for the calculation of the anodic limit. Overall, the functionals that provide the best results are BMK, ωB97M-V and MN12-SX. Acceptable results can be also obtained by M06-2X, M11, M08-HX and M11-L. Among the less computationally expensive functionals, the best ones seem to be CAM-B3LYP and ωB97X-D.

Acknowledgments

References

[1]   Trahey L, Brushett F R, Balsara N P, Ceder G, Cheng L, Chiang Y-M, Hahn N T, Ingram B J, Minteer S D, Moore J S *et al.* 2020 *Proc. Nat. Acad. Sci.* **117** 12550

[2]   Sharma S, Panwar A K, Tripathi M M 2020 *J. Traffic Transp. Eng.* **7** 340

[3]   Yoo H D, Markevich E, Salitra G, Sharon D, Aurbach D 2014 *Materials Today* **17** 110

[4]   Mishra A, Mehta A, Basu S, Malode S J, Shetti N P, Shukla S S, Nadagouda M N, Aminabhavi T M 2018 Materials Science for Energy Technologies 1 182

[5]   Quartarone E, Mustarelli P 2020 *J. Electrochem. Soc.* **167** 050508

[6]   Xu W, Shusterman A J, Marzke R, Angell C A 2004 *J. Electrochem. Soc.* **151**, A632

[7]   Ue M, Murakami A, Nakamura S. 2002 *J. Electrochem. Soc.* **149**, A1572

[8]   Johansson P 2006 *J. Phys. Chem. A* **110**, 12077

[9]   Johansson P 2007 *J. Phys. Chem. A* **111**, 1378

[10] Ong S P, Ceder G 2010 *Electrochim. Acta* **55**, 3804

[11] Carboni M, Spezia R, Brutti S 2014 *J. Phys. Chem. C* **118**, 24221

[12] Haskins J B, Bauschlicher C W, Lawson J W 2015 *J. Phys. Chem. B* **119**, 14705

[13] Karu K, Ruzanov A, Ers H, Ivaništšev V, Lage-Estebanez I, García de la Vega J 2016 *Computation* **4**, 25

[14] Ong S P, Andreussi O, Wu Y, Marzari N, Ceder G 2011 *Chem. Mat.* **23**, 2979

[15] Zhang Y, Shi C, Brennecke J F, Maginn E J 2014 *J. Phys. Chem. B* **118**, 6250

[16] Cheng L, Assary R S, Qu X, Jain A, Ong S P, Rajput N N, Persson K, Curtiss L A 2015 *J. Phys. Chem. Lett.* **6**, 283

[17] Kazemiabnavi S, Zhang Z, Thornton K, Banerjee S 2016 *J. Phys. Chem. B* **120**, 5691

[18] Winget P, Cramer C J, Truhlar D G 2004 Theor. Chem. Acc. **112**, 217

[19] Marenich A V, Ho J, Coote M L, Cramer C J, Truhlar D G 2014 *Phys. Chem. Chem. Phys.* **16**, 15068

[20] Brutti S 2020 *Appl. Sci.* **10**, 8552

[21] Paolone A, Brutti S 2021 *Materials* **14**, 3221

[22] Shao Y, Molnar L F, Jung Y, Kussmann J, Ochsenfeld C, Brown S T, Gilbert A T B, Slipchenko L V, Levchenko S V, O'Neill D P *et al.* 2006 *Phys. Chem. Chem. Phys.* **8**, 3172

[23] Brutti S, Simonetti E, de Francesco M, Sarra A, Paolone A, Palumbo O, Fantini S, Lin R, Falgayrat A, Choi H *et al.* 2020 *J. Power Sources* **479**, 228791

[24] Cimini A, Palumbo O, Simonetti E, de Francesco M, Appetecchi G B, Fantini S, Lin R, Falgayrat A, Paolone A 2020 *J. Therm. Anal. Calorim.* **142**, 1791

[25] Mardirossian N, Head-Gordon M. 2017 *Mol. Phys.* **115**, 2315