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Electronic Supplementary Information

Factors affecting cyclic durability of all-solid-state lithium batteries using poly(ethylene oxide)-based polymer electrolytes and recommendations to achieve improved performance[†]

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Charge Delocalization and Self Interaction Correction

It is a known fact that including some form of Self Interaction Correction (SIC) prevents DFT from erroneously delocalize charges over different sites or molecules.^{1,2} To estimate the importance of this, we considered eight different Density Functionals including varying degrees of exact Hartree Fock (HF) exchange. In fact, HF exchange includes SIC.

The functionals considered are **PBE**^{3,4} (0%), **B3LYP**⁵ (20%), **B3LYP-D3**⁶, with Grimme dispersion correction (20%), **CAM-B3LYP**⁷ (19% at short range, 65% at long range), **PBE0**⁸ (25%), **M06-2X**⁹ (54%), **LC-BLYP**^{10,11} (0% at short range, 100% at long range), **M06-HF**^{12,13} (100%), **HF** (100%), where numbers in parenthesis indicate the percentage of exact HF exchange included in each functional.

For all of these, we computed ionization potential (IP) and charge distribution for the following systems.

1. Five identical DME molecules, 10 Å apart, in vacuum.
2. Five identical TFSI[⊖] anions, 500 Å apart, in vacuum.
3. One TFSI[⊖] anion, surrounded by one, two, and three DMEs, in vacuum.
4. One TFSI[⊖] anion, surrounded by one, two, and three DMEs, with diethylether implicit solvation.
5. One PF₆[⊖] anion, surrounded by one, two, three, and four DMEs, in vacuum.
6. One PF₆[⊖] anion, surrounded by one, two, three, and four DMEs, with diethylether implicit solvation.

Detailed numerical results are reported in the Supplementary Material for another article by E. Fadel et al.¹⁴ recently submitted. We report here only a brief summary and the conclusions.

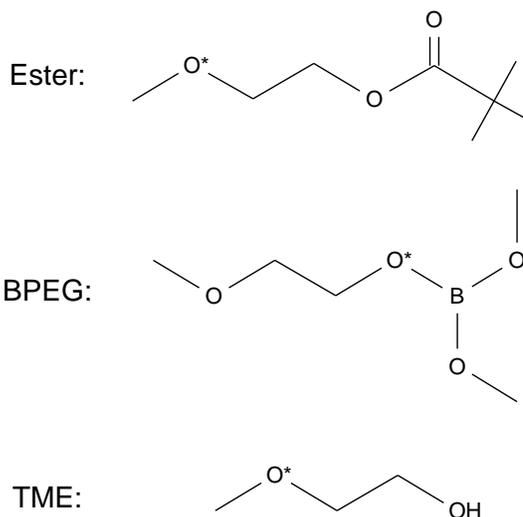
The expected, correct physical behavior involves ionization of one of the molecules and IP values independent from the number of replicas. In all cases, we find that only methods containing 100% of HF exchange at long range (LC-BLYP, M06-HF, and HF) provide the correct physical description.

Comparing these three functionals with higher level computations (MP2 for TFSI[⊖]-DME_n and CCSD(T) for PF₆[⊖]-DME_n), we find that HF yields significantly different optimized geometries and IP values. By contrast, both LC-BLYP and M06-HF provide reasonable geometries and IPs. Hence, we selected these two functionals for our investigation.

Whenever both anions and DME molecules are considered at optimized geometries, ionization invariably occurs from one DME molecule, despite its higher ionization potential. As detailed in Ref.¹⁴, this effect is due to electrostatic stabilization of the positive charge on DME by the nearby negatively charged anion.

Oxidation of other species

We report more detailed results regarding oxidation of species other than DME, mentioned in the section with the same name in the main article. The following species were considered to represent the key features that may be found in the electrolyte.



where the symbol '*' marks a position in the molecule used in the discussion below. These were selected to include one ether-

oxygen similar to that in DME, as well as the functional group of interest. For each of these, we considered different plausible binding geometries to a TFSI[⊖] anion, mainly with the functional group (ester, BO₃, OH) near the TFSI[⊖] nitrogen. We report here only results referring to the lowest energy configuration prior to ionization.

Binding energies to TFSI[⊖], vertical Ionization Potentials for both the isolated molecule S and the pair S-TFSI[⊖], and the percentage of charge coming from the species S are reported in the following table. All computations use diethyl-ether as implicit solvent.

Species	BE(S-TFSI [⊖]) (kcal/mol)	IP(S) (eV)	IP(S-TFSI [⊖]) (eV)	% charge from S
DME	6.3	8.50	7.71	99
Ester	8.9	8.64	7.78	97
BPEG	7.5	9.56	8.63	96
TME	10.1	8.51	7.73	98

We remark that in order to make sure that the ionized state is in fact the lowest energy state, we prepared different initial guesses placing negative charges near different atoms, used these guesses to run several DFT computations for each ionized species, and selected the lowest energy results.

We observe that the charge is consistently removed from the species S coordinating TFSI[⊖], as seen for DME. Ionization potentials for Ester-TFSI[⊖] and TME-TFSI[⊖] are extremely similar to that of DME. In these cases, Mulliken population and spin density analysis indicate that the ionized electron is removed mainly from the oxygen atoms marked with the '*' symbol above, which is chemically equivalent to that of DME. These atoms carry over 80% of the spin density in the ionized state. We conclude that ionization from one of the other oxygens would be less convenient.

In the case of BPEG, ionization occurs mainly from a lone pair of one of the oxygens bound to the boron and it is almost one eV harder. This effect is likely due to the geometry of the BPEG-TFSI[⊖] pair. In fact, the ether-oxygen is further away from the TFSI[⊖] nitrogen and oxygens, yet close enough to one of the CF₃ to have a reduced implicit solvation energy. This combination leads to a higher ionization potential from the ether-oxygen in BPEG-TFSI[⊖] than in BPEG alone. Presumably, for other binding geometries the IP would be lower. This computation is however sufficient to prove that ionizing BPEG near the Boron atom is less convenient than ionizing DME.

Notes and references

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