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Research paper

Benchmarking of computational approaches for fast screening of lithium ion battery electrolyte solvents

Daejin Kim, Hyein Guk, Seung-Hoon Choi, Dong Hyen Chung *

Insilico Co., Ltd., C-602, Korea Bio Park, 700, Daewangpangyo-Ro, Bundang-Gu, Seongnam-Si, Gyeonggi-Do 463-400, Republic of Korea

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ABSTRACT

Electrolyte solvents play an important role in lithium-ion batteries. Hence, investigation of the solvent is key to improving battery functionality. We performed benchmark calculations to suggest the best conditions for rapid screening of electrolyte candidates using semi-empirical (SEM) calculations and density functional theory (DFT). A wide selection of Hamiltonians, DFT levels, and basis sets were used for this benchmarking with typical electrolyte solvents. The most efficient condition for reducing computational costs and time is VWN/DNP+ for DFT levels and PM3 for SEM Hamiltonians.

1. Introduction

Lithium ion batteries (LIBs) are a practical alternative to replace or offset energy from fossil fuels. However, this alternative also has some technical issues that should be addressed to improve its functionality and safety before wider use in a variety of industries. In this regard, the electrolyte solvent is a key component and plays an important and practical role in advancing the whole performance of the LIB device [1,2]. Other components such as the anode and cathode could also be further developed, but this requires improvements in other components including electrolyte solvents. As such, further research and development of the electrolyte is essential for improvements in LIBs, so many researchers have tried to investigate the properties of the electrolyte. Consequently, a virtual library of electrolyte candidates have recently been generated [3–5], and thus, fast and accurate calculations of a large number of molecular structures using quantum mechanical calculation are required to provide estimates of their electronic structure and properties.

Here, we use semi-empirical methods (SEM) and density functional theory (DFT) to calculate the HOMO, LUMO, ionization potential (IP), and electron affinity (EA) of electrolyte molecules. Although the accuracy is not very reliable, the SEM method is often used for the fast calculation and screening of a large number of molecular structures. Conversely, DFT is more accurate, but the calculation time is much longer. As such, if more sophisticated values are required, DFT should be selected. However, for both levels, the calculation results can be altered with the choice of detailed conditions. In other words, the Hamiltonian used in the SEM calculation is critical to the resulting estimated properties. Furthermore, for a successful DFT calculation, more complicated options are carefully selected. We have tested the calculation results for both levels and have established the detailed conditions under which the results are most correlated to higher-level calculations.

2. Materials and methods

As a reference for the investigation of the optimum conditions for SEM Hamiltonians and DFT levels, we selected 20 well-known electrolyte structures, and three levels of DFT calculations were reviewed from the literature [6,7]. Commercially available and commonly used electrolytes were chosen as the input structures for the reference calculations (Fig. 1). Properties such as HOMO, LUMO, Vertical IP, Vertical EA, Adiabatic IP, and Adiabatic EA were calculated at the M05-2x/cc-pvTz, LC-ωPBE/6-31+G(d,p), and B3PW91/6-311G(d,p) reference levels [6,8] and each configuration of options in DFT and SEM. Moreover, we then compared each calculation to find the best conditions for the DFT and SEM calculations that showed the least error from the resultant properties in the reference level DFT calculations.

The reference level DFT calculations are preferable for predictions of electrolyte properties and are comparable to the high-level post HF calculations such as G4MP2. Borodin and coworkers

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* Corresponding author.
E-mail address: dhchung@insilico.co.kr (D.H. Chung).

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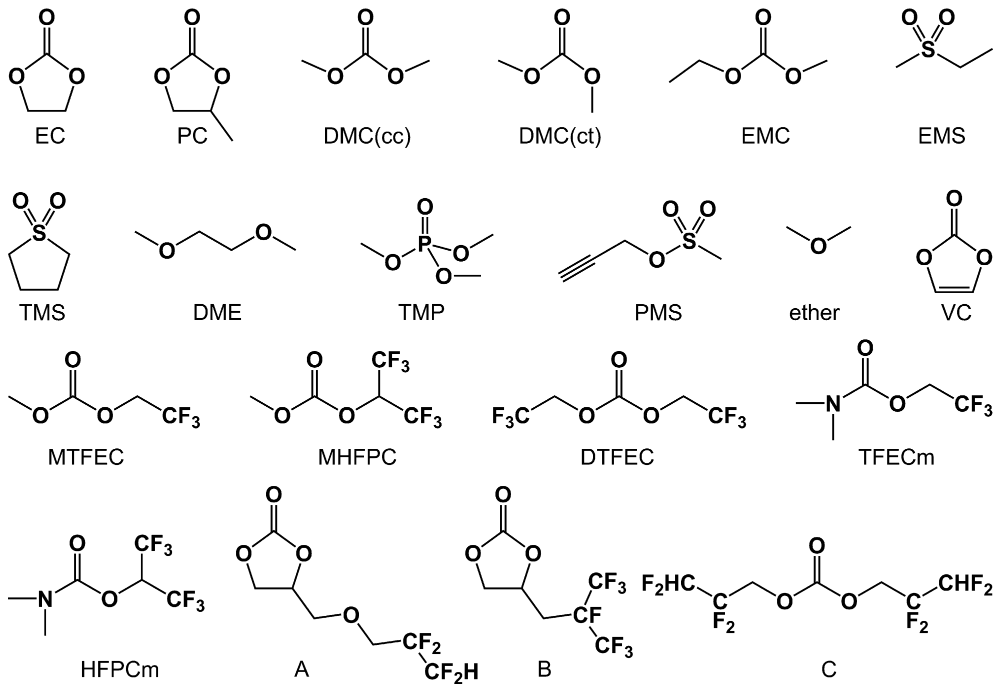

Fig. 1. Molecular structures of lithium ion battery electrolyte solvents as input structure.

used M05-2x/cc-pvTz and LC-ωPBE/6-31+G(d,p) for predictions of oxidation energy and free energy [6]. Han and coworkers used B3PW91/6-311G(d,p) as the descriptor calculation to find the correlation between the structure and electrolyte properties [8].

All the geometries, including the neutral and charged states, were fully optimized, and the minimum energy structure was confirmed by vibrational frequency analysis.

3. Results and discussion

We investigated the performance of the selected DFT levels for predictions of the electronic properties of the solvents. M05-2X/cc-pvTz and Lc-ωPBE/6-31+G(d,p) showed good agreement with high-level post-HF G4MP2 calculations [6], and B3PW91/6-311G(d,p) was used as the computational screening protocol for the efficient development of SEI-forming additives [8]. Therefore, in our benchmarking, electronic properties from these DFT levels (Table 1) were regarded as the standard values for the comparison of various levels and basis sets.

3.1. Optimum method among the SEM Hamiltonians

Despite their inaccuracy compared to DFT levels, semi-empirical calculations are capable of rapid calculation of many physical and chemical molecular properties. Materials Studio VAMP includes six Hamiltonians: AM1, AM*, MNDO, MNDO/d, PM3, and PM6 [9–16]. Using these six Hamiltonians, MS VAMP calculated the electronic properties, and we performed regression analysis with the DFT level calculations. The Pearson correlation coefficients (*R*) are listed in Table 2. Average *R* values for the electronic properties are listed in Table 3. We found that the correlation was around 0.7, which indicates poor agreement. In contrast, the HOMO, Vertical IP, and Adiabatic IP properties showed better correlations compared to the LUMO, Vertical-EA, and Adiabatic-EA, which may be due to limitations on the expression of unoccupied orbitals by SEM Hamiltonians.

Here, we suggest that SEM Hamiltonians for lithium ion battery solvents are limited to HOMO and IP prediction and that PM3 is the best Hamiltonian for this prediction. Recently, Chaban and coworkers reported that the PM7 Hamiltonian can be adequate to describe the solvation of the lithium cation using molecular dynamics simulations [17–19]. When the benchmark calculations are expanded to the interaction with the lithium cation, PM6 or PM7 can show better results, and the benchmark calculations will be more advanced.

3.2. Optimum method among the DFT levels

DFT calculations are generally more accurate than SEM Hamiltonians but require more calculation time, CPU processing power, and RAM. We performed benchmark calculations for the electronic properties of LIB solvents using the different DFT levels and basis sets included in Materials Studio DMol^3 [20,21]. As with the SEM Hamiltonians, 10 DFT levels and 6 basis sets [22–29] were combined resulting in 60 combinations, and the electronic properties of each combination were analyzed in terms of the Pearson correlation coefficient, *R*. The average *R* values for the electronic properties are listed in Table 4. As shown in Table 4, *R* values above 0.9 are found, indicating that DFT level calculations are generally more accurate than SEM Hamiltonians. PW91 and VWN functionals with the DNP+ and TNP basis sets showed good correlation with the B3PW91/6-311G(d,p) results.

We performed this benchmarking using the available SEM Hamiltonians or DFT levels for the electronic properties of LIB solvents in order to reduce the computational cost and thus want to suggest which Hamiltonian or DFT level is best for this purpose. Thus, we also examined the elapsed time for calculation of six electronic properties with one CPU core. Table 5 lists this elapsed time and shows some distinct patterns. The TNP basis set used more CPU time than DNP+, and PW91 also used more CPU time than VWN. Consequently, the VWN/DNP+ DFT level is best for calculation of the properties of LIB solvents.