Theoretical Analysis of the Oxidation Potentials of Organic Electrolyte Solvents

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This study theoretically evaluated oxidation potentials of a wide variety of solvents, using the recently developed highly reliable solvation model, called HSM, combined with the accurate quantum chemical methods. Reasonable agreements with experimental values were observed. Analyses on the characteristics of the highest occupied molecular orbital and chemical hardness of solvents showed qualitative and quantitative correlations with oxidation potentials, respectively. 

Improving the energy density is one of the most crucial issues in lithium-ion secondary batteries. The stabilities of the electrolyte solvents against oxidation play key roles when developing advanced batteries using cathode materials operating at high-voltage. Ue et al.1,2 measured the redox potentials for a number of organic electrolyte solvents. Theoretical investigations on redox reactions were also performed extensively,3 mainly focused on decomposition reactions following oxidations/reductions. For instance, Borodin and coworkers4–6 recently reported that intermolecular hydrogen transfer reactions stabilized the oxidized state.

The present study systematically evaluated oxidation potentials of organic electrolyte solvents using highly accurate quantum chemical models for condensed systems; the results obtained were compared with experimental values. Correlations between oxidation potentials and chemical characteristics of solvents were analyzed from the viewpoints of the highest occupied molecular orbitals (HOMOs) and chemical hardness.

Computational Details

Oxidation potentials of 14 solvents were examined, the names, abbreviations, chemical structural formulas, experimental oxidation potentials,1,4 and HOMOs are shown in Fig. 1. One-electron oxidation potentials \( V_{\text{ox}} \) with respect to the Li+/Li reference electrode were calculated as follows:

\[
V_{\text{ox}} (\text{vs. Li}^+/\text{Li}) = \frac{G[\text{solvent}] - G[\text{solvent}^+]}{F} + E_{\text{vacuum/SHE}} - E_{\text{Li}^+/\text{Li}}/\text{SHE} \tag{1}
\]

where \( F \) is Faraday’s constant, \( G[\text{solvent}] \) and \( G[\text{solvent}^+] \) are Gibbs energies of solvent molecules in cationic and neutral states, respectively. \( E_{\text{vacuum/SHE}} \) and \( E_{\text{Li}^+/\text{Li}}/\text{SHE} \) are the potentials of an electron in a vacuum and of a metallic lithium electrode, respectively, with respect to the standard hydrogen electrode (SHE). Experimental oxidation potentials \( V_{\text{ox}} \) (vs. SCE),3 which were obtained with respect to the saturated calomel electrode (SCE), were converted into \( V_{\text{ox}} \) (vs. Li+/Li) as follows:

\[
V_{\text{ox}} (\text{vs. Li}^+/\text{Li}) = V_{\text{ox}} (\text{vs. SCE}) + E_{\text{SCE/SHE}} - E_{\text{Li}^+/\text{Li}}/\text{SHE} \tag{2}
\]

where \( E_{\text{SCE/SHE}} \) is the potential of an electron in SCE with respect to SHE. Reported values of \( E_{\text{vacuum/SHE}} = -4.28 \text{ V}_0 \), \( E_{\text{Li}^+/\text{Li}}/\text{SHE} = -3.04 \text{ V}_0 \) were utilized.

Geometric structures of the neutral and the cationic states for solvent molecules were optimized by the second-order Möller-Plesset (MP2) perturbation theory, with Dunning’s triple-zeta plus polarization type basis set (cc-pVTZ). Solvent effects were considered by using the conductor-like polarizable continuum model (CPCM).11,12 and so-called the SMD model.13 Experimental permittivities and radii of solvents1,14 Table S1 were employed in CPCM and SMD, throughout. Thermochemical corrections to the electronic energies were evaluated, based on the conventional ideal gas model (IGM).

Furthermore, the harmonic solvation model (HSM) analyses14,15 were performed at the MP2/cc-pVTZ/CPCM level of theory, as an alternative to IGM-based analysis. HSM reproduces thermochemical corrections of molecules in condensed phase accurately and adequately, while IGM occasionally gives unphysical behaviors (Supplemental Appendices 1 and 2).

Single-point energies were evaluated by the coupled cluster method with single, double, and perturbative triple excitations (CCSD(T)), with the complete basis set (CBS) limit estimation using extrapolation schemes with an adjustable parameter for improved evaluations. The detailed schemes on CBS are found in the previous literatures.16,17

DFT calculations were also performed with the B3LYP hybrid functional.18–22 Geometric structures were optimized at the B3LYP/cc-pVTZ level of theory with CPCM and SMD. Frequency analyses were performed at the same level of theory. Single-point electronic energies were evaluated using inversely exponential type extrapolations with cc-pVXZ (\( X = 2–4 \)).19 Chemical hardness of solvents, \( \eta \), was evaluated at the B3LYP/CBS/CPCM level of theory, as follows:

\[
\eta = \frac{1}{2} \left( \frac{\partial^2 E}{\partial N^2} \right) = \frac{1}{2} (E(N+1) + E(N-1) - 2E(N)) \tag{3}
\]

where \( N \) means the number of electrons in a solvent molecule at the neutral state. \( E(N) \), \( E(N+1) \), and \( E(N-1) \) mean the total energies at the neutral, anionic, and cationic states of the solvent molecule, calculated for the geometric structure of the neutral state.23

All calculations except for HSM were performed using the Gaussian 09 program,24 while the HSM analyses were conducted using the GAMESS program,25 combined with our original code.

Results and Discussion

Vertical ionization energies of the solvents in the gas phase were compared with available experimental values26 (Table S2). The results obtained by the CCSD(T) and B3LYP calculations showed reasonable agreements with experimental values, with less than 0.1 eV of differences. The B3LYP results commonly underestimated those for CCSD(T) by ca. 0.3 eV, consistent with the previous study.27

Fig. 2 plots the correlations between experimental and calculated oxidation potentials at the CCSD(T)/CBS/CPCM and...
Figure 1. Names, abbreviations, chemical structural formulas, experimental oxidation potentials, and HOMOs analyzed at the B3LYP/cc-pVTZ/CPCM level of theory of the 14 organic electrolyte solvents, utilized in the present study.

B3LYP/CBS/CPMC levels of theory with thermochemical collections by HSM. Mean absolute errors (MAEs), as well as the equations expressing the linearly fitted relationships between experimental and calculated values are shown. The numerical data for Fig. 2, as well as results with SMD and/or IGM, are summarized in Table S3.

It should be mentioned that experimental values are dependent on the experimental conditions, such as species and concentration of salt, while the reference experimental values were obtained under an identical experimental condition. Therefore, we expect that we can compare the tendencies of oxidation potentials on solvent species, or at least the present analysis would serve as the reference value that is so-called intrinsic oxidation potentials of solvent molecules.

The CCSD(T)/CBS/CPCM calculations reproduced the experimental values with MAE of 0.5 V, which is attributed to the neglected contributions of explicit solvents, salt, and so forth. Thermochemical contributions (ΔG(HSM)−ΔE) were generally negative (0.0−0.4 V). Quasi-linear correlation with R² = 0.8 was observed, while the CCSD(T)/CBS/CPCM level of calculations commonly overestimated experimental values except for BC (#2) and MPN (#9).

The results of B3LYP/CBS/CPMC commonly underestimated the CCSD(T)/CBS/CPMC values, consistent with the observation for vertical ionization energies. MAE was slightly decreased to 0.4 eV. The use of SMD instead of CPCM resulted in slight decrease of oxidation potentials except for EMC (#3) at the CCSD(T)/CBS level of theory calculation, while remarkable differences from CPCM results were not observed. Appendix 2 (supplemental material) gives more detailed discussions on thermochemical contributions, in which HSM and IGM were compared, with emphasis on the evaluation of entropies of quasi-translational and rotational motions of a molecule in the condensed phase.

Dependencies of oxidation potentials on the chemical characteristics of the solvents were investigated by analyzing the DFT results. HOMOs of the solvents, shown in Fig. 1, showed a systematic trend: i.e., oxidation potentials of the solvents were in the order of π(cyano) > π(carbonyl) > π(sulfonyl) > π(nitro) > n(ether) > n(amino), with some exceptional cases.

Figure 2. Correlations between experimental and calculated oxidation potentials of the 14 organic electrolyte solvents. Red squares and blue circles correspond to the results obtained at the CCSD(T)/CBS/CPCM/HSM and B3LYP/CBS/CPMC/HSM levels of theory, respectively. The linearly fitted lines are shown as red solid and blue dashed lines, with their equations. The ideal line, in which the experimental and calculated values are equal to each other, is shown as the dotted line.

Relationship between the calculated oxidation potential and chemical hardness of the solvents (Table S4) is shown in Fig. 3.

Figure 3. Correlation between the calculated oxidation potential and chemical hardness of the solvents.
Characteristics of HOMOs of typical solvents are also summarized in the figure as arrows showing the ranges of oxidation potentials. A quasi-linear correlation with $R^2 = 0.88$ was observed except for NE (#8), which possesses a highly electronegative nitro group, leading to a high electron affinity. This observation is consistent to the previous study for small molecules. The present result suggests that chemical hardness, quantifying the characteristics of HOMOs, as well as the lowest unoccupied molecular orbitals, can be a semi-quantitative indication of oxidation potentials of the solvents.

Conclusions

In the present study, we systematically evaluated the oxidation potentials of organic electrolyte solvents. Highly accurate quantum chemical models for condensed phase systems, i.e., HSM combined with the CCSD(T)/CBS method, as well as the standard methodologies were utilized. Both methodologies based on HSM and standard solvation models basically showed reasonable agreements with the experimental values, as well as the previous theoretical contributions. However, the analysis on thermochemical corrections suggests the non-negligible contributions, for which the conventional IGM-based analyses would fail qualitatively. Furthermore, HSM-based analysis revealed that $V_{ox}$ slightly decreases with the higher temperature mainly due to the entropic effects (Supplemental Appendices 1 and 2), consistent with the experimental observation. We should mention that the errors due to IGM would be enhanced especially in the case of the number of solvated molecules changes, such as decomposition reaction, for instance.

Analysis of the characteristics of solvent molecules showed systematic trends in the oxidation potentials, based on the characteristics of HOMOs. Chemical hardness showed a quasi-linear correlation with oxidation potentials. Considering our recent work on de-solvation of carrier ions, in which the de-solvation energies showed linear correlations with chemical hardness, chemical hardness of solvents is suggested to be a good chemical index for the design of advanced electrolyte solvents.

Acknowledgment

Parts of the calculations were performed at the Research Center for Computational Science, Okazaki Research Facilities, National Institutes of Natural Sciences. This study was supported in part by “Elements Strategy Initiative for Catalysts & Batteries” supported by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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