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Computational comparison of oxidation stability: Solvent/salt monomers vs solvent–solvent/salt pairs

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HIGHLIGHTS

- The oxidation stabilities of high-voltage electrolyte components were simulated.
- A fundamental understanding of the electrolyte oxidation processes is provided.
- A methodological scheme to properly predict the anodic stability of electrolytes is proposed.
- Simple comparisons of HOMO energies can be misleading.
- Oxidatively driven intermolecular reaction has a great influence on the anodic stability of electrolytes.

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ABSTRACT

A fundamental understanding of the anodic stabilities of electrolytes is important for the development of advanced high-voltage electrolytes. In this study, we calculated and systematically compared the oxidation stabilities of monomeric solvents and anions, and bimolecular solvent–solvent and anion–solvent systems that are considered to be high-voltage electrolyte components, using ab initio calculations. Oxidation stabilities of solvent or anion monomers without considering specific solvation molecules cannot represent experimental oxidation stabilities. The oxidation of electrolytes usually forms neutral or cationic radicals, which immediately undergo further reactions stabilizing the products. Oxidatively driven intermolecular reactions are the main reason for the lower oxidation stabilities of electrolytes compared with those of monomeric compounds. Electrolyte components such as tetramethylene sulfone (TMS), ethyl methyl sulfone (EMS), bis(oxalate)borate (BOB^-), and bis(trifluoromethane)sulfonamide ($TFSI^-$) that minimize such intermolecular chemical reactions on oxidation can maintain the oxidation stabilities of monomers. In predictions of the theoretical oxidation stabilities of electrolytes, simple comparisons of highest occupied molecular orbital energies can be misleading, even if microsolvation or bulk clusters are considered. Instead, bimolecular solvent complexes with a salt anion should be at least considered in oxidation calculations. This study provides important information on fundamental and applied aspects of the development of electrolytes.

1. Introduction

Research on the exploitation of new energy sources and energy-storing materials is being performed globally [1–4], because of the limitations of carbon-based fuels and the environmental problems associated with the increasing use of such fuels [5–7]. Li-ion batteries are among the most efficient energy-storing devices, and have been commercialized. High-voltage cathode materials are being developed for higher-energy-storage devices for large-scale battery applications such as electric vehicles [8], requiring to also develop new high-voltage electrolytes [9–14]. High-voltage cathode materials such as $LiCoPO_4$, $Li_3V_2(PO_4)_3$, Li_2CoPO_4F, and $LiNi_{0.5}Mn_{1.5}O_4$ have recently been reported [15–17]. The voltage ranges of such cathode materials are usually beyond the electrochemical ranges of conventional electrolytes, being typically applicable to conventional Li-ion batteries. High anodic stability of electrolytes would be an important issue in the development of not only high-voltage Li-ion batteries but also new-generation of

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battery technologies [18–23] such as Na-ion-based devices [24], because the battery performance is limited by the operating voltage. In the development of high-voltage electrolytes, while the ion conductivity, volatility, flammability, thermal stability, and reductive stability are all important factors, a fundamental understanding of the electrolyte oxidation processes is crucial.

Electrolyte oxidation involves loss of one electron from the highest occupied molecular orbital (HOMO) of solvents or anions in the electrolytes. The HOMO energies usually correlate well with the first ionization energies (IE_1) of molecular systems. However, this correlation between the HOMO energies and IE_1 values breaks down when oxidative reorganization is accompanied by significant geometric relaxation. BF_4^-, PF_6^-, and ClO_4^- have different effects on the anodic stabilities of carbonate solvents [25,26]. H-transport from carbonate solvents decreases the oxidative stability of carbonates [27,28]. Many sulfones have been shown experimentally to have higher anodic stabilities than carbonates, although the IE_1 values of monomeric sulfones are lower than those of monomeric carbonates [29]. The oxidation stability of an electrolyte is therefore significantly influenced by the reaction region involving microsolvation in the presence of Li-salt anions.

In this work, we studied the oxidation stabilities of eight solvent molecules, including systems that are considered to be high-voltage electrolytes. The following solvent molecules were investigated: ethylene carbonate (EC), fluoroethylene carbonate (FEC), 4-[2,3,3,3-tetrafluoro-2-(trifluoromethyl)propyl]-1,3-dioxolan-2-one (HFEC), dimethyl carbonate (DMC), methyl 2,2,2-trifluoroethyl carbonate (FEMC), 1,1,3,3-tetrafluoro-1-(1,1,2,2-tetrafluoroethoxy)propane (HFE), tetramethylene sulfone (TMS), and ethyl methyl sulfone (EMS). The structures and HOMO shapes of the solvent molecules are shown in Fig. 1. Electrolytes consisting of the fluorinated compounds HFE, HFEC, and FEMC have superior anodic stabilities compared with those of EC-based non-fluorinated electrolytes [30]. As well as the advantages of high anodic stabilities, fluorinated carbonates improve the performance and safety [31]. Sulfones, including EMS and TMS, have been reported to be solvents with high anodic stabilities, but the practical applications of sulfone-based electrolytes are limited [32–35], therefore more fundamental studies are needed. In this study, the effects of four different anions, i.e., PF_6^-, BF_4^-, bis(trifluoromethane)sulfonamide ($TFSI^-$), and bis(oxalate)borate (BOB^-) on solvent oxidation were investigated; salts containing these anions are considered to be high-voltage electrolyte components [36]. The structures and HOMO shapes of these anions are shown in Fig. 2. The oxidation stabilities of solvents, anions, solvent–solvent clusters, and anion–solvent clusters were studied, and a detailed comparison with the results of previous studies was performed. The results show that oxidatively driven intermolecular chemical reactions lead to electrolyte oxidation stabilities lower than those of monomeric compounds. PF_6^-- and BF_4^--based carbonate systems have much lower oxidation stabilities than each of the monomers. Sulfone-, BOB^--, and $TFSI^-$-based electrolytes deactivating the intermolecular chemical reactions on oxidation can maintain the oxidation stabilities of monomers.

2. Calculation methods

The oxidation potentials of electrolyte solutions are calculated from Refs. [37–41]

$$V_{ox} = (IE_1 + \Delta G_{red})/F \tag{1}$$

where F is the Faraday constant (1 eV/V). The free energy of Li/Li$^+$ reduction [ΔG_{red}(Li)] is

$$\Delta G_{red}(Li) = G_s(Li) - G_{sol}\left(Li^+\right) - \Phi_M \tag{2}$$

where G_s(Li) is the free energy of solid Li, $G_{sol}(Li^+)$ is the free energy of Li$^+$ in solution, and Φ_M is the work function of the inert metal electrodes.

The Li/Li$^+$ reduction potential in an aqueous medium [$V_{red,aq}$(Li)] is −3.04 V versus the standard hydrogen electrode (SHE), i.e., about −1.4 eV on the physical scale, and is given by

$$\Delta G_{red,aq}(Li) = G_s(Li) - G_{aq}\left(Li^+\right) - \Phi_M \tag{3}$$

where $G_{aq}(Li^+)$ is the free energy of Li$^+$ in the aqueous phase. The

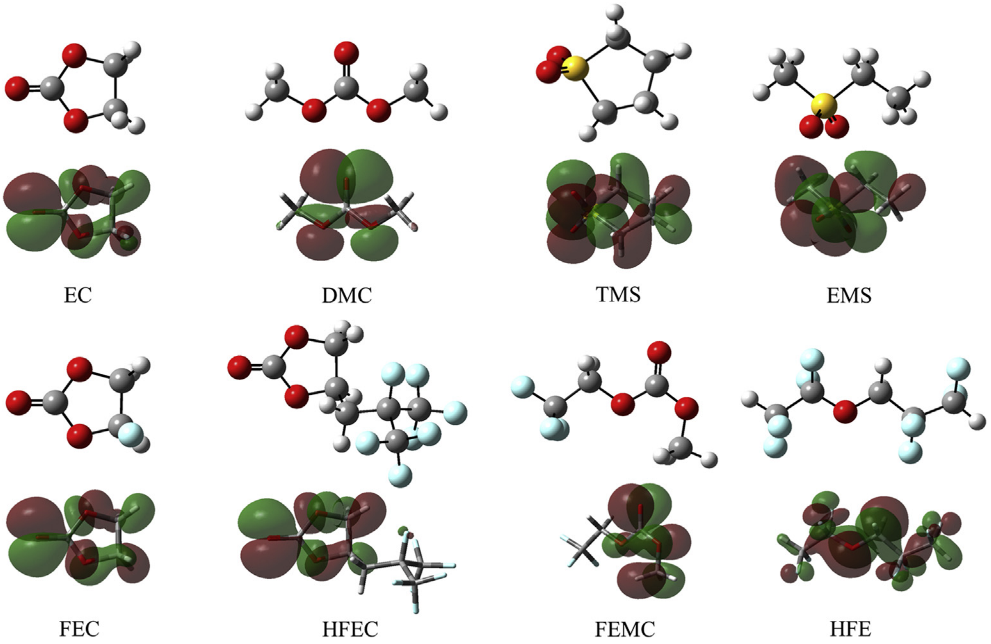

Fig. 1. Structures and HOMO shapes of solvent molecules.