# Oxidation Potentials of Functionalized Sulfone Solvents for High-Voltage Li-Ion Batteries: A Computational Study

Nan Shao,[†] Xiao-Guang Sun,[†] Sheng Dai,[†,‡] and De-en Jiang[*,†]

[†]Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, United States
[‡]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37966, United States

ABSTRACT: New electrolytes with large electrochemical windows are needed to meet the challenge for high-voltage Li-ion batteries. Sulfone as an electrolyte solvent boasts of high oxidation potentials. Here we examine the effect of multiple functionalization on sulfone's oxidation potential. We compute oxidation potentials for a series of sulfone-based molecules functionalized with fluorine, cyano, ester, and carbonate groups by using a quantum chemistry method within a continuum solvation model. We find that multifunctionalization is a key to achieving high oxidation potentials. This can be realized through either a fluorether group on a sulfone molecule or sulfonyl fluoride with a cyano or ester group.

Computed Oxidation Potential vs. Li⁺/Li (V)
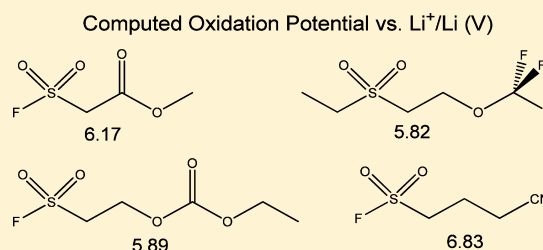
1. INTRODUCTION

Li-ion batteries have great potential to revolutionize the transportation industry. The energy density of Li-ion batteries is proportional to the voltage of the cell, so high voltage leads to high energy density.[1] Often the voltage of the cell is limited by the electrochemical window of the organic solvent in the electrolyte.[2] With the development of high-voltage (≥ 5 V) cathode materials,[3−5] it becomes imperative to develop electrolytes that have high enough oxidation potentials to match the new cathode materials.

The current state-of-art electrolytes for Li-ion batteries are a lithium salt such as $LiPF_6$ dissolved in carbonate mixtures such as ethylene carbonate (EC) with dimethyl carbonate (DMC) or diethyl carbonate (DEC). The electrolyte's electrochemical window can be measured by cyclic voltammetry.[6] Usually, either reduction potential or oxidation potential is measured against a reference electrode such as Li⁺/Li. Quantum mechanical calculations combined with thermodynamic cycles have been used to reproduce the measured one-electron oxidation or reduction potentials of ionic liquids,[7] organic inorganic ions,[8] and organic molecules.[9−12] For high-voltage Li-ion batteries, the oxidation of the electrolyte solvent at the cathode is a major concern, so here we focus our discussion on the oxidation potential; at the graphite anode, the key is whether a good solid−electrolyte interphase (SEI) can be formed, since all organic electrolyte solvents will be reduced well above the potential for Li intercalation into graphite.

Sulfone-based electrolytes have been shown to have high oxidation potentials (>5.0 V)[13−16] and used in Li-ion[17] and Li−S batteries.[18] The aim of this work is to propose new sulfone-based electrolytes which are promising synthesis targets for their high oxidation potentials. Oxidation of a solvent molecule happens by losing one electron from the highest occupied molecular orbital (HOMO), so lower HOMO level usually indicates greater difficulty in removing one electron and hence

higher oxidation potential. This simple correlation can be used as the first guide to search for molecules with large oxidation potential. One straightforward way to change the HOMO level is to introduce additional functional groups to a sulfone molecule. In this work, we consider the fluorine, cyano, ester, and carbonate functionalities both individually and synergistically. The method to compute oxidation potentials is briefly summarized in the next section.

2. COMPUTATIONAL METHODOLOGY

We compute the oxidation potential of the electrolyte solvent by using a thermodynamic cycle. See our previous work[19] for details of the thermodynamic cycles and energetics of each step involved. The key is to obtain the change of free energy as the solvent loses an electron in the liquid state. We have benchmarked our method by reproducing the measured oxidation potentials for several known sulfone solvents, including ether-functionalized sulfones.[19] The MP2 (Møller−Plesset perturbation theory to the second order) method combined with the polarizable continuum model (PCM)[20] is shown to be the most accurate method to predict oxidation potentials of sulfone-based electrolytes with mean deviation less than 0.29 V. The computed free energy of oxidation for the solvent was then referenced to that of the Li⁺/Li couple computed from a separate thermodynamic cycle. Geometry optimizations via Hartree−Fock (HF) and MP2 methods have been employed, with a medium level 6-31+G(d,p) basis set. We also computed the gas-phase adiabatic ionization potential (IP) for the sulfone molecule for comparison of the effect of different functional groups; use of a larger basis bet [6-311+G(2d)] was found to change the IP for ethylmethyl

Table 1. Comparison of Computed Oxidation Potential (V_{ox}) at the MP2/PCM Level with the Measured Value (Relative to Li$^+$/Li);[19] Computed Gas-Phase Adiabatic Ionization Potential (IP) Is Also Shown for Comparison
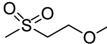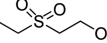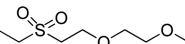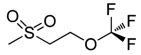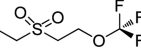
short name	structure	computed V_{ox} (V)	experiment V_{ox} (V)	IP (eV)
EMS		6.11	5.9	10.53
MEMS		5.24	5.6	10.21
EMES		5.39	5.6	10.15
EMEES		5.25	5.3	10.03

Table 2. Computed Oxidation Potential (V_{ox}) at the MP2/PCM Level (Relative to Li$^+$/Li) for Trifluoromethoxyethyl Methyl Sulfone (F-MEMS) and Ethyl Trifluoromethoxyethyl Sulfone (F-EMES); Computed Gas-Phase Adiabatic Ionization Potential (IP) Is Also Shown

short name	structure	computed V_{ox} (V)	IP (eV)
F-MEMS		5.82	10.58
F-EMES		5.82	10.31

sulfone by only 0.13 eV. Unrestricted HF and MP2 calculations were performed for the radical cations and the spin contamination was found to be small ($\langle S^2 \rangle$ is on average < 0.8). All the orbital levels in this paper are from HF; the oxidation potentials and natural population analysis (NPA) charges are from MP2. In the PCM solvation model used, the solute–solvent boundary is represented by the van der Waals surface of the solute; that is, the solute cavity is built using atom-centered spheres with radius equal to 1.1 times the van der Waals atomic radius from the UFF force field. (In this way of defining the cavity, no solvent probe is needed.) A dielectric constant of 10.0 is assumed for most of the proposed new sulfone molecules. All computations were performed with the GAUSSIAN 09 program.[21]

3. RESULTS AND DISCUSSION

Ether-functionalized sulfones such as methoxyethyl methyl sulfone (MEMS), ethyl methoxyethyl sulfone (EMES), and ethyl methoxyethoxyethyl sulfone (EMEES) have been previously shown experimentally to have large oxidation potentials.[14,15] In our previous study, we have examined various methods including HF, density functional theory (DFT), and MP2 in the framework of the PCM method by comparing the computed oxidation potentials with the measured values for those sulfone solvents. We summarize the results in Table 1 to show that a generally good agreement is reached between the MP2/PCM method and the experiment for the four linear sulfone molecules. One can see from Table 1 that adding ether groups decreases the oxidation potential, although it helps to lower the melting point (for example, 2 °C for EMES versus 36.5 °C for EMS). The reason for the lowered oxidation potential is that the oxidation happens now on the more easily oxidizable ether group instead of the sulfone group. The lowered oxidization potential is also reflected by the computed gas-phase ionization potential (IP). A simple strategy

here to recover the oxidation potential to the level of EMS is to use fluorinated ether functionality, as shown below.

Fluorination of the Ether Group. The C−F bonds in organic molecules can positively affect the interfacial chemistry for the Li-ion batteries; for example, fluorinated carbonates have been used as a cosolvent in electrolytes.[22,23] In addition, they are flame-retardant.[24] We considered different degrees of fluorination for the three ether-functionalized sulfones in Table 1. Two structures were found to have a computed oxidation potential of 5.82 V (Table 2): trifluoromethoxyethyl methyl sulfone (F-MEMS) and ethyl trifluoromethoxyethyl sulfone (F-EMES). One can see that by using trifluoromethyl instead of methyl the oxidation potential of the resultant sulfone is recovered to almost the same level as the nonfunctionalized EMS. Changes of natural population analysis (NPA) charges after oxidation (Figure 1) for F-MEMS and F-EMES show that fluorination makes the oxidation happen on the sulfone oxygen, instead of on the ether group where oxidation of nonfluorinated MEMS and EMES happens.[19] So fluorination converts the methoxy group from electron-donating to electron-withdrawing while increases the oxidation potential. The computed gas-
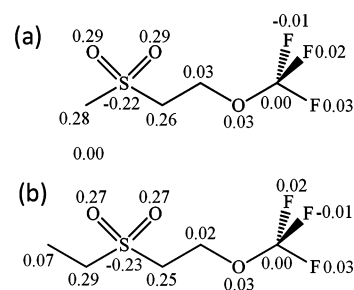

Figure 1. Changes of natural population analysis (NPA) charges between the radical cation and the neutral molecule for (a) F-MEMS and (b) F-EMES.

Table 3. Computed Oxidation Potential (V_{ox}) at the MP2/PCM Level (Relative to Li$^+$/Li) (V_{ox}) for Three Functionalized Sulfones: Methyl Methanesulfonyl Acetate (MMSA), Methyl Cyanopropyl Sulfone (MCPS), and Ethyl Methanesulfonylethyl Carbonate (EMSEC); Computed Gas-Phase Adiabatic Ionization Potential (IP) Is Also Shown

short name	structure	computed V_{ox} (V)	IP (eV)
MMSA		5.82	10.53
MCPS		5.75	10.81
EMSEC		5.81	10.59

phase IP (Table 2) also shows that fluorination now recovers the IP to the level of roughly that of EMS (Table 1).

Nitrile, Ester, and Carbonate Groups. Carbonates are the most commonly used electrolyte solvents in Li-ion batteries.[24] Introducing carbonate functionality into the sulfone structure might improve the SEI formation ability of the sulfone electrolytes, which has partially plagued the practical application of sulfone electrolytes in Li-ion batteries.[14] Moreover, the carbonate, cyano, and ester groups are also electron-withdrawing and may lead to lower HOMO level and thus higher oxidation potentials. Table 3 shows the computed oxidation potentials and gas-phase IPs for carbonate, ester, and cynao-functionalized sulfones. One can see that their oxidation potentials are comparable to those of fluorinated sulfones (F-MEMS and F-EMES). The changes of NPA charges after oxidation (Figure 2) show that the ester carbonyl oxygen is
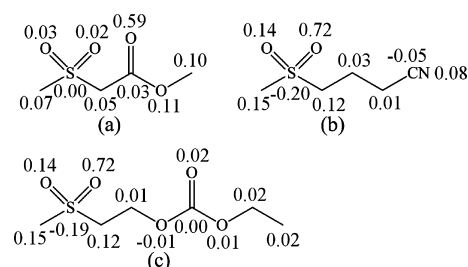

Figure 2. Changes of NPA charge between the radical cation and the neutral molecule for (a) MMSA, (b) MCPS, and (c) EMSEC.

easier to be oxidized than the sulfone oxygen for MMSA. For MCPS and EMSEC, mainly the sulfone group gets oxidized, instead of the cyano or the carbonate group. The gas-phase of

IPs of the three sulfones are also in line with those of EMS, F-MEMS, and F-EMES.

Multifunctionalization of Sulfone. The results above indicate that fluorine, ester, carbonate, and cyano groups can all contribute to the oxidative stability of sulfone molecules. One further strategy is to incorporate multiple functionalities in the sulfone molecule. What we thought of is to replace the methyl group next to sulfone in MMSA, MCPS, and EMSEC (Table 3) with fluorine, leading to MFSA, CPSF, and EFSEC (Table 4), respectively. The three new sulfone molecules all show HOMO levels lower than −13.0 eV. Comparing MFSA and MMSA, one can see that fluorination increases the oxidation potential by 0.35 V upon the ester-functionalized sulfone. Likewise, fluorination of the cyano-functionalized sulfone leads to the highest oxidation potential predicted in this work (6.83 V for CPSF), more than 1 V higher than that of MCPS. This high oxidation potential is due to the fact that two strong electron-withdrawing groups (−F and −CN) locate at both ends of the sulfone group, making much more difficult to lose the electron from the sulfone group (Figure 3b). The higher oxidation potentials of MFSA and CPSF are also corroborated by their higher IPs (Table 4).

When sulfone is functionalized with both fluorine and carbonate (EFSEC versus EMSEC), the oxidation potential also increases, though to a lesser degree. Because of fluorination, the carbonate group gets oxidized predominately (Figure 3c), instead of the sulfone group. The outcome is that EFSEC has an oxidation potential similar to EMSEC.

Besides the wide electrochemical window, a useful electrolyte solvent should have high solubility for lithium salts as well as low melting point and high boiling point to remain liquid in a wide temperature range. A drawback of sulfone is its high

Table 4. Computed Oxidation Potential (V_{ox}) at the MP2/PCM Level (Relative to Li$^+$/Li) (V_{ox}) for Three Multifunctionalized Sulfones: Methyl Fluorosulfonyl Acetate (MFSA), Cyanopropanesulfonyl Fluoride (CPSF), and Ethyl Fluorosulfonylethyl Carbonate (EFSEC); Computed Gas-Phase Adiabatic Ionization Potential (IP) Is Also Shown

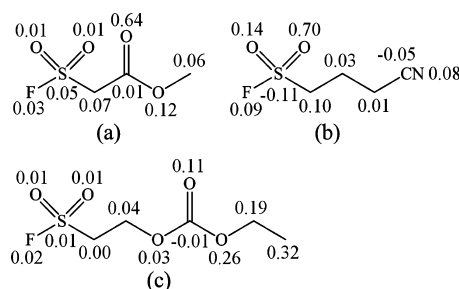| short name	structure	computed V_{ox} (V)	IP (eV)
MFSA		6.17	11.15
CPSF		6.83	12.05
EFSEC		5.89	10.80

Figure 3. Changes of NPA charge between the radical cation and the neutral molecule for (a) MFSA, (b) CPSF, and (c) EFSEC.

melting temperature.[25] Xu and Angell introduced alkyl unsymmetry to lower the melting temperatures. For example, ethylmethyl sulfone (EMS) has a melting point of 36 °C, much lower than that of the symmetric methylsulfonylmethane (109 °C).[13] Further, Sun and Angell synthesized ether-functionalized sulfones (including MEMS, EMES, and EMEES) with melting temperature lower than 15 °C and moderate ionic conductivities.[14,15] Built upon those previous studies of sulfone electrolytes, the present work suggests that multifunctionalized sulfones may have even higher oxidation potentials. They are also expected to have lower melting points; this of course calls for experimental confirmation. Although other important characteristics for an electrolyte solvent such as viscosity and SEI issues on the graphite anode are not considered, we hope that the predicted high oxidation potentials here will attract interest from experimental researchers to synthesize and characterize those novel sulfone electrolyte solvents for Li-ion batteries. In addition, for future work we plan to compute the reduction potentials of the functionalized sulfones to evaluate their full electrochemical windows.

4. CONCLUSIONS

In summary, we computed oxidation potentials of sulfone solvent molecules functionalized with fluorine, cyano, ester, and carbonate groups by quantum mechanical calculations of one-electron oxidation free energies within a continuum solvation model. We showed that although adding the ether group to the sulfone molecule lowers the oxidation potential, using instead the fluoroether group recovers the oxidation potential to almost the level of the nonfunctionalized sulfone. In addition, sulfones functionalized with a cyano, ester, or carbonate group also maintain the high oxidation potential, and they are expected to have lower melting point than the nonfunctionalized counterpart. We found that two strong electron-withdrawing groups such as −F and −CN located at the two ends of the sulfone molecule can greatly enhance the binding of the electron to the sulfone group, thereby making the electron more difficult to lose and leading to a higher oxidation potential than the nonfunctionalized sulfone. The gas-phase ionization potential has been found to be a very useful indicator of oxidation potential. This study shows that multifunctionality might increase the oxidation potentials of sulfone electrolyte solvents. It is hoped that this computational study will attract experimental interest in synthesizing the proposed new sulfone molecules for high-voltage Li-ion batteries.

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: jiangd@ornl.gov; Fax: +1 (865) 576-5235; Tel: +1 (865) 574-5199.

Notes
The authors declare no competing financial interest.

■ REFERENCES

(1) Goodenough, J. B.; Kim, Y. *J. Power Sources* **2011**, *196*, 6688−6694.
(2) Goodenough, J. B.; Kim, Y. *Chem. Mater.* **2010**, *22*, 587−603.
(3) Wang, F.; Yang, J.; NuLi, Y. N.; Wang, J. L. *J. Power Sources* **2010**, *195*, 6884−6887.
(4) Du, G. D.; Nuli, Y. N.; Yang, J.; Wang, J. L. *Mater. Res. Bull.* **2008**, *43*, 3607−3613.
(5) Amine, K.; Yasuda, H.; Yamachi, M. *Electrochem. Solid-State Lett.* **2000**, *3*, 178−179.
(6) Bard, A. J. F.; Faulkner, L. R. *Electrochemical Methods - Fundamentals and Applications*, 2nd ed.; John Wiley & Sons: New York, 2000.
(7) Maeshima, H.; Moriwake, H.; Kuwabara, A.; Fisher, C. A. J. *J. Electrochem. Soc.* **2010**, *157*, A696−A701.
(8) Ue, M.; Murakami, A.; Nakamura, S. *J. Electrochem. Soc.* **2002**, *149*, A1572−A1577.
(9) Han, Y. K.; Jung, J.; Cho, J. J.; Kim, H. J. *Chem. Phys. Lett.* **2003**, *368*, 601−608.
(10) Zubatyuk, R. I.; Gorb, L.; Shishkin, O. V.; Qasim, M.; Leszczynski, J. *J. Comput. Chem.* **2010**, *31*, 144−150.
(11) Phillips, K. L.; Sandler, S. I.; Chiu, P. C. *J. Comput. Chem.* **2011**, *32*, 226−239.
(12) Fu, Y.; Liu, L.; Yu, H. Z.; Wang, Y. M.; Guo, Q. X. *J. Am. Chem. Soc.* **2005**, *127*, 7227−7234.
(13) Xu, K.; Angell, C. A. *J. Electrochem. Soc.* **1998**, *145*, L70−L72.
(14) Sun, X. G.; Angell, C. A. *Electrochem. Commun.* **2009**, *11*, 1418−1421.
(15) Sun, X. G.; Angell, C. A. *Electrochem. Commun.* **2005**, *7*, 261−266.
(16) Xu, K.; Angell, C. A. *J. Electrochem. Soc.* **2002**, *149*, A920−A926.
(17) Abouimrane, A.; Belharouak, I.; Amine, K. *Electrochem. Commun.* **2009**, *11*, 1073−1076.
(18) Ji, X. L.; Lee, K. T.; Nazar, L. F. *Nat. Mater.* **2009**, *8*, 500−506.
(19) Shao, N.; Sun, X. G.; Dai, S.; Jiang, D. E. *J. Phys. Chem. B* **2011**, *115*, 12120−12125.
(20) Tomasi, J.; Mennucci, B.; Cammi, R. *Chem. Rev.* **2005**, *105*, 2999−3093.
(21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; et al. *Gaussian 09, Revision A*; Gaussian, Inc.: Wallingford, CT, 2009.
(22) Smart, M. C.; Ratnakumar, B. V.; Ryan-Mowrey, V. S.; Surampudi, S.; Prakash, G. K. S.; Hu, J.; Cheung, I. *J. Power Sources* **2003**, *119*, 359−367.
(23) Nanbu, N.; Watanabe, S.; Takehara, M.; Ue, M.; Sasaki, Y. *J. Electroanal. Chem.* **2009**, *625*, 7−15.
(24) Xu, K. *Chem. Rev.* **2004**, *104*, 4303−4417.
(25) Matsuda, Y.; Morita, M.; Yamada, K.; Hirai, K. *J. Electrochem. Soc.* **1985**, *132*, 2538−2543.