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Theoretic Calculation for Understanding the Oxidation Process of 1,4-Dimethoxybenzene-Based Compounds as Redox Shuttles for Overcharge Protection of Lithium Ion Batteries

Tiantian Li,[†] Lidan Xing,[†] Weishan Li,[*,†,‡,§] Bin Peng,[†] Mengqing Xu,[†,‡,§] Fenglong Gu,[†,‡,§] and Shejun Hu[†,‡,§]

[†]School of Chemistry and Environment, [‡]Key Laboratory of Electrochemical Technology on Energy Storage and Power Generation of Guangdong Higher Education Institutes, and [§]Engineering Research Center of Materials and Technology for Electrochemical Energy Storage (Ministry of Education), South China Normal University, Guangzhou 510006, China

ABSTRACT: The effect of substituents on the oxidation potential for the one-electron reaction of 1,4-dimethoxybenzene was understood with a theoretical calculation based on density functional theory (DFT) at the level of B3LYP/6-311+G(d). It is found that the oxidation potential for the one-electron reaction of 1,4-dimethoxybenzene is 4.13 V (vs Li/Li$^+$) and can be changed from 3.8 to 5.9 V (vs Li/Li$^+$) by substituting electron-donating or electron-withdrawing groups for the hydrogen atoms on the aromatic ring. These potentials are in the range of the limited potentials for the lithium ion batteries using different cathode materials, and thus the substituted compounds can be selected as the redox shuttles for the overcharge prevention of these batteries. The oxidation potential of 1,4-dimethoxybenzene decreases when the hydrogen atoms are replaced with electron-donating groups but increases when replaced with electron-withdrawing groups. The further oxidation of these substituted compounds was also analyzed on the basis of the theoretic calculation.

Degradation pathway for one-electron oxidation of TFDMOB
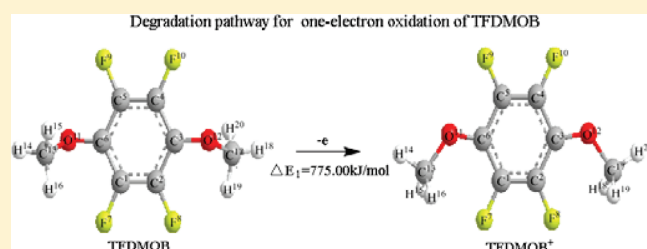
1. INTRODUCTION

Lithium ion batteries (LIBs) have been used widely to power portable electronic devices and demonstrated to be promising for large-scale applications, such as hybrid or pure electric vehicles.[1−3] A typical LIB system consists of a transition metal oxide cathode (such as LiMn$_2$O$_4$, LiCoO$_2$, LiNiO$_2$, etc.), a graphite anode, a separator, and a nonaqueous electrolyte solution.[4,5]

There are several limitations that need to be overcome for the practical application of LIBs in hybrid or pure electrical vehicles. The most important problem with a LIB is its safety.[6−8] The organic solvents in a LIB tend to decompose on anode or cathode when the LIB is overcharged.[9,10] The LIB becomes thermally unstable and sometimes smokes, ignites, or even explodes during overcharge.[11−13] Commercial LIBs are usually equipped with external protection devices, such as positive temperature coefficient resistors or integrated circuits. The external protection depends on the reliability of the electronic devices and thus cannot avoid absolutely the decomposition reactions that take place inside the battery. Therefore, internal overcharge protection is necessary for LIBs.

The use of solid polymer or ionic liquid electrolytes provides a safe solution to the decomposition of organic solvents, but the ionic conductivity of these electrolytes is too low to be used in practice. Alternatively, electrolyte additives, polymerizable compounds, and redox shuttles have been used for the overcharge protection of LIBs.

Several polymerizable compounds, called "shutdown additives", are found to be effective for the overcharge protection of LIBs.[14,15] When a LIB is overcharged, polymerizable compounds are electrochemically polymerized, forming an insulating polymer layer that blocks charged current flows.[16] Unfortunately, the overcharged LIB cannot be reused due to the formation of the insulating polymer layer.

Different from the shutdown additives, redox shuttles do not damage the LIB. The redox shuttles remains inert during the normal operation of the LIB. When a LIB is overcharged, the redox shuttle (S) is oxidized on the cathode, forming a radical cation (S$^+$). The S$^+$ diffuses through the electrolyte to the anode and is reduced on the anode back to S, which returns back to the cathode for the next redox cycle. The "oxidation−diffusion−reduction−diffusion" cycle shuttles the charged current.[17−20]

Considering the mechanism of overcharge protection by redox shuttles, the oxidation potential of the additives needs to be more positive than the end-of-charge potential of the cathode but more negative than the decomposition potential of organic solvents. Thus, the oxidation potential of redox shuttles is important for the overcharge protection of LIBs. For current LIBs, the end-of-charge potential of the cathode varies from 3.4 V
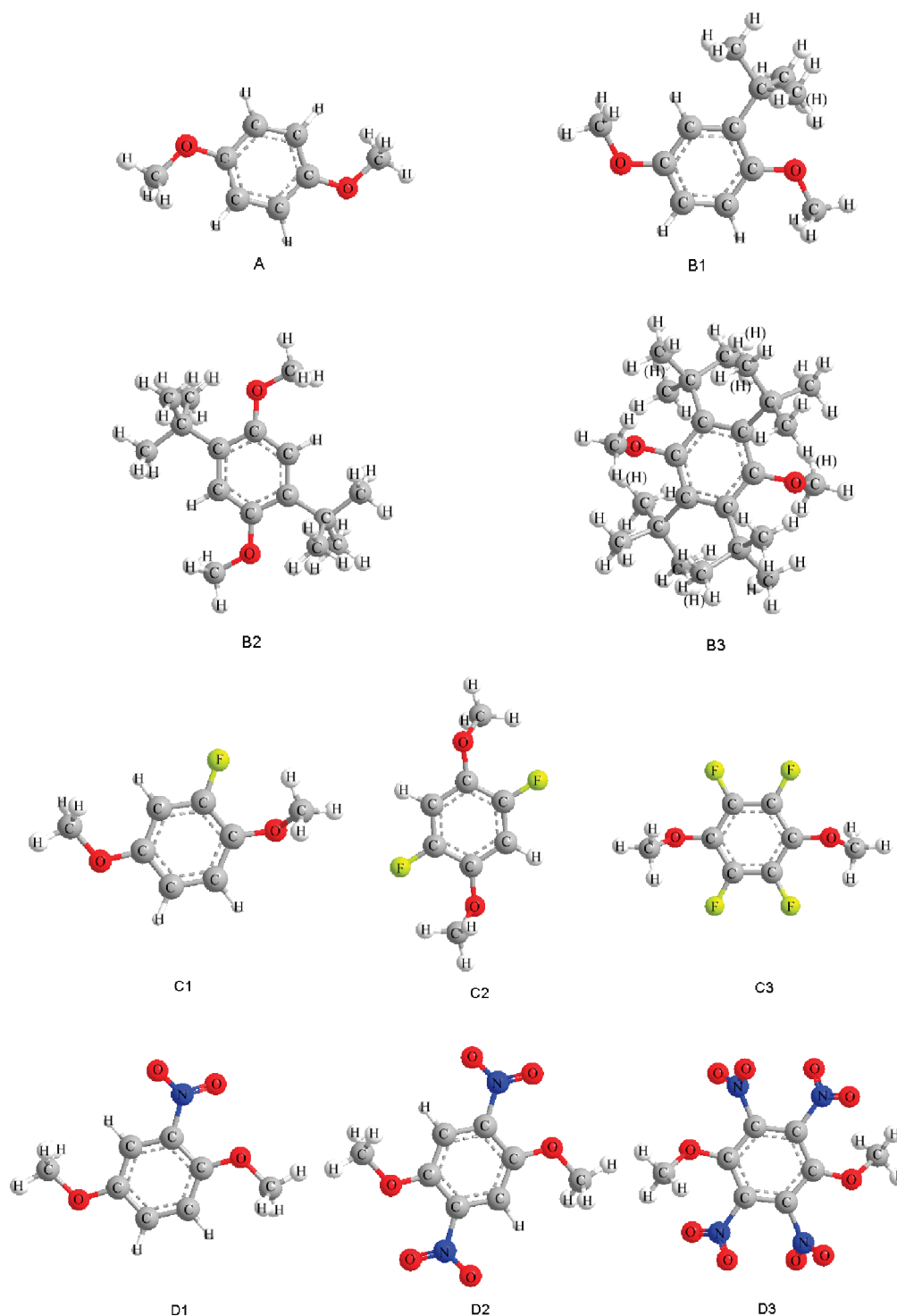
Figure 1. The optimized geometric structures of 1,4-dimethoxybenzene-based compounds.

for LiFePO$_4$ to 4.2 V for LiCoO$_2$. To meet the demand for higher energy density of the power for electric vehicle use, cathode materials with their end-of-charge potentials over 5 V, such as LiNi$_{0.5}$Mn$_{1.5}$O$_4$, have to be used. Therefore, it is necessary to design various redox shuttles with different oxidation potentials.

1,4-Dimethoxybenzene was first reported by Adachi et al. as a promising redox shuttle for overcharge protection of LIBs.[21,22] The methoxyl groups of this compound provide enough resonance

structures to help stabilize the oxidized state. Several compounds based on 1,4-dimethoxybenzene have been reported as redox shuttles.[23-27]

Theoretic calculation has become a powerful tool for predicting the chemical properties of chemicals.[28-30] Density functional theory (DFT) is a popular method for calculating the oxidation potentials of redox shuttles for LIBs.[31,32] In this work, the effect of substituents on the oxidation potential of 1,4-dimethoxybenzene

Table 1. Frontier Molecular Orbital Energy and Ionization Potential (IP) of 1,4-Dimethoxybenzene-Based Compounds EC and PC in the Gas Phase (g)

	HOMO (eV)	LUMO (eV)	E (hartree)	E^+ (hartree)	IP (kcal/mol)
A	−5.64	−0.45	−461.406 626 4	−461.139 569 1	167.58
B1	−5.55	−0.32	−618.688 732 7	−618.430 086 7	162.30
B2	−5.46	−0.21	−775.971 411 7	−775.720 388 9	157.52
B3	−5.73	−0.74	−1090.411 865 3	−1090.163 378 1	155.93
C1	−6.16	−0.60	−560.671 077 5	−560.396 581 0	172.25
C2	−6.56	−0.91	−659.932 482 2	−659.652 116 8	173.93
C3	−7.17	−1.06	−858.446 589 9	−858.151 406 4	185.23
D1	−6.36	−2.49	−665.963 448 5	−665.673 326 8	182.05
D2	−6.97	−3.33	−870.515 128 6	−870.204 830 1	194.71
D3	−7.92	−4.14	−1279.581 133 1	−1279.244 357 6	211.33
PC	−8.38	−0.37	−381.826 928 5	−381.444 811 7	239.78
EC	−8.46	−0.28	−342.498 329 3	−342.108 175 1	244.82

was understood with the calculation based on DFT at the level of B3LYP/6-311+G(d). The oxidation processes of these substituted compounds were also analyzed on the basis of the theoretic calculation.

2. COMPUTATIONAL DETAILS

All the calculations have been performed using the Gaussian 03 package.[33] The geometries are optimized by the B3LYP method[34] in conjunction with the 6-311+G(d) basis set.[35] The solvent effects are based on the integral equation formalism of the polarizable continuum model (IEFPCM).[36] A dielectric constant of 31.3 is adopted and is a weighted average value between the dielectric constants of ethylene carbonate (EC, 89), dimethyl carbonate (DMC, 3), and ethylmethyl carbonate (EMC, 2) (EC/DMC/EMC = 1:1:1). To confirm each optimized stationary point and make zero-point energy (ZPE) corrections, frequency analyses are done with the same basis set. Enthalpies and Gibbs free energy are obtained at 298.2 K. Charge distribution is analyzed by the natural bond orbital (NBO) theory.

The absolute potential (φ_{abs}) for the oxidation of an organic compound (M) was obtained based on[37]

$$\varphi_{abs}(M) = IP + [-T\Delta S + \Delta G^0_S(M^+) - \Delta G^0_S(M)]/F$$

where IP is the ionization potential, ΔS is the entropy difference between M and M^+ in the gas phase, ΔG^0_S is the Gibbs free energy change of M or M^+ between the gas phase and solvent, and F is Faraday's constant. The oxidation potential, $\varphi(M)$, of the compounds in this paper was given with respect to $\varphi_{abs}(Li/Li^+)$, which is 1.4 V.

3. RESULTS AND DISCUSSION

3.1. Oxidation Potential of 1,4-Dimethoxybenzene-Based Compounds.
The hydrogen atoms on the benzene ring of 1,4-dimethoxybenzene are replaced with tertiary butyl, fluorine, and nitro groups, forming a series of 1,4-dimethoxybenzene-based compounds. Figure 1 presents the optimized geometric structures of these compounds.

Table 1 lists the frontier molecular orbital energy (in eV), thermodynamic properties (in hartree), and the ionization potential (IP, in kcal/mol). On the basis of the molecular orbital theory, the ability of a molecule to lose one electron depends on the energy

level of the highest occupied molecular orbital (HOMO). It can be known that the HOMO energy of A, PC, and EC is −5.64, −8.38, and −8.46 eV, respectively, and the corresponding ionization potential is 167.58, 239.78, and 244.82 kcal/mol, respectively. When the hydrogen atom on the aromatic ring of 1,4-dimethoxybenzene is replaced with one group [−C(CH₃)₃, −F, or −NO₂], the compounds, B1, C1, and D1, are obtained. The HOMO energy of B1, C1, and D1 is −5.55, −6.16, −6.36 eV, respectively. This indicates that the oxidative activity is in the order B1 > A > C1 > D1 > PC > EC. The same results can be obtained from the IP data. The entropy (in cal/mol·k⁻¹) and Gibbs free energy (in hartree) of 1,4-dimethoxybenzene-based compounds and their radical cations in gas phase (g) and solvent (s) are presented in Table 2. With these data, we can obtain the theoretical oxidation potentials of these compounds, which are presented in Table 3. It can be seen from Table 3 that the theoretical oxidation potential of B1, C1, and D1 is 4.04, 4.35, and 4.63 V (vs Li/Li⁺), respectively.

When the hydrogen atoms on the aromatic ring of 1,4-dimethoxybenzene are replaced with two of the same groups [−C(CH₃)₃, −F, or −NO₂], we obtain the HOMO energy of B2, C2, and D2, which is −5.46, −6.56, and −6.97 eV, respectively. It can be known that the oxidative activity is in the order B2 > A > C2 > D2 > PC > EC. The IP of B2, C2, and D2 is 157.52, 173.93, and 194.71 kcal/mol, respectively, showing the same results as those obtained from the comparison of their HOMO energy. The calculated oxidation potential is 3.94, 4.42, and 5.04 V (vs Li⁺/Li) for B2, C2, and D2, respectively, as shown in Table 3.

When the hydrogen atoms on the aromatic ring of 1,4-dimethoxybenzene are replaced with four of the same groups [−C(CH₃)₃, −F, or −NO₂], we obtain the HOMO energy of B3, C3, and D3, which is −5.73, −7.17, −7.92 eV. The oxidative activity is in the order B3 > A > C3 > D3 > PC > EC. The IP of B3, C3, and D3 is 155.93, 185.23, and 211.33 kcal/mol, respectively, also showing the same results as those obtained from the comparison of HOMO energy. The calculated oxidation potential is 3.86, 4.82, and 5.84 V (vs Li/Li⁺), respectively, as shown in Table 3.

On the basis of the above results, it is found that the oxidation potential of 1,4-dimethoxybenzene can be changed from 3.8 to 5.9 V (vs Li/Li⁺) by substituting electron-donating or electron-withdrawing groups for the hydrogen atoms on the aromatic ring. These values are in the range of the limited potentials for the lithium ion batteries using different cathode materials. The

Table 2. Entropy (in cal/mol·k^{-1}) and Gibbs Free Energy (in hartree) of 1,4-Dimethoxybenzene-Based Compounds and Their Radical Cations in Gas Phase (g) and Solvent (s)

	S_g^+	S_g	G_s^+	G_s	G_g^+	G_g
A	96.815	95.471	−461.082 300	−461.286 513	−461.009 136	−461.276 476
B1	121.621	119.890	−618.258 657	−618.459 417	−618.193 380	−618.452 126
B2	146.489	144.149	−775.435 854	−775.632 915	−775.377 507	−775.628 396
B3	194.900	185.582	−1089.661 517	−1089.855 234	−1089.608 272	−1089.852 777
C1	101.783	101.004	−560.349 320	−560.561 314	−560.276 036	−560.550 930
C2	106.498	108.288	−659.614 829	−659.832 823	−659.541 314	−659.823 235
C3	116.467	118.138	−858.135 676	−858.364 981	−858.059 627	−858.356 185
D1	112.626	109.594	−665.629 168	−665.851 039	−665.545 868	−665.834 834
D2	128.862	125.235	−870.172 129	−870.408 921	−870.080 666	−870.389 060
D3	154.874	153.051	−1279.213 421	−1279.478 804	−1279.124 307	−1279.459 472

Table 3. Oxidation Potential (vs Li/Li$^+$) of 1,4-Dimethoxybenzene-Based Compounds

	A	B1	B2	B3	C1	C2	C3	D1	D2	D3
φ_{cal}	4.13	4.04	3.94	3.86	4.35	4.42	4.82	4.63	5.04	5.84
φ_{exp}	3.9[38]	—	3.9[24]	—	4.04[22]	4.3[25]	4.6[39]	4.46[39]	—	—

Scheme 1. Polymerization Reaction of 1,4-Dimethoxybenzene
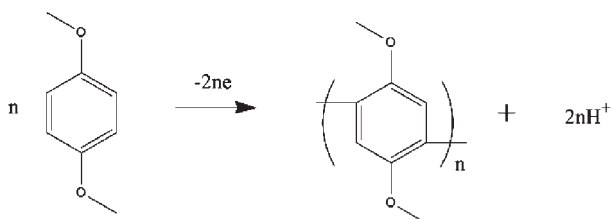
Scheme 2. Degradation Pathway of TFDMOB Oxidation

oxidation potential of 1,4-dimethoxybenzene decreases when the hydrogen atoms are replaced with electron-donating groups but increases when the hydrogen atoms are replaced with electron-withdrawing groups. Upon increasing the electron-absorbing ability of the substituted groups, the oxidation potential of 1,4-dimethoxybenzene-based compounds is enhanced. The calculation results are approximate to those experimental values that have been reported in the literature, as shown in Table 3. The theoretic calculation provides a simple way for the designing of redox shuttles used for the overcharge protection of LIB.

3.2. Degradation Pathway of 1,4-Dimethoxybenzene-Based Compounds. The oxidative and reductive states of a redox shuttle should be transformed reversibly. It has been reported that 1,4-dimethoxybenzene undergoes a radical polymerization reaction when it is oxidized through a two-electron reaction,[40] as shown in Scheme 1. In this case, 1,4-dimethoxybenzene cannot be used as a redox shuttle. Therefore, it is necessary to understand the degradation pathway of the compounds that might be used as redox shuttles. Many researchers have confirmed experimentally that 1,4-dimethoxybenzene-based compounds can be used as redox shuttles.[18,22−25] Here, we take 2,3,5,6-tetrafluoro-1,4-dimethoxybenzene (TFDMOB) and 2,3,5,6-tetra-*tert*-butyl-1,4-dimethoxybenzene (TTBDMOB) as examples of electron-drawing and electron-donating substituted compounds, respectively, to understand the degradation pathway of 1,4-dimethoxybenzene-based compounds through theoretical calculation.

The frontier molecular orbital energy and IP of TFDMOB and the solvent molecules propylene (PC) and ethylene (EC), as shown in Table 1, indicate that TFDMOB is oxidized prior to PC and EC. This is important for TFDMOB to be used as a redox shuttle. Scheme 2 presents the degradation pathway of TFDMOB oxidation. The ΔE_1 and ΔE_2 in Scheme 2 are the energy changes for the reactions TFDMOB − e → TFDMOB$^+$ and TFDMOB$^+$ − e → TFDMOB^{2+}, respectively. The geometric structures of the compounds involved in the decomposition of TFDMOB are shown in Figure 2.

Table 4 presents the charge distribution on atoms in TFDMOB, TFDMOB$^+$, and TFDMOB^{2+}, obtained by natural population analysis (NPA). The bond lengths of C^3−O^{12}, C^6−O^{11}, O^{11}−C^{13}, and O^{12}−C^{17} in TFDMOB, TFDMOB$^+$, and TFDMOB^{2+} are presented in Table 5. The initial oxidation of TFDMOB involves a one-electron reaction forming TFDMOB$^+$, and the corresponding energy ΔE_1 is 775.00 kJ/mol. The bond lengths of C^3−O^{12}, C^6−O^{11}, O^{11}−C^{13}, and O^{12}−C^{17} in TFDMOB are 1.358 10, 1.358 12, 1.438 06, and 1.438 07 Å, respectively. After one-electron reaction of TFDMOB, the bond lengths of C^3−O^{12} and C^6−O^{11} are shortened (1.299 67 and 1.299 68 Å, respectively), but those of O^{11}−C^{13} and O^{12}−C^{17} are lengthened (both are 1.464 88 Å). The standard bond lengths of C−O and C=O are 1.43 and 1.22 Å, respectively. The bonds
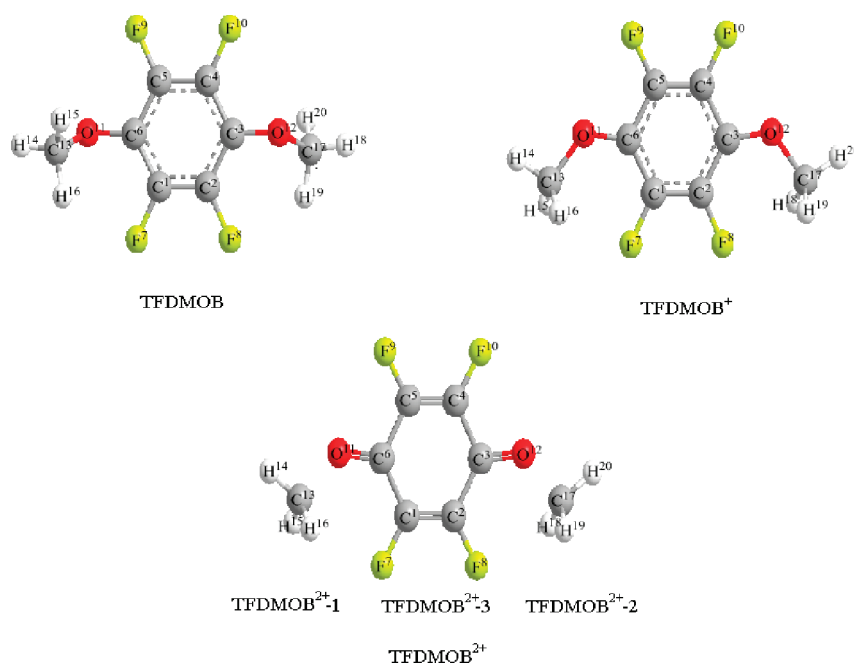
Figure 2. The optimized geometric structures of the compounds involved in the decomposition of TFDMOB.

Table 4. Charge Distribution on Atoms in TFDMOB, TFDMOB$^+$, and TFDMOB^{2+} Obtained by Natural Population Analysis (NPA)

	TFDMOB	TFDMOB$^+$	TFDMOB^{2+}
C^1	0.321 62	0.330 68	0.360 42
C^2	0.321 54	0.330 68	0.360 42
C^3	0.207 42	0.341 86	0.498 08
C^4	0.328 36	0.356 69	0.377 75
C^5	0.328 38	0.356 69	0.377 76
C^6	0.207 36	0.341 86	0.498 08
F^7	−0.328 10	−0.287 88	−0.239 10
F^8	−0.328 14	−0.287 88	−0.239 10
F^9	−0.321 20	−0.271 14	−0.220 23
F^{10}	−0.321 19	−0.271 14	−0.220 23
O^{11}	−0.550 38	−0.406 68	−0.320 21
O^{12}	−0.550 33	−0.406 67	−0.320 22
C^{13}	−0.191 38	−0.199 41	−0.181 36
H^{14}	0.189 88	0.221 53	0.251 68
H^{15}	0.174 58	0.207 17	0.236 48
H^{16}	0.169 22	0.207 18	0.236 50
C^{17}	−0.191 42	−0.199 41	−0.181 35
H^{18}	0.189 89	0.221 53	0.251 68
H^{19}	0.174 64	0.207 17	0.236 48
H^{20}	0.169 22	0.207 18	0.236 50

Table 5. Bond Lengths of TFDMOB, TFDMOB$^+$, and TFDMOB^{2+} (Å)

	TFDMOB	TFDMOB$^+$	change	TFDMOB^{2+}	change
C^3−O^{12}	1.358 10	1.299 67	−0.058 43	1.249 98	−0.049 69
C^6−O^{11}	1.358 12	1.299 68	−0.058 44	1.249 98	−0.049 70
O^{11}−C^{13}	1.438 06	1.464 88	0.026 82	1.518 14	0.053 26
O^{12}−C^{17}	1.438 07	1.464 88	0.026 81	1.518 14	0.053 26

lengths of C^3−O^{12} and C^6−O^{11} are significantly shortened (both are 1.249 98 Å), but those of O^{11}−C^{13} and O^{12}−C^{17} are significantly lengthened (both are 1.518 14 Å). This suggests that the bonds C^3−O^{12} and C^6−O^{11} in TFDMOB^{2+} are double bonds and the bonds O^{11}−C^{13} and O^{12}−C^{17} would cleave. TFDMOB^{2+}-3 is the stable 2,3,5,6-tetrafluoroquinone. Therefore, the second electron oxidation reaction of TFDMOB is irreversible. The sum of the charges of TFDMOB^{2+}-1 and TFDMOB^{2+}-2 are 0.543 30 and 0.543 31, respectively. These are characteristic of methyl radicals that may polymerize, forming ethane. This theoretical calculation confirms the experimental analysis in which one of the final oxidation products from 2, 3, 5, 6-tetrafluoro-1,4-ditertbutybenzene was identified as quinone.[24]

The energy for the second electron oxidation of TFDMOB is far larger than that for its first electron oxidation, indicating that the second electron oxidation reaction of TFDMOB is less possible. Therefore, the one electron transformation between TFDMOB and TFDMOB$^+$ is a good redox shuttle for the overcharge protection of a lithium ion battery.

Similar results can be obtained by the oxidation of TTBDMOB. The frontier molecular orbital energy and IP of TTBDMOB are also shown in Table 1. It can be found from Table 1 that TTBDMOB can be also oxidized prior to PC and EC. Scheme 3 presents the degradation pathway of TTBDMOB oxidation. The ΔE_a and ΔE_b in Scheme 3 are the energy changes

C^3−O^{12} and C^6−O^{11} in TFDMOB$^+$ are between a single bond and double bond, suggesting that TFDMOB$^+$ is unstable and can gain one electron and return back to TFDMOB; i.e., the initial one-electron reaction is reversible.

If TFDMOB$^+$ loses one electron, there are three possible products: TFDMOB^{2+}-1, TFDMOB^{2+}-2, and TFDMOB^{2+}-3. The corresponding energy ΔE_2 is 1261.32 kJ/mol. The bond
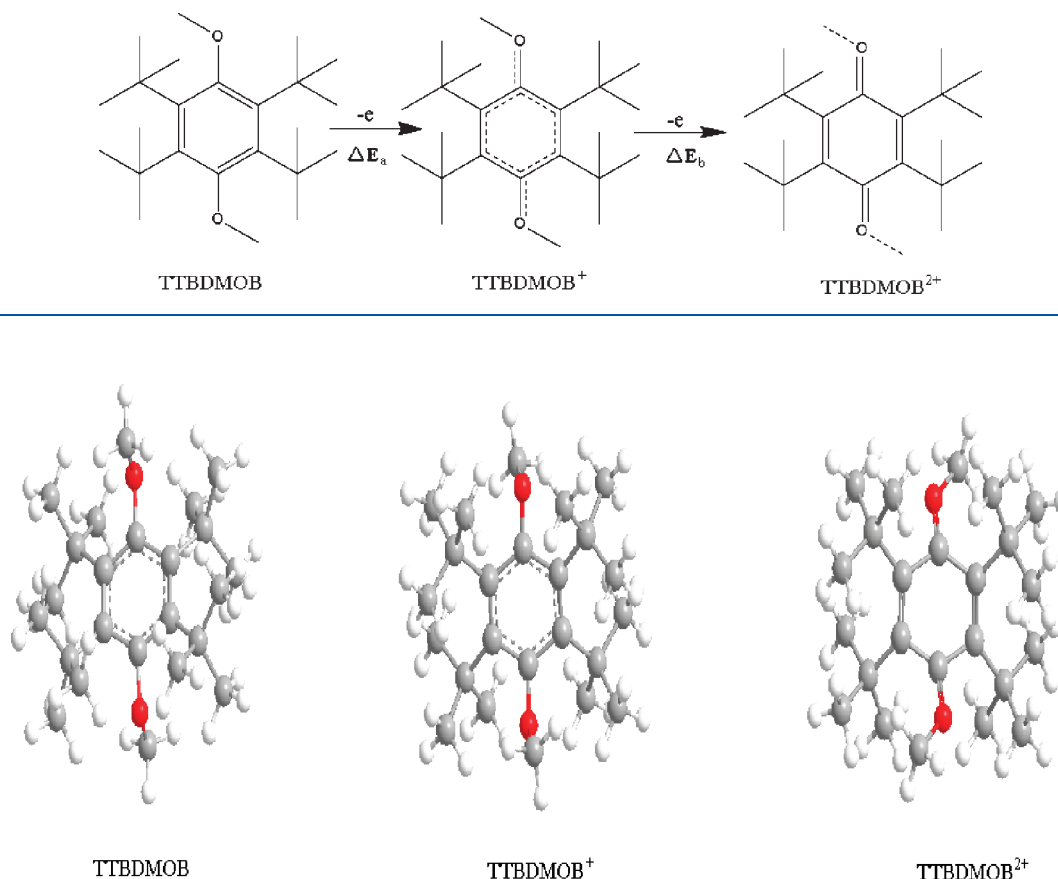
Scheme 3. Degradation Pathway of TTBDMOB Oxidation

Figure 3. The optimized geometric structures of compounds involved in the decomposition of TTBDMOB.

for the reactions TTBDMOB $-$ e $\rightarrow$ TTBDMOB$^+$ and TTBDMOB$^+$ $-$ e $\rightarrow$ TTBDMOB^{2+}, respectively. Figure 3 presents the geometric structures of the compounds involved in the decomposition of TTBDMOB. The energy ΔE_a for the initial oxidation of TTBDMOB to TTBDMOB$^+$ is 652.40 kJ/mol, while the energy ΔE_b for the further oxidation of TTBDMOB$^+$ is 977.04 kJ/mol. It can be also inferred that the initial one-electron reaction of TTBDMOB is reversible and the second electron oxidation reaction of TTBDMOB is less possible. Therefore, the one-electron transformation between TTBDMOB and TTBDMOB$^+$ is also a good redox shuttle for the overcharge protection of a lithium ion battery.

4. CONCLUSIONS

The oxidation potential for the one-electron reaction of 1,4-dimethoxybenzene decreases when the hydrogen atoms on its benzene ring are replaced with electron-donating groups but increases when replaced with electron-withdrawing groups. Therefore, 1,4-dimethoxybenzene-based compounds with different substituents can be used as the redox shuttles for lithium ion batteries that have different end-of-charge potentials. The initial one-electron oxidation of these compounds is responsible for the overcharge protection, while the further oxidation reaction of these compounds is irreversible and hardly happens when they are used for overcharge protection of lithium ion batteries.

■ AUTHOR INFORMATION

Corresponding Author

*Tel:+86 20 39310256. Fax: +86 20 39310256. E-mail: liwsh@scnu.edu.cn.

■ ACKNOWLEDGMENT

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