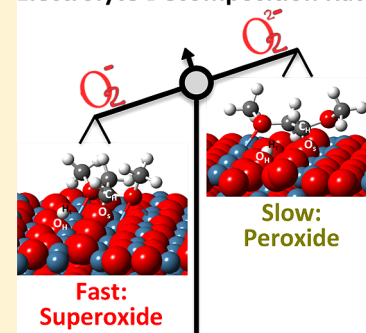


Surface-Mediated Solvent Decomposition in Li–Air Batteries: Impact of Peroxide and Superoxide Surface Terminations

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ABSTRACT: A viable Li/O₂ battery will require the development of stable electrolytes that do not continuously decompose during cell operation. Recent experiments suggest that reactions occurring at the interface between the liquid electrolyte and the solid lithium peroxide (Li₂O₂) discharge phase are a major contributor to these instabilities. To clarify the mechanisms associated with these reactions, a variety of atomistic simulation techniques, classical Monte Carlo, van der Waals-augmented density functional theory, ab initio molecular dynamics, and various solvation models, are used to study the initial decomposition of the common electrolyte solvent, dimethoxyethane (DME), on surfaces of Li₂O₂. Comparisons are made between the two predominant Li₂O₂ surface charge states by calculating decomposition pathways on peroxide-terminated (O₂²⁻) and superoxide-terminated (O₂¹⁻) facets. For both terminations, DME decomposition proceeds exothermically via a two-step process comprised of hydrogen abstraction (H-abstraction) followed by nucleophilic attack. In the first step, abstracted H dissociates a surface O₂ dimer, and combines with a dissociated oxygen to form a hydroxide ion (OH⁻). The remaining surface oxygen then attacks the DME, resulting in a DME fragment that is strongly bound to the Li₂O₂ surface. DME decomposition is predicted to be more exothermic on the peroxide facet; nevertheless, the rate of DME decomposition is faster on the superoxide termination. The impact of solvation (explicit vs implicit) and an applied electric field on the reaction energetics are investigated. Our calculations suggest that surface-mediated electrolyte decomposition should out-pace liquid-phase processes such as solvent auto-oxidation by dissolved O₂.

Electrolyte Decomposition Rate



■ INTRODUCTION

The high theoretical specific energy of the Li/O₂ battery^{1–6} makes it a promising candidate for energy storage in electric vehicles (EVs). However, several performance gaps must be overcome for these systems to become commercially viable. One of the primary issues relates to decomposition of the organic electrolyte.^{7–18} Decomposition processes have been associated with undesirable phenomena such as high charging overpotentials and limited cycle life.^{1,3,4,19,7,15,16,18} Therefore, a deeper understanding of these reactions is an important step in developing practical Li/O₂ batteries.

Identifying a stable electrolyte for Li/O₂ batteries continues to be a challenge. Carbonates, a popular class of solvents for Li-ion batteries, appear to be incapable of providing^{7,9,10,12,14,15} long cycle life and high round-trip efficiencies in these systems. For example, it has been shown that the primary discharge/charge reaction in a Li/O₂ battery using a carbonate-based electrolyte is not reversible formation/decomposition of Li₂O₂, but instead involves highly stable phases such as Li₂CO₃ and other compounds that are generated by side reactions involving the electrolyte.^{7,9,14,15}

More recent experiments have demonstrated an improvement with ether-based electrolytes, presumably due to their higher stability with respect to decomposition during cell operation.^{3,6,13} Despite this higher stability, several stud-

ies^{8,15,16,18,20} have found evidence that side reactions persist in these systems. McCloskey et al.¹⁸ quantified the yield of Li₂O₂ in a Li/O₂ cell with a dimethoxyethane (DME) based electrolyte to be at best 91%. Based on the dependence of the Li₂O₂ yield and columbic efficiency on discharge rate, it was concluded that the dominant parasitic reactions were chemical reactions between the Li₂O₂ surfaces and the electrolyte. Specifically, the Li₂O₂ yield increased with discharge rate while the columbic efficiency remained close to the ideal 2 e⁻/O₂, suggesting that shortening the exposure time of Li₂O₂ surfaces to the electrolyte reduced the extent of side reactions. Freunberger et al. used FTIR, XRD, and NMR to characterize discharged Li/O₂ batteries that used a tetraglyme-based electrolyte.⁸ By the end of the first discharge cycle, decomposition products such as Li₂CO₃, HCO₂Li, CH₃CO₂Li, polyethers, CO₂, and H₂O were present (in addition to Li₂O₂). It was shown that changing either the salt, from LiPF₆ to LiTFSI, or the solvent, from tetraglyme to triglyme or diglyme, did not stop the formation of side products. Indeed, the accumulation of side reaction products has been suggested to

Received: January 9, 2015

Revised: March 25, 2015



contribute to poor voltaic efficiency and poor capacity retention.^{20,21}

In addition to chemical decomposition, other mechanisms for electrolyte degradation include the oxidation/reduction of the solvent or the salt anion, and oxidation of electrolyte components by dissolved molecular oxygen or superoxide.^{22–24} Bryantsev et al.^{22–24} computationally screened a large number of solvents for reactivity with O_2 and O_2^- species that may be present in Li/ O_2 batteries. It was suggested that the primary decomposition pathway of glymes was autooxidation to hydroperoxides and subsequent attack by O_2^- . In addition, Assary et al.²⁵ studied the decomposition of a representative ether solvent, DME, on Li_2O_2 clusters.²⁶ It was found that DME preferred to decompose via H-abstraction on a Li–O–Li site that was suggested to be present as a defect or on small Li_2O_2 nanoparticles. This defect oxide (O^{2-}) species was predicted to be more reactive than the peroxide (O_2^{2-}) or superoxide (O_2^-) species generally found on the low-energy Li_2O_2 surfaces. Finally, Laino et al.²⁷ used first-principles metadynamics simulations to study the stability of various solvents in the presence of a peroxide terminated Li_2O_2 surface. A long chain glyme, PEGDME, was proposed to be relatively stable.

These foregoing studies underscore the importance of understanding the mechanisms associated with electrolyte decomposition reactions. Revealing these mechanisms can suggest a rational pathway to developing electrolytes suitable for Li/ O_2 batteries. Toward this goal, the present study focuses on parasitic chemical reactions occurring at the Li_2O_2 /electrolyte interface, which are motivated by recent experimental reports.¹⁸ Revealing these mechanism(s) remains a challenge due to the complex nature of the liquid electrolyte/solid electrode interface. For example, recent computational studies²⁸ have suggested that both peroxide and superoxide dimers can be present on Li_2O_2 surfaces. Likewise, the impact of solvation by the electrolyte and the role of electric fields in the electrochemical double layer remain poorly understood. In principle all of these factors can impact the kinetics and thermodynamics of surface-mediated electrolyte decomposition.

The present study systematically explores these effects. More specifically, we examine DME decomposition atop low-energy peroxide and superoxide terminated Li_2O_2 crystalline surfaces in order to discern the role of surface charge state on electrolyte decomposition. DME is predicted to decompose according to a two-step process on both surfaces; the first step involves H-abstraction from DME and subsequent bonding to a surface O_2 dimer. This interaction splits the dimer into an OH^- ion and an isolated O ion. In the second step, this residual O nucleophilically attacks the C site from which the H was abstracted, forming a strong bond between the broken DME and the surface. Regarding energetics, our calculations indicate that the decomposition reaction is more exothermic on the peroxide terminated surface; nevertheless, the activation energy for decomposition is lower on the superoxide surface, suggesting that this termination will be more reactive. Finally, the influence of solvation and electric fields on DME decomposition reactions is examined. An explicit solvation model generated from a snapshot of an ab initio MD simulation of a realistic electrolyte/ Li_2O_2 interface is compared with a continuum model and to a system where solvation effects are omitted. We find that the activation barriers are very similar across all three of these cases, suggesting that the energetics is dominated by

short-ranged interactions. Effects due to an applied electric field are also discussed. This work clarifies the mechanisms associated with electrolyte decomposition in Li/ O_2 batteries and reveals the influence of surface charge state on those mechanisms.

METHODOLOGY

Van der Waals (vdW) augmented DFT calculations were performed using the Vienna ab initio Simulation Package (VASP).^{29–31} Our prior studies examining the adsorption of small molecules in MOFs^{32–34} reveal that vdW corrections are essential for reproducing experimental adsorption enthalpies. The projector-augmented wave (PAW) scheme^{35,36} was used to treat core–valence electron interactions, with the wave functions of the valence electrons expanded in a 400 eV plane wave basis set. All calculations were spin polarized. The PBE exchange–correlation functional³⁷ in conjunction with a fully self-consistent technique for treating dispersion interactions (optB88-vdW)^{38–40} was the primary exchange correlation functional employed; additional spot-checking was performed using the HSE06 hybrid functional.^{41,42}

Oxygen dimers on Li_2O_2 surfaces were previously predicted to be electron-deficient in some low-energy terminations.²⁸ To isolate the role of the surface oxygen charge state on surface-mediated electrolyte decomposition, two low-energy terminations that exhibit similar geometries but different charge states were selected. These are the so-called ($11\bar{2}0$) stoichi and the ($11\bar{2}0$) O-rich-2 surfaces from refs 28 and 43. These surfaces are nearly degenerate in energy, and are predicted to exist as low-energy facets on the equilibrated Li_2O_2 crystallites. The oxygen dimers at the ($11\bar{2}0$) stoichi surface are exclusively peroxides (O_2^{2-}), whereas the oxygen dimers at the ($11\bar{2}0$) O-rich-2 surface are exclusively superoxides (O_2^-). Figure 1a,b depicts these two surfaces. Additional information regarding these surfaces is provided elsewhere.^{28,43}

The computational cell used for DME/ Li_2O_2 calculations consisted of a five-layer-thick Li_2O_2 slab expanded 4×2 times in the surface plane, for a total of 160 atoms. The bottom three layers of the slabs were held fixed at their bulk positions; all other atoms were allowed to relax until the forces were less than 0.05 eV/Å. The dimensions of the simulation cell was $10.95 \text{ Å} \times 15.38 \text{ Å} \times 24 \text{ Å}$, which allows for the two surfaces of the Li_2O_2 slab to be separated by 13.5 Å when the DME is adsorbed on the surface, ensuring minimal interaction between periodic images. As the molecule is placed only on one side of the slab, we examined the impact of dipole corrections and found that they had minimal effect (less than 0.02 eV) on the energetics. Hence, these corrections were not used in subsequent calculations.

Static and climbing-image nudged elastic band (NEB)⁴⁴ calculations were performed with Gamma point k-space sampling to estimate activation energies for DME decomposition reactions. Occasional spot check calculations were performed with higher k-point densities ($2 \times 2 \times 1$) and cutoff energies (550 eV). NEB barriers calculated using the denser k-point grid exhibit at most a ~ 0.01 eV increase in barrier height in comparison to the corresponding Gamma point calculation. The effect of increasing the plane-wave cutoff energy was also observed to be small: The DME adsorption energy increased by at most 8% at the 550 eV cutoff.

Starting configurations involving a single DME molecule adsorbed atop peroxide and superoxide terminated surfaces (Figure 2a,d) were obtained using a two-step procedure. First, a

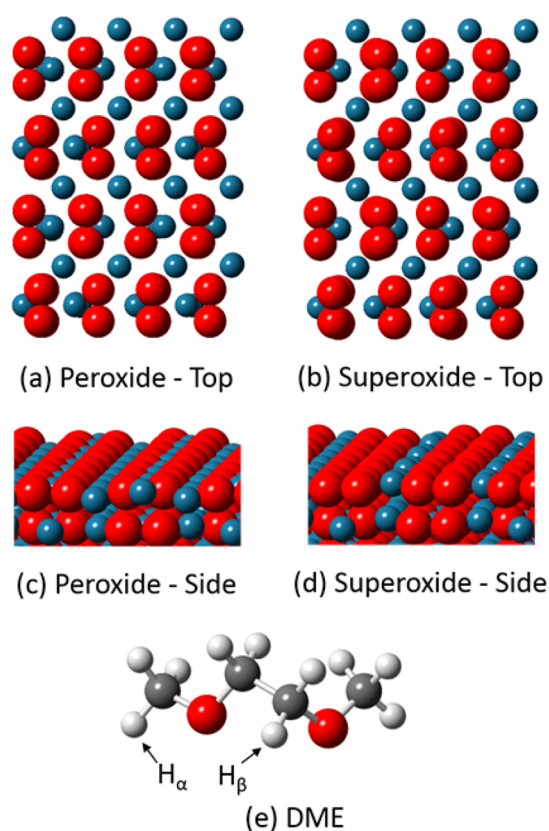


Figure 1. (a/c and b/d) Top/side view of the surfaces used for DME decomposition calculations. (a/c) Peroxide-terminated (11 $\bar{2}$ 0) “stoichi” surface; (b/d) superoxide-terminated (11 $\bar{2}$ 0) “O-rich-2” surface; (e) Molecular structure of isolated DME with hydrogens labeled according to their location at primary $-\text{CH}_3$ (H_α) and secondary $-\text{CH}_2-$ (H_β) carbon sites. The Li deficiency in the superoxide terminated Li_2O_2 surface is visible in the side view (d) as missing Li ions within the O_2 dimer rows. Li, O, C, and H are shown with blue, red, gray, and white, respectively.

classical Monte Carlo (MC) technique was used to sample the minimum energy configurations for DME adsorption on static Li_2O_2 surfaces. The Universal Force Field (UFF) was used for these simulations,⁴⁵ with atomic partial charges determined by the Bader charge partitioning scheme.^{46–49} More than 7000 conformations of DME were considered; these were generated by varying the torsion angles of the DME molecule. In addition, a large number of adsorption configurations (10^7) were explored, using equal probabilities for rotation and translation with respect to the surface, and selection of different conformers.

In the second step of the procedure the 20 lowest energy configurations from the MC search were taken as starting configurations for geometry relaxations using vdW-DFT. Finally, the lowest energy DFT configurations were then used to study adsorption and decomposition energetics. A detailed search for low-energy DME configurations following H-abstraction was performed on the lowest energy DME adsorbed configuration on both peroxide and superoxide terminated Li_2O_2 surfaces. In this case, the 12 hydrogens of the adsorbed DME were removed one by one and placed on various O_2 dimers on the surface. This process resulted in 70 configurations, from which the most stable H-abstracted configurations were selected as the most likely decomposition products. As described below, these products correspond to

scenarios where the abstracted hydrogen resides on the O_2 dimer closest to the adsorbed DME.

The influence of an electric field normal to the surface plane was accounted for by including a charge dipole layer in the vacuum region at the simulation cell boundary.^{50,51} The magnitude of the electric field was set to an average of 0.1 V/Å, which was selected to reproduce the expected potential drop for a typical electrochemical double layer. This value is obtained assuming a drop of ~ 1 V across a few nanometer thick electric double layer atop the electrode. Other electric field strengths (0.01 and 0.001 V/Å) were also tested and found to have little impact on the reaction barrier.

The effects of solvation were included at two levels. First, a continuum solvation model (VASPsol code^{52–55}) was used with the dielectric constant set to the value for DME ($\epsilon = 7.2$).⁵⁶ Next an explicit model was explored by extracting a snapshot from an ab initio molecular dynamics (AIMD) run. This model was comprised of three regions: (i) A four-layer thick Li_2O_2 slab, constructed from a 3×2 supercell of the surface unit cell containing 168 atoms; (ii) A liquid electrolyte containing 19 DME molecules and 2 LiBF_4 molecules, corresponding to a concentration of approximately 1 M; (iii) A ~ 14 Å vacuum region. The cell was orthorhombic, with dimensions $15.4 \text{ Å} \times 16.4 \text{ Å} \times 32.0 \text{ Å}$. The initial geometry was equilibrated for ~ 20 ps using the UFF⁴⁵ as implemented in GULP.⁵⁷ During this equilibration, the Li_2O_2 slab was held fixed. The system was then further equilibrated with AIMD using the QBox^{58,59} code. These calculations were performed using the PBE GGA exchange correlation functional³⁷ with the D2 dispersion corrections of Grimme.⁶⁰ Gamma-point k-space integration was used. Norm-conserving HSCV pseudopotentials⁶¹ were employed, with the hydrogen mass set to that of deuterium in order to improve time step convergence. The bottom layer of the Li_2O_2 slab was kept fixed. A time step of 1 fs and temperature of 298 K was used for both classical and AIMD. Snapshots after ~ 20 ps of AIMD were extracted, relaxed to a local minimum, and subsequently used as starting points for NEB calculations. In addition, the energy barriers calculated using the NEB method were compared to a Metadynamics^{62–65} simulation of the same. The simulation parameters for the Metadynamics run were identical to those used in the AIMD simulation. A Gaussian-shaped bias potential of 0.05 eV height and width was applied after every 25 fs of MD run-time to the bond connecting a β -hydrogen and C in the DME molecule.

RESULTS

Adsorption and Decomposition of DME. Figure 1 shows the peroxide (O_2^{2-}) and superoxide (O_2^-) terminated surfaces of Li_2O_2 used for DME decomposition calculations. The DME molecule (Figure 1c) adsorbs exothermally on both surfaces (Figure 2a,d); we refer to these adsorbed geometries in which the DME does not spontaneously decompose as “intact” configurations. The calculated adsorption energies of an isolated DME molecule are -1.52 and -1.18 eV for the peroxide and superoxide terminated surfaces, respectively. The relaxed geometry suggests that there is a strong electrostatic interaction between the surface Li and ethereal (DME) O: on the peroxide surface, these Li–O distances are 2.04 and 2.10 Å, and on superoxide surface they are 2.03 and 2.02 Å. These bonds are slightly shorter than the Li–O bonds (2.16 Å) in the bulk peroxide.

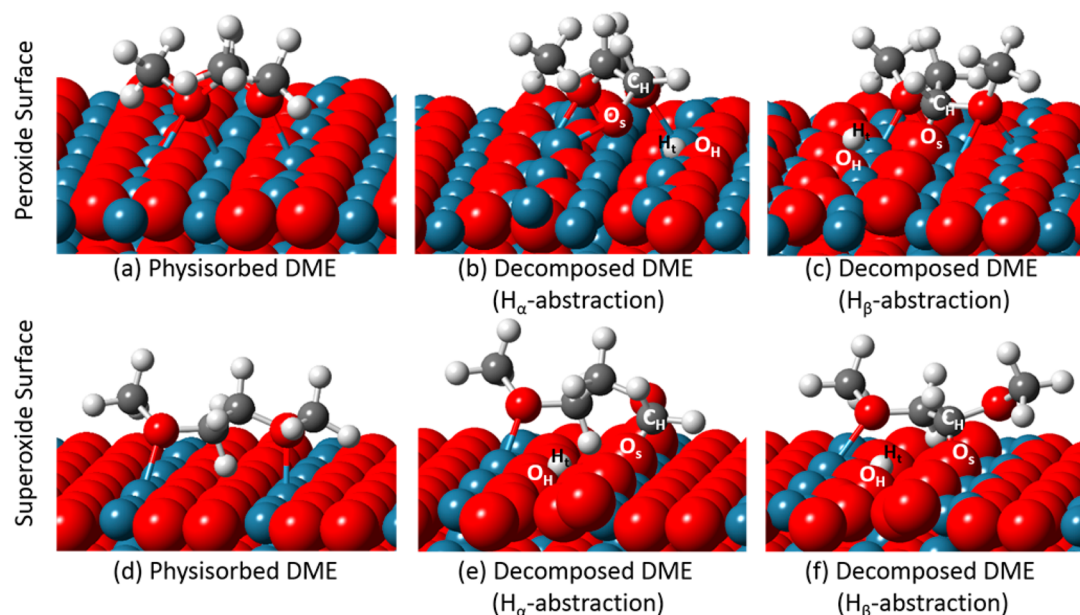


Figure 2. Side view of the low-energy configuration for adsorbed DME on peroxide (a) and superoxide surfaces (d). H-abstracted DME adsorbed atop peroxide (b, c) and superoxide surfaces (e, f). Abstracted H can detach from either $-\text{CH}_3$ (a, c) or $-\text{CH}_2-$ (b, d) positions within the adsorbed DME molecule. In all cases, H-abstraction results in splitting of an O_2 dimer on the Li_2O_2 surface, generating an $-\text{OH}$ and a surface O that nucleophilically attacks the C from which H was abstracted. H_α : The H that is transferred from DME to the surface O_2 . C_{H} : The C of DME from which H_α is abstracted. O_{H} : One of the surface O of O_2 dimer that bonds with H_α . O_β : The other surface O of O_2 dimer that nucleophilically attacks the C_{H} .

Potential decomposition pathways for adsorbed DME include C–O and C–H bond breaking reactions. The calculated activation barrier for C–O bond breaking was 2.5 and 1.7 eV for the superoxide and peroxide surfaces, respectively. These relatively high barriers suggest that DME decomposition is unlikely to proceed along such a pathway; hence, this mechanism was not considered further. A similar conclusion was also reported in a previous work.²⁵ On the other hand, decomposition of DME via an H-abstraction reaction was found to exhibit lower barriers on both types of Li_2O_2 surfaces. In this case a hydrogen atom detaches from either the primary (H_α) or secondary (H_β) position of DME (Figure 1e) and bonds to a surface O_2 dimer. This process splits the O_2 dimer, resulting in the formation of a surface-bound hydroxyl (OH) species, and a residual, electron-rich oxygen atom on the surface. This residual O then nucleophilically attacks the H-deficient C of the DME molecule. These two reactions, H-abstraction and nucleophilic attack, are roughly consecutive and result in highly exothermic products. Figure 2 illustrates the final configurations for decomposed DME fragments resulting from abstraction reactions involving H_α or H_β on both surface terminations.

Figure 3 provides a summary of the thermodynamics and kinetics associated with the most favorable DME decomposition pathways for both surface terminations. The energies of the intact and decomposed states are given with respect to that of the separated components (an isolated DME molecule and the appropriate Li_2O_2 surface). The activation energy for H-abstraction is given with respect to the intact configuration. It can be seen that the superoxide surface has a smaller (less exothermic) DME adsorption energy but lower activation energy for H_β -abstraction than the peroxide surface.

The overall decomposition reaction comprises an exchange of a hydrogen and an oxygen between the DME and surface O_2

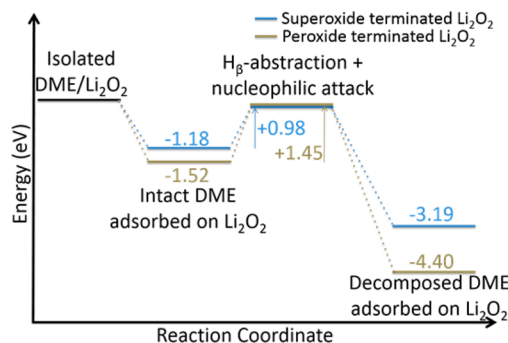
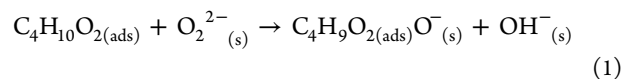
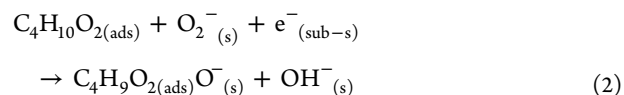


Figure 3. Energy landscape for H_β -abstraction from DME on peroxide and superoxide terminated Li_2O_2 surfaces. “Isolated $\text{DME}/\text{Li}_2\text{O}_2$ ” refers to a configuration where DME and the Li_2O_2 surface are separated. The activation barrier for H-abstraction is with respect to the “DME adsorbed on Li_2O_2 ” configuration, while the other energies are relative to the “Isolated $\text{DME}/\text{Li}_2\text{O}_2$ ” configuration.

dimer. As shown by Bader analysis below, the net reaction on the peroxide-terminated surface can be summarized as



and that on the superoxide termination as



Here, $\text{C}_4\text{H}_{10}\text{O}_{2(\text{ads})}$ refers to the adsorbed (intact) DME, while $\text{O}_2^{2-}(\text{s})$ and $\text{O}_2^-(\text{s})$ are the peroxide and superoxide units on the respective surfaces that subsequently react with abstracted hydrogen. The product $\text{C}_4\text{H}_9\text{O}_{2(\text{ads})}\text{O}^-(\text{s})$ species corresponds to H-abstracted DME bonded to a surface oxygen that is shared between DME and the surface; this species

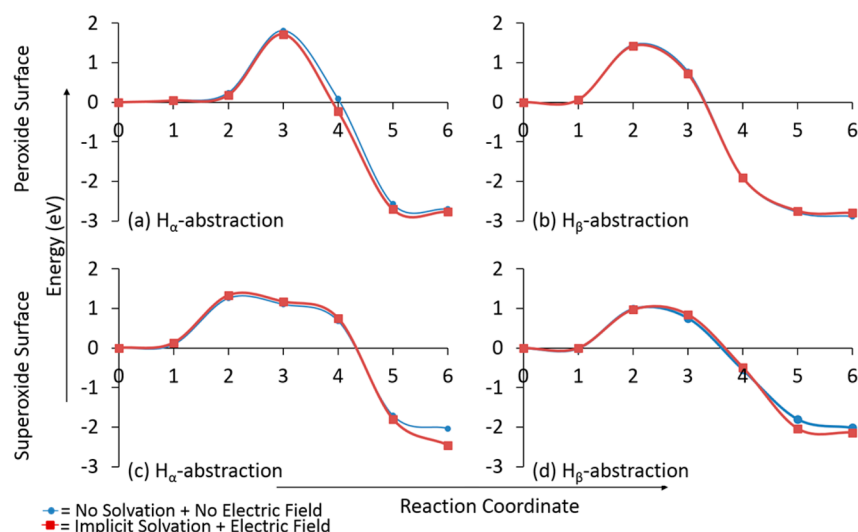


Figure 4. Energy profile for H-abstraction from DME adsorbed atop peroxide (a, b) and superoxide surfaces (c, d), computed at $T = 0$ K using the NEB method with (red square) or without (green circle) implicit solvation and electric field. In H-abstraction, H can detach from either $-\text{CH}_3$ (a, c) or $-\text{CH}_2-$ (b, d) position of the DME molecule. Image 0 corresponds to the intact configuration and Image 6 corresponds to the H-abstracted configuration for respective surfaces (Figure 2 shows these configurations). The 0 of y-axis correspond to the energy of the intact configuration.

Table 1. Energy Barriers for H-Abstraction from DME on the Peroxide- and Superoxide-Terminated Li_2O_2 Surfaces as Obtained from Methods Described in the Text

site	functional	solvation	electric field	barrier: peroxide termination (eV)	barrier: superoxide termination (eV)
H_α	optB88-vdW	none	none	1.81	1.26
	optB88-vdW	implicit	away from surface	1.72	1.33
H_β	optB88-vdW	none	none	1.45	0.98
	optB88-vdW	implicit	away from surface	1.43	0.97
	optB88-vdW	implicit	toward surface		1.33
	optB88-vdW	explicit	none		0.97
	optB88-vdW	explicit	away from surface		0.96
	HSE06@optB88-vdW	none	none	1.78	1.32

originates from the splitting of the $\text{O}_2^{2-/1-}(\text{s})$ dimer due to interaction with abstracted H. Finally, $\text{OH}^-(\text{s})$ represents the surface hydroxyl group formed from the dissociated $\text{O}_2^{2-/1-}(\text{s})$ and abstracted H. In the latter case, as discussed below, one electron ($e^-_{\text{sub-s}}$) is transferred from peroxide moieties in the subsurface region of the slab.

For the peroxide surface, the products of eq 1 are 2.70 and 2.88 eV lower in energy than the intact configuration when abstraction occurs at the H_α and H_β sites, respectively. On the superoxide surface the products are 2.03 (H_α) and 2.01 eV (H_β) lower in energy than the intact configuration. These energetics indicate that the thermodynamic driving force for DME decomposition is larger on the peroxide surface.

Reaction Barriers for DME Decomposition. The rate of the decomposition reaction is determined by the size of the reaction barrier(s) that must be surmounted to reach the reaction products. Figure 4 shows the reaction pathway for both H_α and H_β -abstraction from DME on the peroxide and superoxide terminated surfaces. The transition states for both abstraction sites correspond to a configuration where the abstracted H dissociates an O_2 dimer forming an $-\text{OH}$ and an electron rich O on the surface. The activation energies for these reactions on the peroxide surface are 1.81 and 1.45 eV for the H_α and H_β -abstraction, respectively. A similar trend with respect to the hydrogen sites is seen for the superoxide surface, where the reaction barriers are 1.26 and 0.98 eV for H_α and H_β -abstraction, respectively. Taken together, these calculations

suggest that abstraction of an H_β is more facile than abstraction of H_α , independent of surface termination. In addition, the lower barrier found on superoxide-terminated surfaces indicates that this termination is more reactive toward solvent decomposition than is the peroxide termination. The influence of using a hybrid functional (HSE06) on these two barriers was also examined by performing single point calculations on the relaxed energy pathway for H_β -abstraction. We find that the barrier increases consistently by 0.35 eV for both surfaces, but the trends observed between surface terminations or abstraction sites remain unchanged.

Effect of Solvation and Electric Fields. The calculations described above are for an idealized case involving an isolated DME molecule adsorbed on a Li_2O_2 surface. This may not be representative of the interface between the liquid electrolyte and a Li_2O_2 surface in a Li/O_2 cell due to the presence of salt/solvent molecules surrounding the DME undergoing H-abstraction and also the presence of an electrochemical double layer that gives rise to an electric field in the vicinity of the interface due to charge separation.⁶⁶ In order to estimate the significance of these effects we have calculated abstraction barriers with a continuum solvation model and an electric field for hydrogen extraction from both sites (H_α and H_β) on both terminations (peroxide and superoxide). The magnitude and direction of electric field that most closely represents the environment of the Li_2O_2 /electrolyte interface in a Li/O_2 cell is unknown. We assume a nominal field magnitude of 0.1 V/Å,

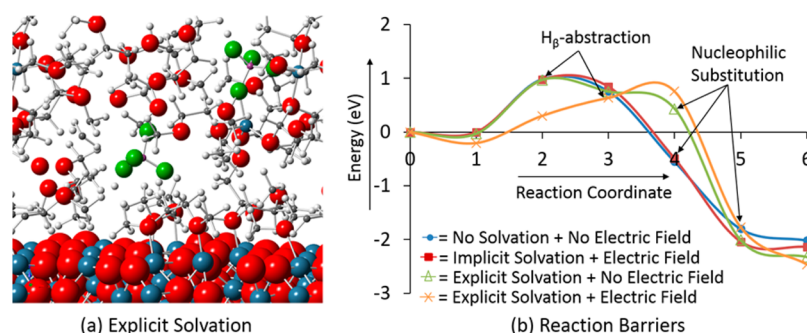


Figure 5. (a) Snapshot of an explicit electrolyte with 1 M LiBF_4 salt/DME on the superoxide-terminated Li_2O_2 surface. (b) Energy profile for H_β -abstraction from DME on the superoxide-terminated Li_2O_2 surface, computed at $T = 0$ K using the NEB method. The 0 of y-axis corresponds to the energy of the intact configuration. “ H_β -abstraction” and “Nucleophilic Substitution” labels in (b) identify the mechanisms associated with the respective images in the NEB pathways. Li, O, C, H, B, and F are shown in blue, red, gray, white, light pink, and green, respectively.

motivated by the fact that electrochemical double layers typically exhibit potential drops on the order of a 1 V and thicknesses on the order of 1 nm.⁶⁷ We first consider the case where the field is oriented away from the surface, motivated by the predicted alignment of energy levels in Li_2O_2 relative to the Li/O_2 redox potential.⁶⁸

We find that inclusion of implicit solvation and a 0.1 V/Å electric field directed away from the surface has a small effect (at most ~ 0.1 eV) on the activation energy, as shown in Table 1 and Figure 5. For example, the H_β -abstraction barrier decreases by only 0.02 and 0.01 eV for both peroxide and superoxide terminated surfaces, respectively. This effect is somewhat larger for the H_α -abstraction where the barrier decreases by 0.09 eV on the peroxide and increases by 0.07 eV on the superoxide-terminated surfaces. Interestingly, when the direction of the electric field is reversed, i.e. pointing into the surface, the H_β -abstraction barrier on the superoxide-terminated surface is increased by a larger amount, from 0.97 to 1.33 eV.

The effect of solvation on the activation energy was further tested using a solvation model where both electrolyte and salt (1 M LiBF_4) molecules are explicitly included. This was accomplished by extracting a representative configuration from large-scale ab initio MD and then relaxing this configuration to a local energy minimum. While we believe that our starting structure for the explicit electrolyte case is well equilibrated, variations in the local electrolyte composition close to the DME, for example, a locally higher or lower concentration of salt ions, could in principle impact the barrier height. This would be an interesting topic for additional investigation, but is beyond the scope of the present study. Due to the large computational cell used in these calculations, only the reaction with the lowest barrier from the isolated DME molecule calculations, that is, H_β -abstraction on the superoxide terminated surface, was revisited in this scenario. We find that the size of the primary energy barrier obtained using the explicit solvation model is similar (0.97 eV) to that previously discussed for a single molecule (0.98 eV). The overall energy profile (Figure 5b, green curve with triangular data points) is similar to the single molecule case, with the exception of the step where the surface O nucleophilically attacks the C of DME (image 4 in Figure 5b). This step is slightly less endothermic in the explicit electrolyte model, compared to the single molecule (blue curve, image 3 in Figure 5b), which can be explained by the fact that the neighboring electrolyte molecules may stabilize the H_β -abstracted DME, rendering it less susceptible to

nucleophilic attack by the surface O. We also note that the DME fragment product resulting from the H_β -abstraction reaction (image 6 in Figure 5b) is more stable when it is coordinated by explicit electrolyte (-2.46 eV vs the intact adsorbed DME) than in the single molecule case (-2.14 eV).

Additional quantification of the reaction barrier for H_β -abstraction was performed using a Metadynamics simulation. In this case, the reaction barrier for H_β -abstraction was calculated to be 1.04 ± 0.01 eV, in very good agreement with the NEB result.

The effect of an electric field (0.1 V/Å) on the explicitly modeled electrolyte was also tested (Figure 5b, orange curve with “x” data points). We find that the activation energy is reduced slightly to 0.96 eV, as can be seen by comparing image 4 (transition state) to image 1 (minimum energy configuration along the pathway). Interestingly, neither H_β -abstraction (image 3) nor nucleophilic attack (image 5) corresponds to the transition state in this case. Rather, the transition state occurs during the reorientation of the H_β -abstracted DME (approximately image 4) in preparation for nucleophilic attack. (In order to eliminate the lowering of energy for image 1, we repeated this barrier calculation with a relaxed version of image 1 as the starting configuration. But, the lowering of energy persisted. This could be explained by the presence of local minima in other degrees of freedom within the electrolyte.)

Table 1 summarizes the decomposition energetics of DME under the various scenarios considered in this work. For a fixed direction of the applied electric field, the activation energy for the H-abstraction reaction is similar in all cases, regardless of whether an explicit electrolyte, with (0.97 eV) or without (0.96 eV) electric field, or a single molecule, with (0.97 eV) or without (0.98 eV) solvation and electric field, is used. The similarity between reaction barriers obtained across the different models suggests that the key kinetic pathways for DME decomposition are largely determined by the local chemistry between the adsorbed DME molecule and the Li_2O_2 surface, and are relatively insensitive to environmental effects.

Charge Transfer Analysis. A Bader charge analysis for the single DME molecule decomposition reaction shows that for both surface terminations a total of one electron (e^-) is transferred from the DME to the Li_2O_2 slab. Table 2 shows the charges on these atoms before and after reaction steps involving H_β -abstraction and nucleophilic attack on both surfaces. As expected, the pristine peroxide and superoxide terminated surfaces start with around 1 and 0.5 e^- on each O, respectively. Roughly half an e^- is transferred when H_β is abstracted

Table 2. Bader Charges of the Atoms Participating in the Decomposition Reaction as a Function of Charge Surface Termination and H-Abstraction Site (α vs β)^a

superoxide	Δq slab	Δq DME-H _t	q (O _s)	q (H _t)	q (O _H)	q (C _H)
intact	0.0	0.0	−0.5	0.1	−0.4	0.4
H _{β} -abstracted	−1.0	0.6	−1.3	0.6	−1.3	0.9
H _{α} -abstracted	−1.1	0.6	−1.2	0.7	−1.5	0.9
peroxide	Δq slab	Δq DME-H _t	q (O _s)	q (H _t)	q (O _H)	q (C _H)
intact	0.0	0.0	−0.8	0.1	−0.9	0.4
H _{β} -abstracted	−1.1	0.6	−1.3	0.6	−1.5	1.0
H _{α} -abstracted	−1.1	0.6	−1.3	0.7	−1.6	0.9

^a Δq corresponds to the change in charge with respect to the intact configuration; q corresponds to the value of the charge on the various atoms. The labels H _{β} , O_s, O_H, and C_H are shown in Figure 2.

(comparing column 2 and column 3 of Table 2) and the other half is transferred after O_s nucleophilically attacks the C_H (column 3 of Table 2). Interestingly, at the end of the reaction the O_s and O_H have similar charge states on both surface terminations, although the peroxide O₂ dimers start with essentially twice the charge as found initially on the superoxide O₂ dimers. Since 1 e[−] is transferred to the Li₂O₂ surface from the DME for both terminations, it would appear that there is some “unaccounted for” charge transferred to these atoms in the case of the superoxide termination. The source of the additional charge transferred to the superoxide surface can be identified by analyzing the charges on the neighboring O₂ dimers both along the surface and in the subsurface region. Charge transfer from subsurface peroxide moieties to the surface O₂ dimer that participates in the H-abstraction reaction was identified as the source of the additional transferred electrons.

DME Decomposition via Alternative Reaction Routes.

Alternative reaction routes for H _{β} -abstraction of DME on the superoxide-terminated surface were also explored. Figure 6a shows one such reaction route that consists of three reaction steps. The first reaction is H_t transfer from DME to a surface O₂ where it forms a stable HOO[−] species on the surface, and the C_H remains in a metastable sp² state. The barrier for this reaction is 1.09 eV. It is interesting to note that a stable OOH species can be observed on the superoxide-terminated surface. However, on the peroxide-terminated surface, the presence of H_t near O₂ spontaneously splits the O₂ dimer. In the second step, H_t diffuses to a neighboring O₂, again forming an HOO[−] moiety on the surface and leaving the previously attached O₂ intact. The barrier for this H-diffusion is high (1.48 eV). Finally, the O₂ nucleophilically attacks the C_H in an exothermic reaction step. The reaction energy profile shows that this reaction route is limited by H-diffusion. The high barrier for H-diffusion encouraged us to look for other nucleophilic attack routes, such as the one shown in Figure 6b. In this pathway, DME decomposition proceeds via two reaction steps. The first reaction is same as in the previous pathway: H_t is abstracted from the DME and subsequently bonds to a surface O₂. The second step corresponds to a nucleophilic attack by an O₂ dimer that is located behind the DME molecule. The barrier for the second reaction is also high (1.36 eV). This high barrier could be due to the large distortion of DME that is needed to position the C_H in closer proximity to the surface O₂ dimer that initiates the nucleophilic attack.

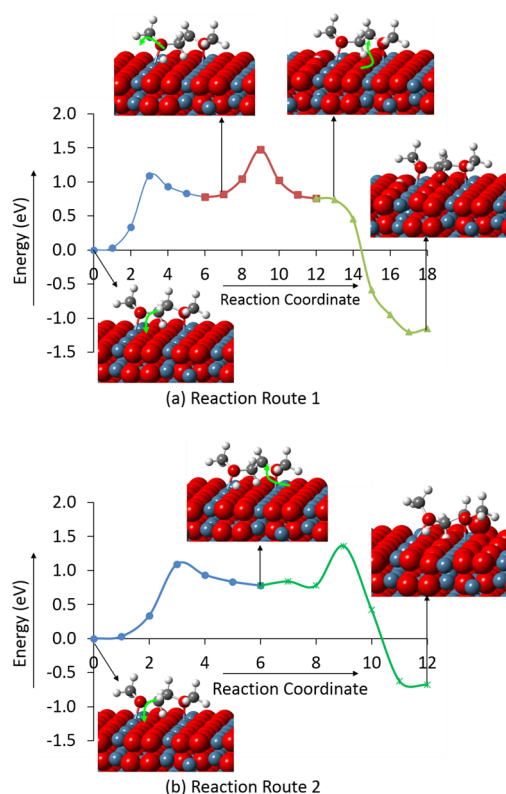


Figure 6. Energy profile for two reaction routes for DME decomposition on the superoxide surface, computed at $T = 0$ K using the NEB method. The plots in different colors correspond to different parts of the reaction. The first part (•) of both reaction routes is an H-abstraction reaction where a stable OOH species is formed on the surface. This is followed by (a) H-diffusion and O₂^{2−} nucleophilic attack on the H-abstracted C of DME or (b) direct nucleophilic attack by an oppositely placed O₂^{2−} dimer on the H-abstracted C of DME. The 0 of y-axis correspond to the energy of the intact configuration.

DISCUSSION

Connection to Experiments. A recent experiment¹⁸ characterized the quantities of side reaction products formed in DME-based Li/O₂ cells and found that the yield of Li₂O₂ was at best ~91%, thereby confirming the presence of (non-Li₂O₂ forming) parasitic reactions. Furthermore, ref 25 found evidence that the dominant solvent degradation mechanism during discharge was the chemical reaction between DME and Li₂O₂ surfaces. The present calculations suggest that hydrogen abstraction from solvent molecules adsorbed on Li₂O₂ surfaces may be the first step in this process.

To explore the hypothesis that chemical reactions between the solvent and Li₂O₂ surfaces are responsible for the observed side reactions in Li/O₂ cells, we use our predicted reaction barriers to estimate how much DME would be decomposed in a typical Li/O₂ experiment. We assume that the reaction rate for solvent decomposition can be described by classical reaction theory; consequently, the number of moles of solvent that are decomposed per gram of cathode during a time t is given by $N = ctA\nu \exp(-E_a/k_B T)$, where A is the specific area of the discharge product, c is the concentration of active sites, ν is a frequency factor, and E_a is the activation energy. Setting $A = 100 \text{ m}^2/\text{g}_{\text{carbon}}$ (typical for carbon blacks⁶⁹), $c = 10^{19} \text{ m}^{-2}$ (based on the density of surface O₂ sites), $t = 6 \text{ h}$, $\nu = 10^{13} \text{ Hz}$,^{25,70} and $E_a = 1 \text{ eV}$ (our calculated reaction barrier) yields $5 \times 10^{-3} \text{ mol/}$

g_{carbon} . (Using instead the HSE06 reaction barrier (1.32 eV) yields 2×10^{-8} mol/ g_{carbon}). These quantities represent rough estimates: assuming that the values of A , c , and ν are uncertain to within a factor of 4, and that E_a can vary by ± 0.1 eV, then the amount of solvent degraded would exhibit an uncertainty of approximately 2 orders of magnitude.) Considering that the amount of Li_2O_2 generated during a discharge to a capacity of 1000 mAh/ g_{carbon} is 2×10^{-2} mol/ g_{carbon} , we conclude, and in agreement with experimental observations,^{16,18} that the decomposition products generated via chemical reaction with Li_2O_2 surfaces upon cycling could comprise a significant fraction of the discharge product and ultimately degrade cell performance. Furthermore, we note that the surfaces examined here do not contain defects of the type examined in prior computational studies.²⁵ If present in high enough concentrations, these defects could further accelerate the rate of electrolyte decomposition.

Relation to Earlier Computational Studies and to Liquid Phase Degradation Processes. A few prior theoretical studies have also examined reactions between Li_2O_2 and various solvents. A recent study used first-principles metadynamics to study the stability of common solvents on a Li_2O_2 surface.²⁷ This study differs from ours in that (i) rather than DME, a long-chain glyme (PEGDME) was considered and (ii) a different Li_2O_2 surface was examined. Our prior calculations found that the surface used in ref 27 (which we refer to as 1–100 stoich-1) had a high surface energy of >100 meV/ \AA^2 ; in contrast, the surfaces used in the present work have surface energies of only 26 and 52 meV/ \AA^2 .^{2,28} Since surfaces having higher surface energies tend to be more reactive, one might expect that the decomposition reactions explored in ref 27 would exhibit lower activation energies. Nevertheless, despite the differences in chain length and surface termination, the results of ref 27 are largely consistent with ours: the decomposition of PEGDME was found to initiate with hydrogen abstraction, with a barrier of 0.90 eV at the PBE level of theory, and a barrier of 1.10 eV with the PBE0 hybrid functional.

In another computational study by Assary et al.,²⁵ the decomposition of DME via H-abstraction was examined on cluster models of Li_2O_2 , including the effects of a continuum model for solvation by an acetone solvent ($\epsilon = 21$). It was found that DME decomposition was most favorable (0.66/1.01 eV activation energy using B3LYP/MP2, respectively) via H_α -abstraction on a defective surface “Li–O–Li” site. Decomposition at peroxide and superoxide O_2 moieties was found to yield higher barriers of 1.42/1.51 (H_β -abstraction) and 1.12/1.32 eV (H_α -abstraction), respectively. The lower barriers observed for decomposition at superoxide sites is consistent with the trends reported in the present study between superoxide and peroxide-terminated surfaces.

Bryantsev et al.^{22–24} calculated the stability of DME with respect to reaction with solvated O_2 and O_2^- molecules. Because of the large barrier for H_α -abstraction by O_2^- (~ 1.4 eV), it was concluded that hydrogen abstraction by superoxide species in solution was not competitive with disproportionation or electrochemical reduction. Our calculated H_α -abstraction barrier of 1.26 eV on the superoxide surface is similar the B3LYP barrier calculated by Bryantsev et al.²⁴

Alternatively, it was suggested²² that decomposition of ether-based electrolytes was due to autoxidation of DME in the presence of dissolved O_2 . The autoxidation process forms ether hydroperoxides that can then decompose in the presence of

O_2^- . How then does the rate of DME autoxidation compare to the rate of chemical attack of DME by Li_2O_2 surfaces? As described above, this rate depends on the reaction barrier and the number of active surface sites or dissolved O_2 molecules. The reaction barrier for DME autoxidation calculated by Bryantsev et al.²² (1.67 eV) is larger than the barriers for H-abstraction on Li_2O_2 surfaces calculated in the present work. Additionally, the number density of surface dimers in a Li/ O_2 cell during discharge will likely be larger than the number density of dissolved O_2 molecules: assuming similar properties to those described above (area of the discharge product = 100 $\text{m}^2/g_{\text{carbon}}$; density of surface sites = 10^{19} m^{-2} ; density of the carbon electrode = 1 $g_{\text{carbon}}/\text{cm}^3$), we calculate a density of $\sim 10^3$ mol/ m^3 of surface sites in the electrode. This is 2 orders of magnitude larger than the solubility of O_2 gas in DME: ~ 10 mol/ m^3 .⁷¹ These data suggest that hydrogen abstraction at Li_2O_2 surfaces likely dominates autoxidation during the discharge of Li/ O_2 cells using DME-based electrolytes.

Comparing our results to prior calculations suggests two trends: the environment of a superoxide molecule (i.e., solvated, defective cluster, or clean surface) appears to influence the reaction barrier for H-abstraction from DME by a few tenths of an eV; and (2) the barriers for H abstraction from DME predicted by hybrid functionals tend to be a few tenths of an eV larger than those predicted by semilocal functionals. The later observation can be attributed to the enhanced localization of electrons typical of hybrid functionals, which may cause an increase to energy barriers for transition states that involve charge transfer.⁷²

Solvent Effects. We emphasize that the barrier computed for DME solvated with explicit electrolyte approximates the electrolyte as a glassy solid rather than as true liquid. A similar approach has been used in other recent studies.^{73–76} The validity of this approach is further supported by the fact that the reaction barrier for H_β -abstraction calculated using Metadynamics (in combination with the explicit electrolyte) is nearly identical. It should be noted that the explicit electrolyte model includes different physics than the model based on implicit solvation: The explicit case includes the effects of local chemical bonding between DME and the solvent. However, because it relies on locally relaxed solvent configurations rather than full dynamics, it largely omits dipolar or dielectric response and likely underestimates the solvent reorganization. On the other hand, the implicit solvation model includes the liquid dielectric and electrostatic response but neglects chemical bonding with the solvent. The fact that the reaction barriers are essentially identical for both models implies that the aforementioned effects (chemical bonding with solvent + dielectric/electrostatic/reorganization response) are less important than the specific interaction between DME and the surface. In other words, in this case we can reasonably conclude that the collective solvent effects are relatively minor.

SUMMARY

Electrolyte decomposition remains one of the primary obstacles to realizing efficient, high-capacity Li/ O_2 batteries. The identification of mechanisms resulting in the irreversible reaction of the electrolyte with soluble and insoluble reaction products is a crucial step in engineering electrolytes suitable for long-term use in these systems. Toward this goal, the present study examines the initial decomposition reaction of the prototype electrolyte solvent, DME, using vdW-augmented

DFT calculations combined with several other theoretical techniques.

We find that the dominant decomposition reaction of DME on Li_2O_2 surfaces consists of an initial H-abstraction step wherein a secondary hydrogen (H_β) detaches from DME and bonds to an O_2 dimer on the surface. The abstracted hydrogen dissociates the O_2 dimer, resulting in the formation of an $-\text{OH}$ group and an electron rich O. This residual oxygen subsequently attacks the under-coordinated C_H in the DME, resulting in a DME fragment strongly bound to the Li_2O_2 surface. Calculated activation energies reveal that it is easier to abstract H_β than H_α for both peroxide and superoxide terminations. Moreover, we find that barriers for H_β -abstraction are smaller on superoxide-terminated surfaces (0.97 eV) than on peroxide-terminated surfaces (1.45 eV). The effects of an implicit solvation model and electric field on the DME decomposition were explored. An electric field (0.1 V/Å) pointing away from the surface decreases the H_β -abstraction barrier at most by 0.02 eV. However, when the field direction is reversed, the H_β -abstraction barrier increases from 0.97 to 1.33 eV. H_β -Abstraction was also studied using an explicit solvation model that includes coordination effects from a multi-component (salt + solvent) liquid electrolyte. The explicit model corroborates the results predicted by the continuum solvation approximation, as the barriers obtained by the two models are similar (0.97 eV). The presence of an electric field with explicit solvation reduces the barrier by a negligible amount. A Bader charge analysis shows a total of 1 e^- transferred from DME to slab for both the peroxide- to superoxide-terminated Li_2O_2 surfaces. Moreover, a charge transfer from bulk peroxide to the surface superoxide moieties is seen on the superoxide-terminated surface. A combination of our calculated activation energies with classical rate theory indicates that hydrogen abstraction at Li_2O_2 surfaces could account for the degradation of ether solvents in Li/ O_2 cells observed by experiments. These surface-mediated decomposition processes are expected to outpace liquid-phase processes such as solvent autooxidation by dissolved O_2 . Our findings point to the need for surface engineering strategies that can chemically passivate reactive Li_2O_2 surfaces, or to chemical modifications of the solvent that impede abstraction processes.⁷⁷

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Notes

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ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy's U.S.–China Clean Energy Research Center for Clean Vehicles (CERC–CVC), Grant No. DE-PI0000012. B.C.W. acknowledges support from the LLNL Laboratory Directed Research and Development Grant 12-ER-053. Computing support came from the LLNL Institutional Computing Grand Challenge program. Part of work was performed under the auspices of the U.S. Department of Energy by LLNL under Contract DE-AC52-07NA27344. The authors also thank Dr. Erik Draeger for

his assistance with QBox and Dr. Kevin Leung for useful feedback.

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