

# Accelerating Electrolyte Discovery for Energy Storage with High-Throughput Screening

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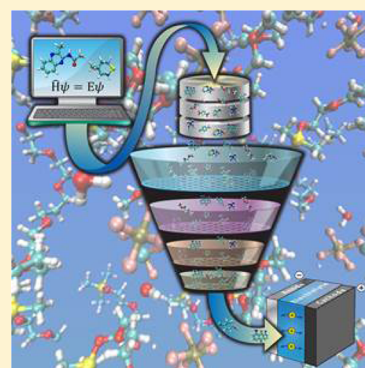
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## S Supporting Information

**ABSTRACT:** Computational screening techniques have been found to be an effective alternative to the trial and error of experimentation for discovery of new materials. With increased interest in development of advanced electrical energy storage systems, it is essential to find new electrolytes that function effectively. This Perspective reviews various methods for screening electrolytes and then describes a hierarchical computational scheme to screen multiple properties of advanced electrical energy storage electrolytes using high-throughput quantum chemical calculations. The approach effectively down-selects a large pool of candidates based on successive property evaluation. As an example, results of screening are presented for redox potentials, solvation energies, and structural changes of ~1400 organic molecules for nonaqueous redox flow batteries. Importantly, on the basis of high-throughput screening, *in silico* design of suitable candidate molecules for synthesis and electrochemical testing can be achieved. We anticipate that the computational approach described in this Perspective coupled with experimentation will have a significant role to play in the discovery of materials for future energy needs.



The worldwide demand for energy has spurred research for advanced electrical energy storage devices needed for the electrical grid system to level out the irregularities in power supply<sup>1</sup> and for high-capacity, cost-efficient batteries for electric vehicles to reduce dependence on finite petroleum resources. The drive to develop more efficient and reliable batteries has led to much research interest in energy storage technologies beyond Li-ion batteries. New battery systems, such as redox flow,<sup>2</sup> chemical transformation,<sup>3</sup> and multivalent batteries<sup>4</sup> are promising candidates for next-generation energy storage systems (Figure 1). Redox flow batteries employ, instead of solid electrodes, two separate electrolyte reservoirs with redox-active chemical components dissolved in nonaqueous or aqueous liquids to store energy. The system is scalable and can potentially provide high electrical storage capacity, especially by employing a nonaqueous solvent with a wider electrochemical stability window than water. The concept of multivalent batteries is to replace monovalent Li<sup>+</sup> in traditional Li ion batteries with di- and trivalent ions such as Mg<sup>2+</sup>, Ca<sup>2+</sup>, and Al<sup>3+</sup>. These batteries have potentially very high capacities due to the multivalent nature of cations and low cost because earth-abundant elements are used as cations. Chemical transformation systems such as Li–O<sub>2</sub>, Li–S, and Na–S batteries store energy through chemical bonds instead of intercalation. The major advantages of this type of battery are its high energy density stored in covalent bonds and low cost due to the earth abundance of sulfur or oxygen used as oxidizers. Success in developing these technologies will require breakthroughs not only in materials but also in device technology and engineering.

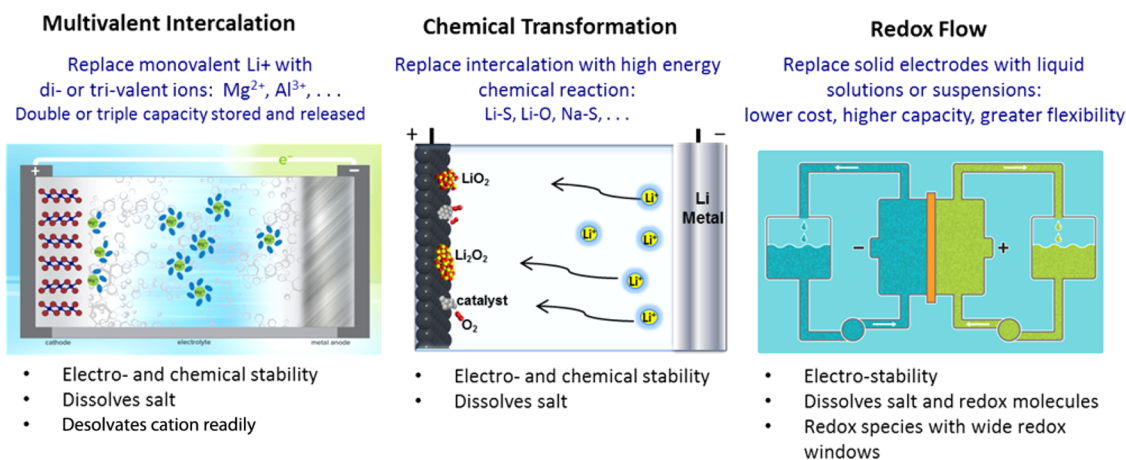
Hence, new investment has been devoted worldwide to research in electrical energy storage systems. As one example, the Joint Center for Energy Storage Research (JCESR),<sup>5,6</sup> a U.S.-based partnership among universities, national laboratories, and industry established in 2013, is focused on electrical energy storage research and development beyond Li ion technologies. The mission is to address key questions in electrochemical energy storage along the full technology development pipeline, from basic scientific research through manufacturing and delivery to market.

One of the main challenges in developing new batteries beyond the Li ion is the selection and discovery of suitable electrolyte materials.

One of the main challenges in developing new batteries beyond the Li ion is the selection and discovery of suitable electrolyte materials. Generally, the minimal requirement for the solvents and salts that make up the electrolyte is that they need to be stable within the electrochemical window of the battery in order to not degrade performance or safety, and the solvent must

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**Figure 1.** Illustration of beyond Li ion battery concepts and basic requirements (bullet points) for the corresponding electrolyte materials. Middle figure adapted from ref 6 (reproduced with permission of the American Institute of Physics).

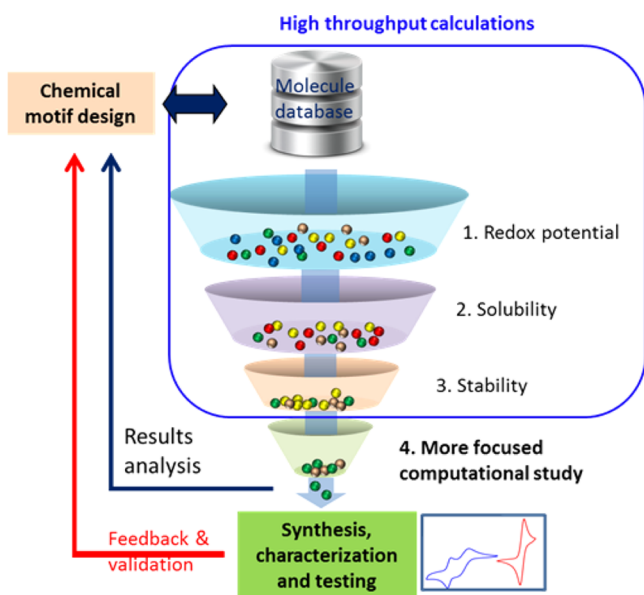
provide good solubility for the salt to ensure sufficient ionic conductivity. Furthermore, the specific energy storage technologies can present additional requirements for the electrolytes. Some performance requirements of electrolytes for different beyond Li ion batteries are summarized in Figure 1. For example, in a multivalent battery, the solvent(s) and salts need to be anodically stable and allow reversible Mg deposition/dissolution.<sup>7</sup> For nonaqueous redox flow (NRF) batteries, redox-active molecules that undergo reversible redox events to store energy need to have wide redox windows and high solubility to attain high energy density. The required properties of the electrolytes are determined both by the microscopic nature of each component as well as the macroscopic properties of the combined liquid. While computational studies are providing key understanding of the properties of the electrolytes being explored for these beyond Li ion technologies as well as Li ion battery electrolytes,<sup>8–12</sup> there is a broad horizon of new approaches with the potential to speed up the discovery of electrolytes with the necessary properties.

Advances in computer technologies and theoretical methodologies have recently started enabling new approaches based on high-throughput screening to accelerate the search for optimal electrolytes to be used in electrical energy storage systems.

Advances in computer technologies and theoretical methodologies have recently started enabling new approaches based on high-throughput screening to accelerate the search for optimal electrolytes to be used in electrical energy storage systems. The goal of such high-throughput computational screening is to establish a database of properties of electrolytes for future searches and to identify the most promising electrolyte molecular candidates at an early stage for further experimental synthesis and testing. Although high-throughput computational screening has been successful in finding new inorganic materials for cathode materials for batteries,<sup>13–16</sup> application of screening techniques to electrolytes for electrical energy systems presents new and different challenges that are starting to be addressed. Halls et al. screened redox properties of >7000 carbonate-based molecules

for Li ion batteries using a semiempirical method to evaluate their application as electrolyte additives.<sup>17</sup> They found that the effect of fluorination leads to a maximum electron affinity much larger than that of the alkylation and illustrated a new approach for exploring the property limits of structural motifs for lithium battery electrolyte additives. Korth has presented large-scale high-throughput calculations of 23 000 aprotic candidates selected from a public database with a comparison of semiempirical quantum chemical and selected density functional calculations of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies.<sup>18</sup> A combined semiempirical mechanical and wave function theory approach was suggested as the screening strategy. Aspuru-Guzik et al. has used a high-throughput framework to study potential candidate organic molecules for photovoltaics using density functional theory (DFT)<sup>19,20</sup> with a similar approach now being used to search for new organic molecules for flow battery applications.<sup>21</sup> In this Perspective, a hierarchical computational scheme for screening multiple properties of a large number of electrolyte materials for advanced electrical energy storage systems is described. This approach considers not only redox potentials but also other important properties such as solubilities and structural stability. By using high-throughput quantum chemical predictions of properties, it is shown how it is possible to eliminate many unpromising candidates and uncover structure–property relationships for developing design principles. It is also shown how descriptor-based screening can be used to further accelerate the computation and discovery process. Finally, the challenges that remain to be overcome for successful high-throughput of electrolytes are discussed, as well as an outlook for the opportunities that this presents for electrical energy storage research.

*Screening Strategy for Electrical Energy Storage Electrolytes.* The general screening strategy is to down-select a pool of candidates based on successive property evaluations obtained from high-throughput computations, as shown in the scheme in Figure 2. In this strategy, there are three tiers of selection. The order and property selection scheme can change depending on the system; for example, in multivalent systems, the ligand and surface effects become dominant; hence, the explicit solvation shell and speciation on the surface need to be determined systematically before redox potentials are calculated. However, in redox flow and most monovalent Li battery systems, such surface and ligand effects are less important; hence, redox potentials and solvation energies that can be relatively easily calculated are used in the first



**Figure 2.** Schematic of down-selection of candidate molecules for electrical energy storage applications based on high-throughput computations using quantum chemical calculations of specific properties. Selected molecules based on screening can be subjected to further focused computational studies and proposed for synthesis and testing. Reproduced with permission of the American Institute of Physics.

tier selection in these systems to reduce the number of candidates for further more expensive calculations. As the pool of molecules pass through each tier, those that meet the selection metrics of that particular tier “permeate” down to the next tier for further selection. Thus, candidates are selectively removed as they go down each tier. In the top three tiers shown in Figure 2, the properties that are universally important for electrolytes in all types of batteries, redox potential, solubility, and stability, are calculated using automated, robust, high-throughput calculations. After the top three tiers of selection, the unpromising candidates are excluded, while the promising candidates can be subject to more detailed studies, if needed. Molecules that meet performance metrics are proposed for validation by experiment.

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The generation, collection, and analysis of quantum chemical data can be facilitated by software development. A software infrastructure, referred to as the Electrolyte Genome, has been developed as part of the Joint Center for Energy Storage Research<sup>5,6</sup> for the automated high-throughput computing of electrolyte properties (unpublished results). This software architecture includes automatic input file generation, result parsing, data storage framework, and job management. The high-throughput code leverages the pymatgen package.<sup>22</sup> The geometries, energies, and so forth from the high-throughput calculations stored in the database enable uncovering

of structure–property relationships to develop design principles.

As mentioned, the performance metrics used for the top three tiers of selection are not necessarily the same for all electrical energy storage concepts. As more understanding is gained of the storage concepts, these criteria will likely change. As part of a dynamic infrastructure, these parameters can be updated with new innovations in materials and/or cell architectures that change the status of the battery technology. Moreover, the cutoff criteria for each property can be flexible and inclusive because a good candidate might not be rated the best for each property but rather be a good compromise when different properties are considered.

*Generation of Electrolyte Candidates.* The chemical structures of electrolyte candidates for the high-throughput screening can be generated through an automated molecule generator. This can be done by creating derivatives of molecules that are already under investigation in the literature or, alternatively, proposed molecules. For example, the quinoxaline molecule shown in Figure 3 has been demonstrated to undergo two reversible electron reductions.<sup>2</sup> It also has high solubility and low molecular weight; thus, it is considered as a promising candidate for an active low-voltage molecule for NRF batteries. Quinoxaline-based candidates for screening can be created automatically by adding substituents at various positions of the molecule, as shown in Figure 3. The substituents include electron-withdrawing as well as electron-donating functional groups. Either one or multiple positions can be substituted at a time. The molecular generator operates in 3-D space, meaning that all substitutions are done with Cartesian coordinates of the molecules. For one-position substitution of the base molecule (quinoxaline), only symmetry-unique sites (R1, R2, and R3) are involved; for multiple-position substitution, the original molecular symmetry is broken after adding the first group; hence, the number of derivatives that can be created increases dramatically. For example, one-site substitution of quinoxaline with the 16 functional groups in Figure 3 generates 48 derivatives, while with two-site substitution, the number increases to 2352. Force-field-based genetic algorithm optimization, such as implemented in Open Babel,<sup>23</sup> can be used to initially optimize the molecules followed by high-throughput quantum chemical calculations such as those described below.

*Calculation of Screening Properties.* Three key properties, redox potential, solubility, and stability, can be used to initially down-select candidate electrolyte molecules for the three beyond Li ion battery concepts shown in Figure 1. Additional properties can be added as needed for the particular system being studied. Details of these screening properties and the specific quantum chemical methodologies for assessing them in the Electrolyte Genome are discussed in this section.

Structures of all neutral and charged species are optimized using the B3LYP density functional<sup>24</sup> with the 6-31+G(d) basis set and confirmed to be minimum structures by vibrational frequency calculations at the same level. The B3LYP/6-31+G(d) level was previously shown to predict reliable ionization potentials and electron affinities.<sup>25</sup> Solvation free energies are calculated using the Polarizable Continuum Model (PCM)<sup>26</sup> at these gas-phase optimized geometries. The dielectric constant of water (78.36) was used for solvation energy calculations as the effect of the dielectric constant on the solvation energy and the resulting calculated redox potential are minimal once the dielectric constant is over 20. More importantly, the order of the redox potentials of different molecules does not change with the choice of solvent

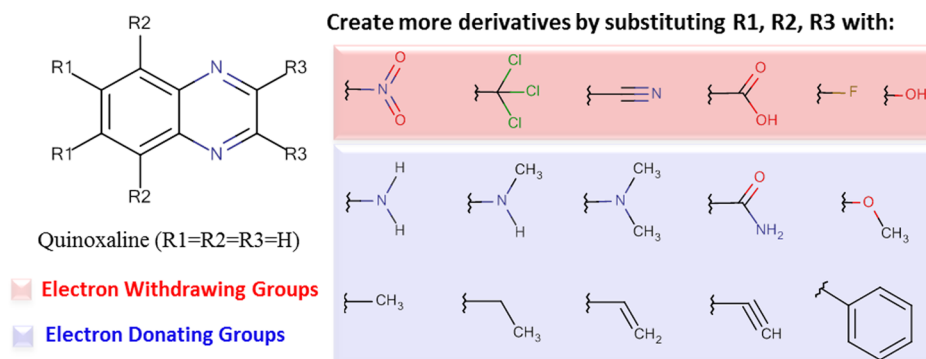


Figure 3. Example of substitution sites (R1, R2, R3) on quinoxaline as a base molecule with various electron-withdrawing and -donating groups.

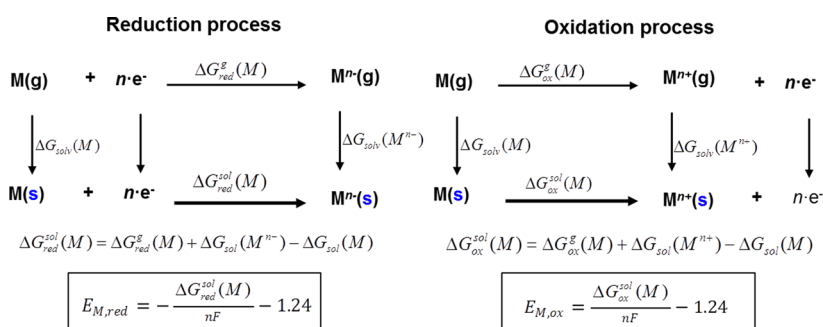


Figure 4. Thermodynamic cycles used to calculate reduction and oxidation potentials. From the  $\Delta G_{\text{red}}^{\text{sol}}$  and  $\Delta G_{\text{ox}}^{\text{sol}}$  values, the redox potential with respect to  $\text{Li}/\text{Li}^+$  ( $E_{\text{red}}$  and  $E_{\text{ox}}$ ), a commonly used experimental convention, is calculated, as shown by the equations in the boxes, where  $n$  is the number of electrons involved in the redox reaction and  $F$  is the Faraday constant. The constant “ $-1.24 \text{ V}$ ” represents the difference between the standard hydrogen electrode (SHE,  $-4.28 \text{ V}$ ) and  $\text{Li}/\text{Li}^+$  redox couple ( $-3.04 \text{ V}$ ).

dielectric constant. See the Supporting Information for more details of the dependence on dielectric constant.

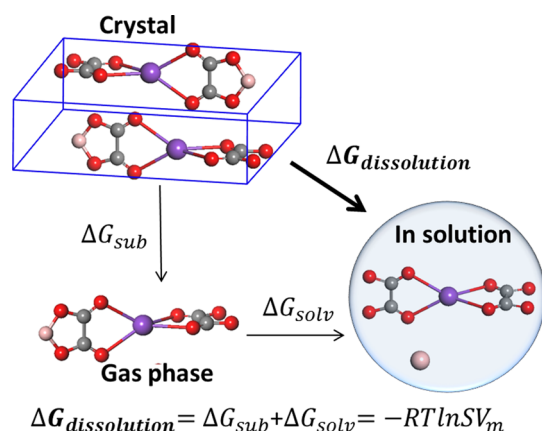
The Electrolyte Genome high-throughput code infrastructure was built to interface with Q-Chem<sup>27</sup> to perform large numbers of automatic calculations. Most DFT calculations reported in this Perspective were done high-throughput with Q-Chem. Other code packages such as Gaussian 09<sup>28</sup> and NWChem<sup>29</sup> can also be interfaced with the infrastructure.

The redox potential, which is a measure of the tendency of a molecule to either gain or lose electron(s), is an essential property of an electrolyte component for any electrochemical storage system. Electrolyte molecules have to be relatively resistant to either reduction or oxidation and, hence, have a wider redox window than the cell operating voltage. Electrolyte molecules are also required to exhibit structural stability in the charged state to ensure reversibility of redox events. For example, in Li ion batteries, the electrolytes (usually carbonates) are stable at the cathode ( $\sim 4 \text{ V}$ , oxidative stability) and at the anode ( $\sim 1 \text{ V}$ , reductive stability). For chemical transformation and multivalent systems, electrolytes also need to be stable at similar conditions to avoid undesirable electrochemical processes at the cell operating voltage. In NRF systems, two reservoirs of electrolyte solution that serve as positive and negative electrodes are referred to as the catholyte and anolyte, respectively. Redox-active components in the catholyte and anolyte set the operating voltage of the device and, hence, must have adequate reversible oxidative stability and reductive stability, respectively, to offer consistent electrochemical performance. In general, materials that possess a high oxidation potential and low reduction potential exhibit large redox windows, which can potentially enable high energy density.

The redox potentials (oxidation and reduction processes) of a molecule in solution can be computed and used to screen a large set of molecules to down-select electrolytes with the desired electrochemical windows. Using the thermodynamic cycles shown Figure 4, solution-phase free-energy changes for reduction or oxidation processes (the  $\Delta G_{\text{red}}^{\text{sol}}$  and  $\Delta G_{\text{ox}}^{\text{sol}}$ ) can be computed.<sup>30</sup> The change in energy of electrons when going from vacuum to nonaqueous solution ( $e_{(\text{gas})}^- \rightarrow e_{(\text{solv})}^-$ ) is approximated as zero. From the  $\Delta G_{\text{red}}^{\text{sol}}$  and  $\Delta G_{\text{ox}}^{\text{sol}}$  values, the redox potential with respect to  $\text{Li}/\text{Li}^+$  ( $E_{\text{red}}$  and  $E_{\text{ox}}$ ) is calculated as shown in Figure 4.

The solubility of active energy storage materials is another property that is essential to the performance of a battery. For example, in NRF batteries, the solubility of anolyte or catholyte redox-active molecules in organic solvents directly affects the capacity of the battery. In chemical transformation and multivalent batteries, salts need to have good solubility and dissociate into cations and anions in a particular solvent in order to effectively transfer charge between electrodes.

Computing the absolute solubility ( $S$ ) of any material requires taking account of its crystalline and liquid-phase interactions. As shown in Figure 5, the sublimation energy ( $\Delta G_{\text{sub}}$ ), molar volume of the crystal ( $V_{\text{m}}$ ), and solvation free energy ( $\Delta G_{\text{solv}}$ ) have to be known to calculate the solubility.<sup>31</sup> Values of the sublimation energy and molar volume, especially for novel compounds, are not available in the literature nor can these values be easily calculated because the crystal structures of the solids are not always known. Hence, it is difficult to predict the solubility. However, using quantum chemical calculations, it is plausible to compute the solvation free energy ( $\Delta G_{\text{solv}}$ ) of a molecule in an organic solvent medium via a continuum model approach that



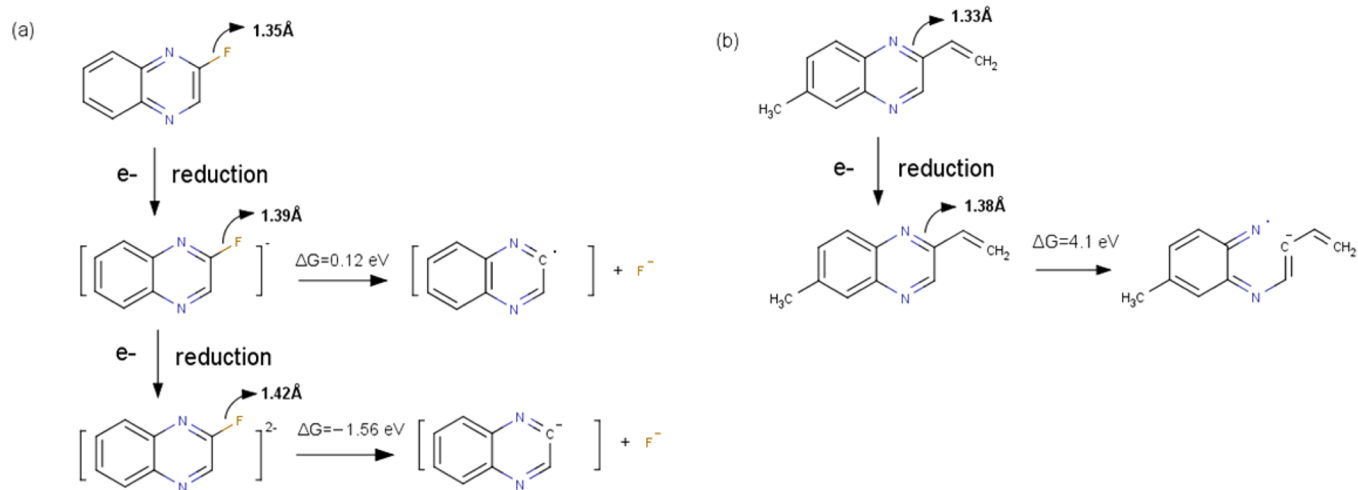
**Figure 5.** Reaction energies needed to calculate the solubility of a molecular solid in solution.

can be used for approximating trends in solubility for use in screening. In general, solvation energy calculations using continuum models are fast and provide reliable trends concerning the solvation effects of adding different substituents to a base molecule. The computed solvation energies can be used to rank solubility of a given molecule in various solvent mediums without performing detailed and expensive condensed-phase free-energy calculations. The solvation free energy can be defined as the difference in energy between the redox-active molecule in the solvent dielectric assessed with a PCM model (see the methods discussed above) and in the vacuum.

The electrochemical or chemical stability of an electrolyte is crucial for the cycle life and safety of batteries. The electrochemical stability depends on whether the electrolytes are likely to decompose upon either reduction or oxidation and, hence, exhibit limited reversibility. Chemical stability of a molecule is related to its reactivity with other species that are likely to exist in the battery cell. For NRF batteries, electrochemical stability of catholyte and anolyte materials is essential for battery cyclability. In a multivalent battery, solvents and salts need to be stable to prohibit the formation of a passivating film on the Mg anode surface.<sup>32</sup> In chemical transformation systems, the chemical stability of the solvent, for example, the reactivity toward reactive intermediate species, is especially problematic.<sup>33</sup>

A screening procedure based on geometry changes can be used to eliminate electrolytes with unsatisfactory electrochemical stability by determining whether the charged molecules exhibit any substantial structural changes compared to the neutral molecules. Those that have significant structural changes indicating potential bond breaking after reduction/oxidation are not likely to undergo irreversible reduction/oxidation reactions. This can be done through an algorithm that detects structural changes with predefined limits for bond lengths. Two examples of potential bond breaking are shown Figure 6 that can be identified using this method. The one-electron and two-electron reductions of 2-fluoroquinoxaline shown in Figure 6a lead to C–F bond elongations of 0.04 and 0.07 Å, respectively. It is possible that the fluoride ion will detach from the aromatic framework and dissolve into the nonaqueous media by cleaving the C–F bond. On the basis of the reaction energies shown in Figure 6a, this is particularly plausible for the two-electron reduction. The second example as shown in Figure 6b is the reduction of 2-vinyl-6-methylquinoxaline where, among all bonds, the C–N elongation of 0.05 Å from the neutral to anion is the greatest. However, the C–N bond breaking that leads to ring opening corresponds to a large endothermic reaction energy of +4.1 eV and should be left in the candidate pool. These examples show that a sufficient bond length change is necessary to predict vulnerability of a bond to fragmentation. Reaction energies calculated for a selection of molecules with significant bond length changes indicated that an increase of 0.1 Å or more was a reasonable criterion to screen out likely resulting unstable species from the bond breaking at those sites. However, in the future, more rigorous methods of checking for thermodynamic stability are desirable.

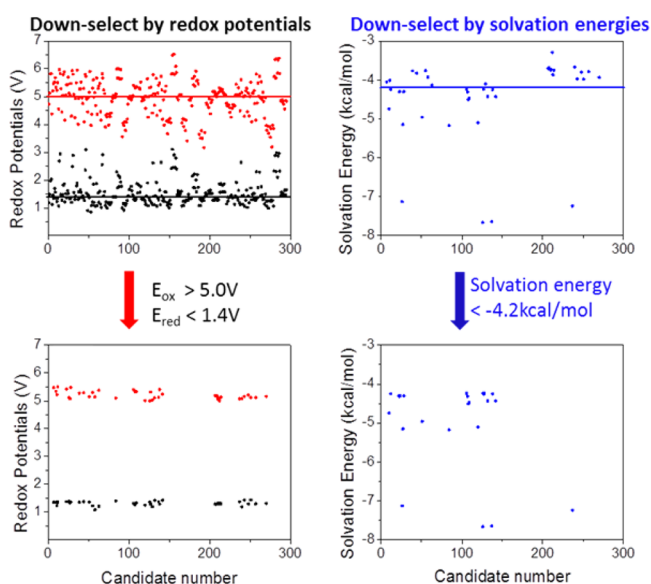
*After-Screening Detailed Computations.* After the screening down-selection, the most promising candidates can be subject to more detailed computational evaluations as needed. In the case of redox potentials, the effect of salt interactions with the redox-active molecule or solvent may have to be investigated as in some cases a significant anion effect has been found on oxidation potentials.<sup>34</sup> For solubility, molecular dynamics simulations with explicit solvent molecules can be used to obtain the solvation structure of salt in solution to help further understanding such as the desolvation of divalent cations<sup>35</sup> or to calculate diffusion coefficients for evaluation of charge-transport efficiency. In the



**Figure 6.** Schematic of (a) the C–F bond elongation of 2-fluoro-quinoxaline upon one- and two-electron reductions and (b) the C–N bond elongation of 2-vinyl-6-methylquinoxaline upon one-electron reduction. Fragmentation reaction energies associated with these bond breakings are also shown.

case of stability, electrolyte degradation after oxidation or reduction may have to be investigated in more detail by calculating selected decomposition reaction barriers.<sup>30,36</sup> The chemical reactions that could cause decomposition of electrolyte molecules depend on the battery type. For example, impurities such as water can cause electrolyte decomposition for all types of batteries, or electrolyte molecules can decompose at defective sites of electrode surfaces for Li–O<sub>2</sub> and multivalent systems. Electrolyte molecules can react with discharge products of Li–O<sub>2</sub> and Li–S batteries and be attacked by radical species from decomposition of salt in all battery types. These more detailed studies of specific properties can only be performed for a small set of promising candidates from the high-throughput tiered screening.

**Application to Anolyte Molecules for NRF Batteries.** As an illustration of the screening process for NRF electrolyte properties using the strategy outlined in the previous section, results are presented for quinoxaline and four other base molecules (anthraquinone, thiane, thiophene, and bipyridine) with up to 2 substituents from the 16 functional groups shown in Figure 3. A total of ~1400 representative molecules were selected from a total of ~12 000 that can be generated from the group substitutions. For the quinoxaline-based molecules, 295 derivatives in total were calculated using high-throughput computations. The calculated redox potentials and solvation energies for this set are illustrated in Figure 7. The screening

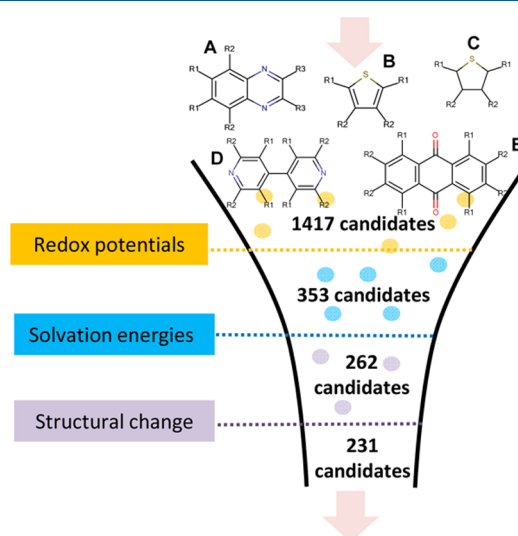


**Figure 7.** Illustration of down-selection of a total of 295 quinoxaline derivatives by the reduction potential (black points), oxidation potential (red points), and solvation energy (blue points).

metrics for the oxidation potential was set to be above 5 V for oxidation, and the reduction potential was set to be lower than that of the base molecule (quinoxaline, 1.4 V). From the 295 molecules, 42 were down-selected (Figure 7) based on the redox potentials, and 20 with solvation free energies lower than the base molecule ( $-4.2$  kcal/mol) were selected. Finally, for stability, we used the screening strategy discussed above, that is, examining down-selected molecules for substantial geometry changes in the charged molecules using an algorithm in our high-throughput screening infrastructure. In this case, none of the 20 down-selected molecules exhibited any broken bond in the reduced and oxidized structures with a bond length change limit of 0.1 Å or more.

Similar selection processes were also carried out for derivatives of anthraquinone, thiane, thiophene, and bipyridine, which can potentially be used as anolyte materials in an NRF battery when coupled with a catholyte with oxidation potentials of 5 V or higher. The selection metrics for the derivatives are not necessarily identical to those of the quinoxaline-based molecules. Because quinoxaline, anthraquinone, and bipyridine have high oxidation potentials, the goal is to select molecules based on these species that correspond to low reduction potentials to widen the potential window. For thiane and thiophene, because the reduction potentials of the base molecules are already very low, the goal is to increase the oxidation potentials, and this is used to select the metrics. Thus, for the redox window, the selection metrics are (i) an oxidation potential higher than 5 V for high oxidation resistivity and (ii) a reduction potential lower than that of the base molecules for a wider potential window. The selection metric for solvation energy is to improve upon the base molecule. More details of the down-select criteria for each base molecule subset are given in the Supporting Information.

The final results for the three-tiered down-select process are summarized in Figure 8. At the first tier of the down-select



**Figure 8.** Down-select results for derivatives of quinoxaline (A), thiophene (B), thiane (C), bipyridine (D), and anthraquinone (E). Selection metrics are discussed in text.

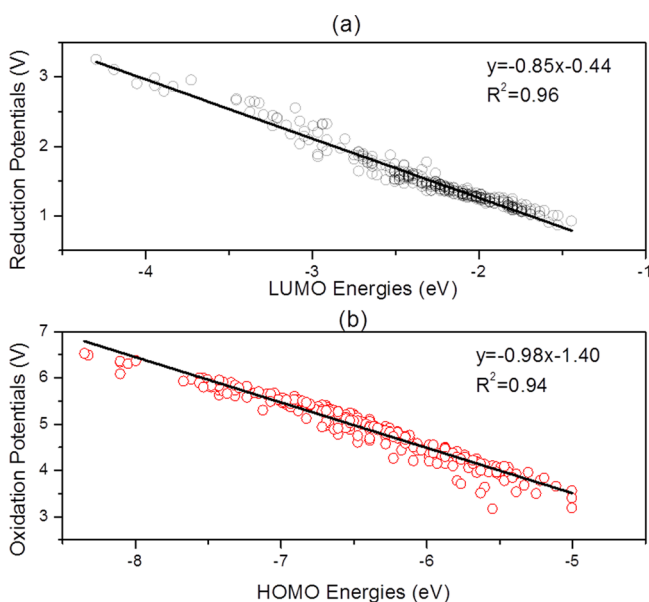
process, that is, redox potentials, the 1417 candidates were reduced to 353. At the second tier, that is, solubility, the 353 candidates were reduced to 262. Finally, the stability screening by examination of structural changes led to a further reduction to 231 candidates. The molecules screened out from the third tier are mainly thiane derivatives where the rings open up upon reduction and meet the bond length increase criterion.

The final set of candidates determined by the down-select process illustrated in Figure 8 provide candidates for testing and can be analyzed for correlation between the screening properties and their molecular properties. Such trends can be very useful for future design of molecules with desired properties. For example, because quinoxaline, anthraquinone, and bipyridine already have high oxidation potentials, it is found that the addition of electron-donating functional groups such as methyl, ethyl, methoxyl, hydroxyl, ethanamide, benzene, and vinyl are able to lower the reduction potential without lowering the oxidation potential to below 5 V, which widens the potential window. However, it is

necessary to avoid stronger electron-donating groups such as amine or methylamine to avoid reducing the oxidation potential of these three base molecules too much. Therefore, all quinoxaline, anthraquinone, and bipyridine derivatives meeting the metrics have these electron-withdrawing and -donating properties. For thiane and thiophene, because the reduction potentials of the base molecules are already very low, it is found that derivatives that satisfy the redox potential requirements mainly have electron-withdrawing groups such as nitro, carboxyl, and cyano to increase the oxidation potentials. For the solubility screening, it is found that certain functional groups can be used to increase the solvation energy (more negative) of the base molecule. More polar groups such as ethanamide, hydroxyl, cyano, and carboxyl are more effective in giving a more favorable solvation energy of the candidate molecule. For example, in Figure 7, the lowest four points in the solvation energy plot correspond to molecules with hydroxyl and ethanamide groups, which also meet the redox window criteria and are potential candidates for experimental testing.

**Descriptor-Based Screening.** Because the total number of derivatives generated by substitution can be very large if all possibilities are considered, use of descriptors that simplify the calculations could significantly speed up the DFT calculations in the high-throughput screening. In this section, it is shown how the HOMO and LUMO energies of the neutral molecules can be used as descriptors for redox potentials, which are responsible for the largest reduction in candidates in Figure 8. Some modification of the descriptors may be required for other specific base molecules that are the subject of high-throughput screening, but these descriptors can accelerate the screening process and enable screening of a substantially larger set of molecules.

A linear fitting can be used to relate oxidation and reduction potentials to HOMO energies and LUMO energies, respectively, of neutral molecules. As shown in Figure 9, a linear fit can be



**Figure 9.** Linear relationship between (a) reduction potentials with LUMO energies and (b) oxidation potentials with HOMO energies of neutral molecules of quinoxaline derivatives.

developed between HOMO/LUMO energies versus oxidation/reduction potentials, and the relationships provide good fits of

the redox potentials of 295 quinoxaline derivatives. The redox potentials in turn can be predicted from calculated HOMO/LUMO energies using these linear equations. The mean absolute deviation between reduction and oxidation potentials predicted from the linear fittings shown in Figure 9 and those calculated is 0.12 eV. These linear equations can be used to predict redox potentials of more molecules in the same series, and the only DFT calculation required for each molecule is the neutral structure optimization to obtain HOMO and LUMO energies. This descriptor approach can substantially accelerate screening because optimizations of charged structures (cation and anion) are no longer necessary.

**Outlook and Challenges.** Advances in computer technologies and theoretical methodologies have enabled new approaches based on high-throughput screening to accelerate the search for optimal electrolytes in electrical energy storage systems. Such high-throughput computational screening can eliminate unpromising electrolyte candidates at an early stage and focus on a few promising molecules for experimental synthesis and testing.

Application of screening techniques to electrolytes for electrical energy systems presents challenges as well as new opportunities that are starting to be addressed by research groups worldwide.

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In this Perspective, strategies are described for hierarchical computational screening of multiple properties of electrolyte materials for their functions in different types of advanced electrical energy storage systems. Such an approach considers not only redox potentials but also other important properties such as solubility and stability. By using high-throughput quantum chemical predictions of properties, it is possible to identify promising electrolyte candidates and provide useful guidelines to experimentalists to improve key properties via molecular modifications. Descriptor-based screening, where simpler, less-expensive calculations are used, is also shown as a way to further accelerate the computational process. In addition, more detailed and focused computations of selected candidates at a later stage can be performed to further understand issues associated with various types of energy storage systems.

Challenges remain to be overcome to advance the state of high-throughput screening of electrolytes. A key required property of electrolytes is stability. As discussed in this Perspective, electrolyte instability can come from a variety of sources. In the hierarchical scheme presented here, stability is screened by the redox window and structural changes. In the future, automated reaction energy evaluations of all bond-breaking possibilities will allow for more thorough thermodynamic stability assessment during screening. Stability issues due to reactions with other species or surfaces as is found in Li-S or Li-O<sub>2</sub> batteries are more difficult to handle in a high-throughput screening scheme, unless it is known specifically which species or surface site is involved. In addition to the thermodynamic stability properties, it may be necessary to evaluate the kinetic stability, which requires evaluation of the activation energies required to break certain

bonds of an electrolyte candidate molecule. At the present time, high-throughput screening is not possible for such activation barriers. Beyond the challenge of adequately addressing stability, there are other properties specific to certain types of electrolytes that may be difficult to assess in a high-throughput manner such as ionic conductivity, viscosity, and so forth. The development of descriptors to speed up calculations such as shown for the redox windows is another challenging area for screening of electrolytes. Finally, all of the property calculations involve some approximations such as a continuum model to represent the surrounding electrolyte environment, choice of density functional, neglect of electrode interface effects, and so forth. For the most part, these approximations work, but occasionally, there are failures, which may cause the screening to fail in some cases.

Despite these challenges, high-throughput screening in combination with closely coupled experimental investigations can provide important avenues for design of suitable candidate molecules. Candidate molecules can be purchased or synthesized for electrochemical testing. Voltage profiles and capacity changes during cycling can be used to evaluate cell performance of predicted electrolytes. In addition, the electrochemical and physical properties of candidate molecules can be characterized by various techniques for additional understanding. For example, redox potentials can be determined by cyclic voltammograms,<sup>2</sup> and solubilities of the candidate molecules in various solvents and temperatures can be measured. We anticipate that the computational approaches such as described in this Perspective along with closely coupled experimentation will have a significant role to play in the discovery of electrolyte materials for future energy needs.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Reduction potentials of five base molecules (quinoxaline, anthraquinone, thiane, thiophene, and bipyridine) in different media and oxidation potentials (V) of the five molecules in water; down-select criteria for each base molecule subset. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## ■ REFERENCES

- (1) Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928–935.
- (2) Brushett, F. R.; Vaughey, J. T.; Jansen, A. N. An All-Organic Non-Aqueous Lithium-Ion Redox Flow Battery. *Adv. Energy Mater.* **2012**, *2*, 1390–1396.
- (3) Bruce, P. G.; Freunberger, S. A.; Hardwick, L. J.; Tarascon, J. M. Li–O<sub>2</sub> and Li–S Batteries with High Energy Storage. *Nat. Mater.* **2012**, *11*, 19.
- (4) Aurbach, D.; Suresh, G. S.; Levi, E.; Mitelman, A.; Mizrahi, O.; Chusid, O.; Brunelli, M. Progress in Rechargeable Magnesium Battery Technology. *Adv. Mater.* **2007**, *19*, 4260.
- (5) Van Noorden, R. A Better Battery. *Nature* **2014**, *507*, 26–28.
- (6) Crabtree, G. W. The Joint Center for Energy Storage Research: A New Paradigm for Battery Research and Development. In *AIP Conference Proceedings*, Melville, New York; Knapp, R. H., Ed.; 2014.
- (7) Muldoon, J.; Bucur, C. B.; Oliver, A. G.; Sugimoto, T.; Matsui, M.; Kim, H. S.; Allred, G. D.; Zajicek, J.; Kotani, Y. Electrolyte Roadblocks to a Magnesium Rechargeable Battery. *Energy Environ. Sci.* **2012**, *5*, 5941–5950.
- (8) Borodin, O.; Smith, G. D. Development of Many-Body Polarizable Force Fields for Li-Battery Components: 1. Ether, Alkane, and Carbonate-Based Solvents. *J. Phys. Chem. B* **2006**, *110*, 6279–6292.
- (9) Johansson, P. Electronic Structure Calculations on Lithium Battery Electrolyte Salts. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1493–1498.



- (10) Assary, R. S.; Curtiss, L. A.; Redfern, P. C.; Zhang, Z. C.; Amine, K. Computational Studies of Polysiloxanes: Oxidation Potentials and Decomposition Reactions. *J. Phys. Chem. C* **2011**, *115*, 12216–12223.
- (11) Zhang, Z. C.; Hu, L. B.; Wu, H. M.; Weng, W.; Koh, M.; Redfern, P. C.; Curtiss, L. A.; Amine, K. Fluorinated Electrolytes for 5 V Lithium-Ion Battery Chemistry. *Energy Environ. Sci.* **2013**, *6*, 1806–1810.
- (12) Wang, Y. X.; Nakamura, S.; Tasaki, K.; Balbuena, P. B. Theoretical Studies to Understand Surface Chemistry on Carbon Anodes for Lithium-Ion Batteries: How Does Vinylene Carbonate Play Its Role as an Electrolyte Additive? *J. Am. Chem. Soc.* **2002**, *124*, 4408–4421.
- (13) Hautier, G.; Jain, A.; Ong, S. P. From the Computer to the Laboratory: Materials Discovery and Design Using First-Principles Calculations. *J. Mater. Sci.* **2012**, *47*, 7317–7340.
- (14) Curtarolo, S.; Hart, G. L. W.; Nardelli, M. B.; Mingo, N.; Sanvito, S.; Levy, O. The High-Throughput Highway to Computational Materials Design. *Nat. Mater.* **2013**, *12*, 191–201.
- (15) Greeley, J.; Jaramillo, T. F.; Bonde, J.; Chorkendorff, I. B.; Norskov, J. K. Computational High-Throughput Screening of Electrocatalytic Materials for Hydrogen Evolution. *Nat. Mater.* **2006**, *5*, 909–913.
- (16) Andersson, M. P.; Bligaard, T.; Kustov, A.; Larsen, K. E.; Greeley, J.; Johannessen, T.; Christensen, C. H.; Norskov, J. K. Toward Computational Screening in Heterogeneous Catalysis: Pareto-Optimal Methanation Catalysts. *J. Catal.* **2006**, *239*, 501–506.
- (17) Halls, M. D.; Tasaki, K. High-Throughput Quantum Chemistry and Virtual Screening for Lithium Ion Battery Electrolyte Additives. *J. Power Sources* **2010**, *195*, 1472–1478.
- (18) Korth, M. Large-Scale Virtual High-Throughput Screening for the Identification of New Battery Electrolyte Solvents: Evaluation of Electronic Structure Theory Methods. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7919–7926.
- (19) Hachmann, J.; Olivares-Amaya, R.; Atahan-Evrenk, S.; Amador-Bedolla, C.; Sanchez-Carrera, R. S.; Gold-Parker, A.; Vogt, L.; Brockway, A. M.; Aspuru-Guzik, A. The Harvard Clean Energy Project: Large-Scale Computational Screening and Design of Organic Photovoltaics on the World Community Grid. *J. Phys. Chem. Lett.* **2011**, *2*, 2241–2251.
- (20) Olivares-Amaya, R.; Amador-Bedolla, C.; Hachmann, J.; Atahan-Evrenk, S.; Sanchez-Carrera, R. S.; Vogt, L.; Aspuru-Guzik, A. Accelerated Computational Discovery of High-Performance Materials for Organic Photovoltaics by Means of Cheminformatics. *Energy Environ. Sci.* **2011**, *4*, 4849–4861.
- (21) Aspuru-Guzik, A. Computational Design of Renewable Energy Materials: A High-Throughput Approach for the Design of Organic Flow Batteries and Photovoltaics. In *248th ACS National Meeting and Exposition*, San Francisco, CA, 2014.
- (22) Ong, S. P.; Richards, W. D.; Jain, A.; Hautier, G.; Kocher, M.; Cholia, S.; Gunter, D.; Chevrier, V. L.; Persson, K. A.; Ceder, G. Python Materials Genomics (Pymatgen): A Robust, Open-Source Python Library for Materials Analysis. *Comput. Mater. Sci.* **2013**, *68*, 314–319.
- (23) *The Open Babel Chemical File Format Conversion Package*. <http://openbabel.sourceforge.net/> (2014).
- (24) Becke, A. D. Density-Functional Thermochemistry. 3. The Role of Exact Exchange. *J. Chem. Phys.* **1993**, *98*, 5648–5652.
- (25) Curtiss, L. A.; Redfern, P. C.; Raghavachari, K.; Pople, J. A. Assessment of Gaussian-2 and Density Functional Theories for the Computation of Ionization Potentials and Electron Affinities. *J. Chem. Phys.* **1998**, *109*, 42–55.
- (26) Lange, A. W.; Herbert, J. M. Polarizable Continuum Reaction-Field Solvation Models Affording Smooth Potential Energy Surfaces. *J. Phys. Chem. Lett.* **2010**, *1*, 556–561.
- (27) Shao, Y.; Molnar, L. F.; Jung, Y.; Kussmann, J.; Ochsenfeld, C.; Brown, S. T.; Gilbert, A. T. B.; Slipchenko, L. V.; Levchenko, S. V.; O'Neill, D. P.; et al. Advances in Methods and Algorithms in a Modern Quantum Chemistry Program Package. *Phys. Chem. Chem. Phys.* **2006**, *8*, 3172–3191.
- (28) 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 D.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (29) Valiev, M.; Bylaska, E. J.; Govind, N.; Kowalski, K.; Straatsma, T. P.; Van Dam, H. J. J.; Wang, D.; Nieplocha, J.; Apra, E.; Windus, T. L.; et al. Nwchem: A Comprehensive and Scalable Open-Source Solution for Large Scale Molecular Simulations. *Comput. Phys. Commun.* **2010**, *181*, 1477–1489.
- (30) Assary, R. S.; Curtiss, L. A.; Moore, J. S. Toward a Molecular Understanding of Energetics in Li–S Batteries Using Nonaqueous Electrolytes: A High-Level Quantum Chemical Study. *J. Phys. Chem. C* **2014**, *118*, 11545–11558.
- (31) Palmer, D. S.; Llinas, A.; Morao, I.; Day, G. M.; Goodman, J. M.; Glen, R. C.; Mitchell, J. B. O. Predicting Intrinsic Aqueous Solubility by a Thermodynamic Cycle. *Mol. Pharmaceutics* **2008**, *5*, 266–279.
- (32) Gofer, Y.; Turgeman, R.; Cohen, H.; Aurbach, D. XPS Investigation of Surface Chemistry of Magnesium Electrodes in Contact with Organic Solutions of Organochloroaluminate Complex Salts. *Langmuir* **2003**, *19*, 2344–2348.
- (33) Assary, R. S.; Lau, K. C.; Amine, K.; Sun, Y. K.; Curtiss, L. A. Interactions of Dimethoxy Ethane with Li<sub>2</sub>O<sub>2</sub> Clusters and Likely Decomposition Mechanisms for Li–O<sub>2</sub> Batteries. *J. Phys. Chem. C* **2013**, *117*, 8041–8049.
- (34) Wang, Y. T.; Xing, L. D.; Borodin, O.; Huang, W. N.; Xu, M. Q.; Li, X. P.; Li, W. S. Quantum Chemistry Study of the Oxidation-Induced Stability and Decomposition of Propylene Carbonate-Containing Complexes. *Phys. Chem. Chem. Phys.* **2014**, *16*, 6560–6567.
- (35) Lapidus, S. H.; Rajput, N. N.; Qu, X.; Chapman, K. W.; Persson, K. A.; Chupas, P. J. Solvation Structure and Energetics of Electrolytes for Multivalent Energy Storage. *Phys. Chem. Chem. Phys.* **2014**, *16*, 21941–21945.
- (36) Lau, K. C.; Lu, J.; Low, J.; Peng, D.; Wu, H.; Albishri, H. M.; Abd Al-Hady, D.; Curtiss, L. A.; Amine, K. Investigation of the Decomposition Mechanism of Lithium Bis(oxalate)borate (Libob) Salt in the Electrolyte of an Aprotic Li–O<sub>2</sub> Battery. *Energy Technol.* **2014**, *2*, 348–354.