Enhancing electrochemical intermediate solvation through electrolyte anion selection to increase nonaqueous Li–O₂ battery capacity

Colin M. Burke, Vikram Pande, Abhishek Khetan, Venkatasubramanian Viswanathan, and Bryan D. McCloskey

Among the “beyond Li-ion” battery chemistries, nonaqueous Li–O₂ batteries have the highest theoretical specific energy and, as a result, have attracted significant research attention over the past decade. A critical scientific challenge facing nonaqueous Li–O₂ batteries is the electronically insulating nature of the primary discharge product, lithium peroxide, which passivates the battery cathode as it is formed, leading to low ultimate cell capacities. Recently, strategies to enhance solubility to circumvent this issue have been reported, but rely upon electrolyte formulations that further decrease the overall electrochemical stability of the system, thereby deleteriously affecting battery rechargability. In this study, we report that a significant enhancement (greater than fourfold) in Li–O₂ cell capacity is possible by appropriately selecting the salt anion in the electrolyte solution. Using "Li NMR and modeling, we confirm that this improvement is a result of enhanced Li⁺ stability in solution, which, in turn, induces solubility of the intermediate to Li₂O₂ formation. Using this strategy, the challenging task of identifying an electrolyte solvent that possesses the anticorrelated properties of high intermediate solubility and solvent stability is alleviated, potentially providing a pathway to develop an electrolyte that affords both high capacity and rechargability. We believe the model and strategy presented here will be generally useful to enhance Coulombic efficiency in many electrochemical systems (e.g., Li–S batteries) where improving intermediate stability in solution could induce desired mechanisms of product formation.

The lithium–oxygen (Li–O₂) battery has garnered significant research interest in the past 10 y due to its high theoretical specific energy compared with current state-of-the-art lithium-ion (Li-ion) batteries (1, 2). Consisting of a lithium anode and an oxygen cathode, the nonaqueous Li–O₂ battery operates via the electrochemical formation and decomposition of lithium peroxide (Li₂O₂). The ideal overall reversible cell reaction is therefore

$$2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2 \ (2\text{e}^- \ \text{process}) \ U = 2.96 \ \text{V}. \ \ [1]$$

One challenge preventing the realization of a modest fraction of the Li–O₂ battery’s high theoretical specific energy is that the discharge product, Li₂O₂, which is generally insoluble in aprotic organic electrolytes, is an insulator (3–5). As Li₂O₂ is conformally deposited on the cathode’s carbon support during discharge, it electronically passivates the cathode, resulting in practical capacities much smaller than theoretically attainable (6). Recently, two reports described the engineering of electrolytes to circumvent this passivation and improve Li–O₂ battery discharge capacity. Aetukuri et al. suggested that adding ppm quantities of water to a 1,2-dimethoxyethane (DME)-based electrolyte increases the solubility of intermediates during Li₂O₂ formation (7). This increased solubility allows a reduced oxygen species shuttling mechanism that promotes deposition of Li₂O₂ aggregated toroid structures. The diffusion of the intermediates away from the electrode surface allows the surface to remain electronically accessible to Li⁺ and O₂, promoting more Li₂O₂ growth, thereby leading to an increase in cell capacity. Of note, this increase in cell capacity with water content in the electrolyte is also consistent with reports by Gasteiger and coworkers (8, 9). Aetukuri et al. reason that this increase could be attributed to water’s significantly higher Gutmann Acceptor Number (AN) than DME, as the AN is a measure of a solvent’s Lewis acidity, and thus quantifies its ability to efficiently solubilize negatively charged species, such as the potential discharge product intermediate, superoxide (O₂⁻) (10). In a related analysis, Johnson et al. showed that an electrolyte solvent with a higher Gutmann Donor Number (DN), a measure of Lewis basicity (11), is more likely to induce toroid formation due to increased Li⁺ stability in solution, inducing solubility of O₂⁻ (12). Johnson et al. further confirmed the presence of O₂⁻ ions in Li⁺-bearing high-DN electrolytes using surface-enhanced Raman spectroscopy (12).

Whereas water and certain organic solvents increase cell capacity via this solution mechanism, there is evidence that both decrease electrolyte stability. Water impurities in Li-ion electrolytes are known to enhance parasitic electrochemical side reactions, and Aetukuri et al. and Cho et al. showed that adding ppm quantities of water in Li–O₂ batteries leads to a decrease in electrolyte stability and increase in irreversible reactions with the

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<td>The Li–air battery has attracted significant interest as a potential high-energy alternative to Li-ion batteries. However, the battery discharge product, lithium peroxide, is both electronically insulating and insoluble in nonaqueous electrolytes. It therefore passivates the battery cathode as it is uniformly deposited and disallows the battery to achieve even a modest fraction of its potential electrochemical capacity. Our objective is to circumvent this challenge by enhancing the solubility of electrochemically formed intermediate species. We present a rational basis for electrolyte (i.e., solvent and salt) selection for nonaqueous Li–air batteries and demonstrate a selection criterion for an electrolyte salt that increases the stability of Li⁺ in solution, thereby triggering a solution-based process that allows significantly improved battery capacities.</td>
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Donor number | solubility | lithium nitrate | NMR | Li–air battery
lithium anode (7, 13). Furthermore, using quantitative measures of battery rechargeability, high-DN solvents, such as DMSO and N-methyl pyrrolidone, have been observed to be less stable than low-DN solvents, such as acetonitrile and DME (14). Recently, Khetan et al. used a thermodynamic analysis to show that an organic solvent’s ability to induce the solution mechanism is anticorrelated with its stability toward nucleophilic attack (15). Thus, Li–O2 cells would benefit from an appropriately engineered electrolyte that both induces Li2O2 intermediate solubility and maintains or exceeds present electrolyte stability.

In this article, we describe the importance of the lithium salt anion in enhancing the solvation of electrochemically formed intermediate species during Li–O2 battery discharge, thereby enhancing discharge capacity. We present a study on two common Li–O2 battery salts, lithium bis(trifluoromethane) sulfonimide (LiTFSI) and lithium nitrate (LiNO3), dissolved in DME. These salts were selected because Schmeisser et al. found that TFSI$^−$ and NO3$^−$ anions provided different DN in ionic liquids with common cations (NO3$^−$-containing ILs having higher DN than TFSI$^−$-containing ILs). We also specifically selected NO3$^−$ because of its reported positive influence on Li–O2 battery rechargeability compared with the more commonly used TFSI$^−$ as the electrolyte anion, while not decreasing battery rechargeability, as measured using quantitative oxygen consumption and evolution. To theoretically quantify this enhancement, we propose an Ising model description of the solvation shell of Li$^+$ . This analysis indicates that the origin of this enhanced solution process is due to the formation of ion pairs (Li$^{+}$-NO3$^−$) in a DME solvent. The theoretical analysis further predicts that ion-pair formation and the associated enhancement in capacity would not be observed when DMSO is used as a solvent, which was subsequently confirmed experimentally. We generalize this analysis to provide a rational basis for selection of electrolyte (solvent + salt) combinations for use in Li–O2 batteries. We believe these results will have profound implications not only for Li–O2 batteries, where a practical outcome of the solubility is an enhancement in battery capacity, but also for other electrochemical systems (e.g., lithium–sulfur batteries) in which intermediate solvation may induce desired mechanisms of product formation.

Results and Discussion

To characterize the effects of the electrolyte salt anion on discharge performance, Li–O2 cells were prepared with electrolytes of varying concentrations of LiNO3 and LiTFSI salts, totaling 1.0 M Li$^+$, in DME. Cell design and preparation are detailed in SI Appendix and follow those described previously (18).

Fig. 1A presents representative galvanostatic discharge profiles of these Li–O2 cells as a function of the LiNO3 salt concentration. Fig. 1A (Inset) shows the average cell capacity for each LiNO3 salt concentration. Cell capacity increases more than fourfold over the LiNO3 concentration range studied, clearly indicating the substantial effect of the Li$^+$ counterion on cell capacity.

Scanning electron microscopy (SEM) was performed on discharged cathodes to investigate changes in Li2O2 morphology, and hence changes in discharge mechanism, with increasing LiNO3 concentration. Fig. 2 presents SEM images of a pristine cathode (Fig. 2A) and images of cathodes from cells of identical electrolyte compositions as those studied in Fig. 1, but discharged at 45 μA/cm$^2$ (Fig. 2B–F). When comparing Fig. 2A–C, the pristine, 0 M LiNO3, and 0.01 M LiNO3 cathodes appear indistinguishable. This implies a conformal coating of discharge product on the 0 M LiNO3 and 0.01 M LiNO3 cathodes, and is consistent with previous reports for 1 M LiTFSI in DME (7, 19).

A conformal coating of discharge product is indicative of a predominant thin-film Li2O2 surface deposition mechanism. Originally outlined by Laoire et al., this mechanism is described by the following elementary steps (20, 21):

$$\textbf{Li}^+ + e^- + \text{O}_2 \rightleftharpoons \text{Li}_2\text{O}_2^* \quad [2]$$

$$\textbf{Li}^+ + e^- + \text{LiO}_2 \rightleftharpoons \text{Li}_2\text{O}_2^* \text{ and/or } 2\text{LiO}_2^* \rightleftharpoons \text{Li}_2\text{O}_2 + \text{O}_2 \quad [3a,b]$$

where "*" denotes a species adsorbed to the cathode/Li2O2 surface. Importantly, in the LiTFSI/DME electrolyte, Li2O2$^*$ is insoluble and therefore remains adsorbed to the electrode surface, where a second charge transfer step (reaction 3a) or a disproportionation reaction (reaction 3b) results in the conformal Li2O2 coating observed in Fig. 2B and C (2, 19–23).

As the LiNO3/LiTFSI ratio increases, the discharge morphology changes perceptibly. As seen in Fig. 2D, when using 0.1 M LiNO3, nodular morphologies appear on the cathode surface. Increasing the LiNO3 concentration to 0.5 M and 0.7 M finds these structures replaced with increasingly larger toroid structures, as seen in Fig. 2E and F, respectively.

![Fig. 1.](image-url)
As described previously, the toroid morphology observed in Fig. 2 D–F is indicative of a solution mechanism of Li₂O₂ growth proceeding through solubility of the LiO₂ intermediate (7, 12, 24). The dissolution of LiO₂* into lithium cations and the redox active superoxide anion, O₂*, follows the equilibrium reaction (7):

\[
\text{LiO}_2^* \leftrightarrow \text{Li}^+ + \text{O}_2^-(\text{sol}).
\]  

Solvated O₂* can then diffuse in solution to a growing Li₂O₂ toroid, where it can combine with Li⁺ to form adsorbed LiO₂* on the toroid surface. LiO₂* can subsequently undergo disproportionation according to Eq. 3b, leading to the formation of Li₂O₃ on the toroid surface (7). The observed toroid formation on discharged cathodes from cells using high LiNO₃:LiTFSI ratios supports the enhancement of this solution mechanism with increasing LiNO₃ concentration.

In further support of the solution mechanism, increasingly larger toroid structures were observed with decreasing current density in cells using 0.5 M LiNO₃ (0.5 M LiTFSI) (SI Appendix, Fig. S1). This observation is consistent with previous reports where Li₂O₂ toroid formation was observed at low currents in electrolytes that promoted the solution Li₂O₂ formation mechanism (7, 12, 24).

Of note, we find that Li₂O₂ yield, as measured using an established peroxide titration technique (18), is generally unaffected by the electrolyte compositions studied here (Fig. 1B), although a slightly higher Li₂O₂ yield may be observed at high LiNO₃ concentrations. Differential electrochemical mass spectrometry was also used, as described previously (18), to quantify the reversibility of the electrochemical reactions (SI Appendix, Fig. S2). The ratio (OER:ORR) of the amount of oxygen evolved during discharge (OER) to the amount of oxygen consumed during discharge (ORR), an important metric of reversibility, is statistically equal for a cell using 1 M LiTFSI and a cell using 0.5 M LiNO₃:0.5 M LiTFSI (OER:ORR ~0.82). Furthermore, only 18O₂ is evolved on charge after a discharge under 18O₂ of a cell using 0.5 M LiLO₂:0.5 M LiTFSI, confirming that NO₃⁻ does not participate in the cathode reaction other than to induce solubility of the intermediates. This result agrees with a similar experiment using pure LiTFSI-based electrolytes (19), implying that electroactive O₂ remains associated during both Li₂O₂ formation and oxidation.

With a change in anion clearly inducing a solution Li₂O₂ growth mechanism, it can be reasoned that the NO₃⁻ anion is affecting LiO₂ solubility via enhanced Li⁺ solvation. The electrolyte anion can affect the electrolyte’s overall donicity [quantified by the Gutmann DN, a measure of Lewis basicity (11)], in turn affecting the electrolyte’s ability to solubilize LiO₂* through enhanced solvation of Li⁺. We used ‘Li NMR to probe the electron donicity felt by Li⁺ ions in our LiNO₃:LiTFSI in DME electrolytes as a proxy measurement of the relative effect of the anion on electrolyte DN.

Using NMR as a proxy for DN is a well-known technique, with Erlich and Popov first proposing 23Na NMR as an effective measurement for a solvent’s DN (25). Erlich and Popov reasoned that a down-field 23Na shift resulted from stronger interaction between the solvation shell molecules and the cation, thereby decreasing the cation’s shielding. The environment of Li⁺ in LiNO₃:LiTFSI in DME electrolytes cannot be determined via 23Na NMR, as adding NaClO₄ to the electrolytes causes a white precipitate to crash out of solution [likely NaNO₃, as discovered by Linert et al. (28)]. Conversely, electrolytes comprising a high-DN solvent with a relatively low DN anion, like ClO₄⁻ (DN = 8.44 kcal/mol) in dimethyl sulfoxide (DN = 29.8 kcal/mol), do

![Fig. 2](https://example.com/fig2.png)

**Fig. 2.** (A) SEM image of pristine XG72 carbon cathode before discharge. (B–F) Discharged cathodes from cells using 1 M total Li⁺ concentration, with 0 M LiNO₃ (1 M LiTFSI), 0.01 M LiNO₃, 0.1 M LiNO₃, 0.5 M LiNO₃, and 0.7 M LiNO₃ respectively. Cells were discharged at 45 μA/cm² to 0.9 mAh/cm² or a 2-V cutoff voltage. All cells had at least 0.5 mAh/cm² capacity. (Scale bars, 1 μm.)
not exhibit a DN dependence on anion concentration. These trends agree with Linert et al., who found via solvatochromic dyes that the effective DN of an electrolyte depended on an interplay between the DN of the solvent, DN of the anion, and AN of the solvent (28). For example, if the solvent’s DN was larger than the anion’s DN, then the electrolyte comprising the two had a DN similar to its solvent’s DN.

If LiNO₃ has a higher DN than DME, then increasing the concentration of LiNO₃ will increase the number of NO₃⁻ ions interacting with any particular Li⁺ ion, which in turn will lead to an increase in the electrolyte’s DN. Thus, we reason that the presence of a concentration dependence on ⁷Li chemical shift, as seen in Fig. 1C, indicates NO₃⁻ ions serving an active role in the electrolyte’s donicity, and the increasingly down-field shift of ⁷Li with increasing LiNO₃ concentration represents increasing donicity.

In contrast, Fig. 3 shows that indeed LiNO₃:LiTFSI salts in the high-DN solvent dimethyl sulfoxide do not exhibit a substantial change in ⁷Li shift with increasing LiNO₃ concentration, and, as therefore expected, no statistically significant capacity increase is observed in DMSO-based electrolytes as the LiNO₃:LiTFSI ratio increases. To confirm the general correlation between enhanced Li⁺ solvation and Li-O₂ battery capacity, another high-DN anion, Br⁻, was studied. As expected, similar trends in ⁷Li NMR chemical shifts and Li-O₂ battery capacity are observed between 0.5M LiBr:0.5M LiTFSI and 0.5 M LiNO₃:0.5 M LiTFSI in DME and DMSO-based electrolytes (SI Appendix, Fig. S10).

We note, however, that extreme care must be taken when using NMR techniques to compare and quantify solvent DN’s, particularly between unlike solvent classes, such as protic and aprotic solvents, as was discussed by Gal and Laurence (29). For the current study, our interest is only in the relative changes of the Li⁺ chemical environment as a function of anion composition in a single aprotic solvent (both for DME and DMSO), such that ⁷Li NMR provides useful qualitative, if not quantitative, values for comparison.

To provide a quantitative basis for the role played by the electrolyte anion, we present a revised thermodynamic model for the solution electrochemical process. The solution-mediated electrochemical growth of Li₂O₂ is triggered by the dissolution reaction given in Eq. 4. The free-energy change involved in this dissolution reaction is given by

\[ \Delta G_{\text{sol}} = \Delta G_{\text{LI}^+} + G_{\text{O}_2^{\text{red}}} - G_{\text{LiO}_2}, \]  

where \( \Delta G_{\text{LI}^+} \) is the free energy of the Li⁺ ions in the electrolyte, \( G_{\text{O}_2^{\text{red}}} \) is the free energy of O₂⁻ ions in the electrolyte, and \( G_{\text{LiO}_2} \) is the free energy of the adsorbed LiO₂ on the Li₂O₂ surface during discharge.

To understand the role of the salt anion on the equilibrium of the dissolution reaction, we need to explore the stabilization of the solvated intermediates in the presence of the anion. The presence of the anion can influence the free energy of Li⁺ ions. To a first approximation, the free energy of the Li⁺ ions and thus the free energy of LiO₂ dissolution is largely dependent on the species that are present in the Li⁺ first solvation shell (30, 31). To be consistent with the experimental data presented in Figs. 1–3, we explicitly model an electrolyte that contains a mixture of LiNO₃ and LiTFSI so that the total Li⁺ concentration is maintained at 1 M. The concentration of O₂⁻ ions in the solution is expected to be much lower than the Li⁺ and salt anion concentrations (7). Thus, we do not expect O₂⁻ ions to play a significant role in the solvation of Li⁺. Hence, to a first approximation, the solvation shell of Li⁺ will comprise only solvent molecules and salt anions (NO₃⁻ and TFSI⁻).

The exact composition of the solvation shell will depend on the energetics of the interactions of the Li⁺ ion with the solvent and the anions. To determine the composition of the first solvation shell and in turn the free energy of stabilization, we develop a modified Ising model for the site occupancy in the solvation shell of Li⁺ (32). The Ising model formalism, originally developed to describe magnetism, provides a systematic basis for treating the energetics of interaction between Li⁺ and the solvent and salt anions (33).

In this model, we develop a site occupancy variable to describe each of the solvation shell sites of Li⁺. The Hamiltonian that governs the solvation shell of Li⁺ is given by

\[ H = h_1 \sum_{i=1}^{N} n_i h_2 \sum_{i=1}^{N} m_i + h_3 \sum_{i=1}^{N} l_i + J_{11} \sum_{i,j} n_i n_j + J_{22} \sum_{i,j} m_i m_j + J_{33} \sum_{i,j} l_i l_j + J_{12} \sum_{i,j} n_i m_j + J_{23} \sum_{i,j} m_i l_j + J_{31} \sum_{i,j} l_i n_j + J_{32} \sum_{i,j} m_i n_j + J_{31} \sum_{i,j} l_i n_j + J_{32} \sum_{i,j} m_i l_j, \]

where \( i = 1 \) to \( N \) represent sites in the solvation shell of a Li⁺ ion and \( (i,j) \) represents the nearest-neighbor pair in the solvation shell. The occupation variables “\( n \),” “\( m \),” and “\( l \)” represent the occupancy of a site by the solvent, the NO₃⁻ anions, and the TFSI⁻ anions, respectively. For any site “\( i \)” occupied by the solvent, \( n_i = 1, m_i = 0, \) and \( l_i = 0 \) and similarly for other cases. Thus, at any given site, \( n_i + m_i + l_i = 1 \), i.e., each site is occupied by either solvent or a salt anion. In our model, \( h_1 \) represents the interaction energy between a Li⁺ ion and a solvent, \( h_2 \) represents the interaction energy between a NO₃⁻ anion and Li⁺, and \( h_3 \) represents the interaction energy between a TFSI⁻ anion and Li⁺.

The coupling constant \( J_{11} \) represents the interaction between neighboring solvent molecules in the Li⁺ solvation shell. Likewise, \( J_{22} \) and \( J_{33} \) represent the interactions between neighboring NO₃⁻ and neighboring TFSI⁻ anions, respectively. The symmetry assumption is invoked, which yields \( J_{12} = J_{21}, J_{13} = J_{31}, J_{23} = J_{32} \). The cross-coupling terms \( J_{12}, J_{13}, \) and \( J_{23} \) represent interactions between neighboring NO₃⁻ and solvent molecules, neighboring TFSI⁻ and solvent molecules, and neighboring TFSI⁻ and NO₃⁻ anions, respectively.

The exact model is not easily analytically tractable; however, we can invoke the mean-field approximation, described in SI Appendix. The mean-field approximation is valid under the assumption that the Li⁺ ions are uniformly distributed in solution and each site in the solution shell experiences an averaged effect of other species present in the electrolyte. The coordination number \( z \) of the solvation shell is expected to be independent of species (anions or solvent) occupying the solvation shell. The mean-field approximation replaces the nearest-neighbor interaction \( \langle n_i n_j \rangle \) by the average interaction \( \langle n \rangle \langle n \rangle \), where assuming spatial invariance, the average occupation of species in the shell can be defined as \( \langle n \rangle = 1/N \sum_i n_i \).

The interaction term \( h_1 \) is dependent on the donating tendency of the solvent molecule to the Li⁺ ions in solution. The free energy of Li⁺ ions can be expressed in terms of the half-wave potential of Li/Li⁺ couple and it has been shown that the half-wave potential of Li/Li⁺ couple is a function of the DN of the solvent (34). Hence the Li⁺–solvent interaction energetics (\( h_1 \)) can be expressed as a function of the DN of the solvent. Similarly, we assume that the terms \( h_2 \) and \( h_3 \) can be expressed as a function of the DN. There is an additional contribution to \( h_2 \) and \( h_3 \) that depends on the concentration of the NO₃⁻ and TFSI⁻ anions. This arises due to a change in the reference chemical potential of the NO₃⁻ and TFSI⁻ anions to account for the configurational entropy associated with that concentration. The coupling constant \( J_{11} \) is a weak attractive van der Waals interaction between solvent molecules, and is estimated to be an order of magnitude less than the donor interactions \( h_1, h_2, \) and \( h_3 \). The constants \( J_{22}, J_{33}, \) and \( J_{32} \) are representative of the repulsive interaction between neighboring anions in the Li⁺ solvation shell and are of the same order of magnitude as \( h_1, h_2 \). The coupling constants \( J_{12}, J_{13} \) for the
interaction between a solvent molecule and the respective anion can be described by the electron accepting tendency of the solvent and can therefore be determined by the solvent’s AN. As we are accounting for the coupling constants in terms of the overall donating and accepting tendencies of the solvent, the overall coordination number is already included in the model, i.e., \( z = 2 \).

Solving the developed model requires the DN of NO\(_3^−\) and TFSI\(^−\) anions to determine the occupation numbers. We use the values determined by Schmeisser et al. via \(^{23}\)Na NMR for ionic liquids with common cations, as discussed earlier (35). Although the quantitative nature of these measurements is still under debate (29), we believe the trends can be well captured from these values. Schmeisser et al. find that TFSI\(^−\) has a very low DN of 11.2 kcal/mol whereas NO\(_3^−\) has a DN of 22.2 kcal/mol (35). Using these values, we can determine the occupation shell of Li\(^+\) as a function of the NO\(_3^−\) anion concentration. As is shown in Fig. 4A, the solvation shell is completely dominated by DME and NO\(_3^−\) anion. As the NO\(_3^−\) anion has a higher DN than DME (DN = 20 kcal/mol), we observe a strong concentration dependence on the NO\(_3^−\) anion. This suggests that increasing NO\(_3^−\) anion concentration will lead to a displacement of low-DN solvents like DME in the Li\(^+\) solvation shell. As we increase the concentration of NO\(_3^−\) in DME, a higher number of NO\(_3^−\) ions occupy the Li\(^+\) solvation shell until the electrostatic repulsion of NO\(_3^−\) ions becomes dominant, leading to a saturation in the number of anions that occupy the first solvation shell.

The corresponding change in the free energy of Li\(^+\) as a function of NO\(_3^−\) concentration in DME is shown in Fig. 4B. The free energy of Li\(^+\) as evaluated from the model is well-correlated with the experimentally measured NMR \(^{7}\)Li chemical shift, as shown in SI Appendix, Fig. S8. This proves that the thermodynamic analysis developed in this work accurately captures the effect of the change in anion concentration in the Li\(^+\) solvation shell. Due to a higher DN of the NO\(_3^−\) anion, there is an overall increase in Li\(^+\) solvation energy; this is accompanied by an enhancement of the rate of the solution process given by \( r_s \sim \exp(\Delta G_{sol}/kT) \). This shows that at 0.5 M LiNO\(_3\):LiTFSI, we would expect an approximately fourfold enhancement in the rate of the solution process. The rate enhancement, \( r_s \sim \exp(\Delta G_{sol}/kT) \), as calculated from the model, shows a positive correlation with the observed capacity enhancement as shown in SI Appendix, Fig. S9.

The model developed can be generalized to map out the entire electrolyte design space. A contour map of the Li\(^+\) stabilization as a function of varying DN of solvent and anion is shown in Fig. 5 and the corresponding contour map of the occupation of the solvent in the solvation shell shown in SI Appendix, Fig. S5. This generalization analysis assumes a constant AN chosen to be the average of DME and DMSO and a 50:50 salt blend of LiTFSI and a varying electrolyte anion. The contour map shows that there is an enhancement when using low-DN solvent, such as DME, and high-DN salt anion, such as NO\(_3^−\) ions. However, an interesting prediction of this generalized analysis is that there is no benefit in using high-DN salt anions in a high-DN solvent such as DMSO (a more detailed analysis of the DMSO case is reported in SI Appendix). This suggests that there is no ion-pair formation in a DMSO solvent and hence, almost no associated change in discharge capacity. This is in excellent agreement with the experiments presented in Fig. 3. To emphasize this agreement, our model predicts that in DMSO, the NO\(_3^−\) anion does not enter the Li\(^+\) solvation shell, and hence there is no change in the Li\(^+\) solvation free energy (SI Appendix, Figs. S3 and S4).

The contour map suggests that using a higher DN anion than NO\(_3^−\) can lead to even greater enhancement of Li\(^+\) solvation, and therefore a study on bromide’s (Br\(^−\)) effect on Li\(^+\) solvation and Li–O\(_2\) capacity was performed (28). Our model predicts that for an electrolyte consisting of DME as a solvent and LiTFSI and LiBr as the salt blend, there is a greater stabilization of Li\(^+\) compared with the LiTFSI and LiNO\(_3^−\) salt blend of similar concentration, as shown in SI Appendix, Fig. S11. The results from the model are consistent with \(^{7}\)Li NMR chemical shifts (SI Appendix, Fig. S104 presents the LiBr \(^{7}\)Li NMR results). We also find a capacity enhancement with the 0.5 M LiBr:0.5 M LiTFSI electrolyte over the 1 M LiTFSI electrolyte (SI Appendix, Fig. S108). Of note, the capacity enhancement obtained in our LiBr and LiNO\(_3\) studies are statistically similar, although using Li\(^+\)
solvent arguments alone, the LiBr-containing cells would be expected to have higher capacities at similar electrolyte concentrations. However, in addition to the free energy of dissolution, $\Delta G_{\text{solv}}$, other factors, such as $O_2$ solubility, and the diffusion coefficients of $O_2^-$ and $Li^+$, govern the overall rate for the solution process and, thereby, the overall capacity enhancement due to the solution process. These other factors likely contribute to suppress the capacity gains expected solely from enhanced solvation when employing the LiBr electrolyte compared to the LiNO$_3$ electrolyte.

The contour map presented in Fig. 5 provides a rational basis for the selection of the total electrolyte, i.e., solvent and anion. An important conclusion of the contour map is that there is minimal capacity enhancement by changing the electrolyte anion in high-DN solvents. We have demonstrated this conclusion using two examples of high-DN anions (Br$^-$, NO$_3^-$) showing almost no enhancement in solvation in a high-DN solvent such as DMSO as shown in the $SI$ Appendix, Figs. S3 and S12. However, there is tre- mendous scope in tuning the electrolyte anion in low-DN solvents. We have demonstrated this conclusion using two important conclusions of the contour map is that there is minimal capacity enhancement by changing the electrolyte anion in high-DN solvents. We have demonstrated this conclusion using two examples of high-DN anions (Br$^-$, NO$_3^-$) showing almost no enhancement in solvation in a high-DN solvent such as DMSO as shown in the $SI$ Appendix, Figs. S3 and S12. However, there is tremendous scope in tuning the electrolyte anion in low-DN solvents to obtain high discharge capacities. Given that it should be sim- pler to identify anions stable to the Li-O$_2$ cathode electrochemistry than high-DN solvents (36, 37), anion selection in combination with low-DN solvents potentially provides a route to avoid the unfavorable capacity/stability trade-off observed in high-DN sol- vents, such as DMSO (14, 15, 38, 39).

Conclusions

In conclusion, we have demonstrated Li$^+$ counterion influence on promoting the solubility of electrochemical intermediates during a Li-O$_2$ battery discharge without further compromising electrolyte stability. Specifically, LiO$_2$ batteries using electrolytes of LiNO$_3$ and LiTFSI in DME displayed increased capacity and increased toroid formation with increasing LiNO$_3$ concentration. We ascribe intermediate solubility to enhanced stability of Li$^+$ in solution by anions with higher effective donor numbers than that of the solvent, thereby also inducing increased stability of the electrochemically formed anion, $O_2^-$, in solution. This strategy can potentially be combined with current efforts to identify novel, stable electrolytes, including those in which organic molecules are entirely removed from the electrolyte [a fascinating idea being explored by researchers at Luxix Power, Inc. (40)], to develop a practical electrolyte that could enable high-energy, long-life Li-air batteries. Further, we have de- veloped a generalized model that predicts Li$^+$ solvation shell occu- pation and the resulting stability of Li$^+$ in electrolytic solutions. We envision this strategy for intermediate stabilization to be generally applicable to numerous nonaqueous systems in which stabilization of desired intermediates may lead to improved electrochemical efficiency. For example, in Li-S batteries, polysulfide intermediate speciation could potentially be controlled by simply tuning the Li$^+$ salt anion, perhaps providing a route for increased sulfur utilization.

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Enhancing electrochemical intermediate solvation through electrolyte anion selection to increase nonaqueous Li-O₂ battery capacity

Supplemental Information

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Materials. Lithium nitrate (BioUltra) and lithium bromide (ReagentPlus) were purchased from Sigma Aldrich and were dried under vacuum in a heated glove box antechamber at 150°C for 24 hours before use. Lithium bis(trifluoromethane) sulfonimide (LiTFSI), 1,2-dimethoxyethane, and dimethyl sulfoxide were purchased from BASF and used as received. Whatman QM-A glass fiber filters were purchased from VWR. PTFE (60 wt% dispersion in H₂O) was purchased from Sigma Aldrich. Vulcan XC72 was purchased from Fuel Cell Store and was filtered through a 60 mesh screen. T316 stainless steel 120 mesh, with wire diameter 0.0026”, was purchased from TWP Inc. Research-grade oxygen and argon were purchased from Praxair. 99%¹⁸O₂ was purchased from Sigma Aldrich. All electrolyte, cell, and NMR sample preparation was completed in an argon-filled glove box with <0.1ppm O₂ and <0.1ppm H₂O.

In preparing the electrolytes, we found the solubility limit of LiNO₃ in DME is approximately 1M. The capacity variability of the 0.7M LiNO₃ cell in Figure 1 is likely due to concentration polarization effects in the electrolyte, as 0.7M begins to approach the solubility limit of LiNO₃ in DME, such that LiNO₃ precipitation at the anode may occur. The LiNO₃ concentration range (<0.7M) we report was limited by this effect.

Cathode preparation. Cathodes were prepared via a similar method to that described previously.(1) A mixture of 3:1 w:w ratio of Vulcan XC72 to PTFE binder in IPA and water (4:1 water:IPA; and 15mL total for 400mg C) was sonicated for 30
seconds and homogenized for 6 minutes. A Badger model 250 air-sprayer was used to spray the slurry onto a piece of stainless steel mesh roughly 4.5” square, which had been rinsed with IPA and acetone and dried at 150°C for ten minutes prior to use. After letting the spray-coated mesh air-dry, 12mm diameter cathodes were punched out, rinsed with IPA and acetone, and dried at 150°C under vacuum for at least 12 hours. The cathodes were then transferred, while hot, into the glove box, and stored on a hot plate at 200°C.

**Carbon loading.** Cell capacities depend on carbon loading. To keep carbon loading consistent, the cathodes used for any particular data set, such as the capacity measurements displayed in Figure 1 or the cathode morphology images in Figure 2, were all from the same batch of spray-coated cathodes. As a control, the capacity measurements presented in Figure 1 were repeated with a second batch of cathodes. All capacities changed proportionally (a slight increase for all cases), with the capacity of the cell using 0.5M LiNO₃:0.5M LiTFSI in DME maintaining just over a three-fold increase from the capacity of the cell employing 1M LiTFSI in DME. Cathodes contained on average 1.5-2.0 mg/cm² carbon.

**Cell preparation.** The Li-O₂ cells used throughout this paper followed the same Swagelok design as described previously.(2) All cells employed a 7/16” diameter lithium foil, a 1/2” diameter Whatman QM-A glass fiber separator, a 12mm diameter cathode of Vulcan XC72 carbon on stainless steel mesh, and a 1mm thick, 1/2” diameter stainless steel ring. The QM-A separators, like the cathodes, were rinsed with IPA and acetone and dried under vacuum at 150°C under vacuum for at least 12 hours before being transferred to the glove box and stored on a hot plate at 200°C. Each battery contained 80 μL of electrolyte.

**Scanning electron microscopy.** Discharged cathodes were characterized via scanning electron microscopy immediately after discharge. After replacing discharged cells’ headspaces with argon, the cells were transferred into the glove box, and the cathodes were removed. The cathodes were each rinsed with two 1 mL aliquots of DME and were subsequently dried under vacuum for at least five minutes in the glove box antechamber. The cathodes were then sealed in septa vials,
removed from the glove box, and taken to the SEM. Immediately before imaging, the cathodes were removed from the argon-filled septa vials, placed on carbon tape on the SEM holder, and inserted into the SEM. From discharge completion to SEM insertion was typically one hour. From removing the cathodes from the septa vials to SEM insertion was typically less than 30 seconds. SEM was performed on a JEOL JSM-7500f.

**Titration.** The Li_2O_2 titration protocol used here followed that described previously. (1) After replacing the discharged cells’ headspaces with argon, the cells were transferred into the glove box, and the cathodes were removed. Each cathode was placed in a 20mL septa vial. The cathodes were placed under vacuum for at least three minutes to evaporate any residual solvent before the vial caps were tightly sealed and the vials were removed from the glove box. 2mL of ultrapure water (18.2MΩ cm, Millipore) was injected through the septa to react the Li_2O_2 into LiOH and H_2O_2. LiOH was quantified by using phenolphthalein as an indicator and HCl as a titrant. H_2O_2 was quantified via an iodometric titration employing potassium iodide, sulfuric acid, and a molybdate catalyst solution to create I_2 and sodium thiosulfate as a titrant for the I_2. Starch was used to sharpen the end point, which turned from dark blue to clear at the end of the titration. The Li_2O_2 percent yield is defined as the amount of Li_2O_2 formed during discharge, as quantified via an iodometric titration, to the amount of Li_2O_2 expected from coulometry, assuming an ideal 2e^-/Li_2O_2 process. (1) Of note, no titratable I_2 was observed from titrations on the separator alone, confirming the following two points: a) no NO_2^- that may have formed at the Li metal anode is present in the separator, and therefore NO_2^- does not result in a falsely higher Li_2O_2 yield as measured using the iodometric titration (NO_2^- also oxidizes I^-); b) Li_2O_2 only forms on the cathode and not the separator.

**Nuclear Magnetic Resonance Spectroscopy.** ⁷Li and ²³Na nuclear magnetic resonance spectroscopy measurements were completed on a Bruker AM-400 magnet with a 5mm Z-gradient broad brand probe. Reference samples, those employing a chloride salt in D_2O, were prepared outside the glove box and were flame-sealed in melting point capillaries. Electrolyte samples were prepared inside the glove box and were placed, along with a reference capillary, in a Wilmad screw-
cap NMR tube. All reference samples were 3M of the chloride salt in D₂O. For the ²³Na NMR, 0.2M NaClO₄ was added. These molarities were taken from Schmeisser et al.(3). ²³Na NMR spectra are not reported here because of the poor solubility of NaNO₃ in DME. NMR spectra of only the reference and only the sample were taken to verify the identity of each peak. A representative ⁷Li NMR spectrum of a 0.5M LiTFSI:0.5M LiNO₃ in DME electrolyte is shown in Figure S7.

**Water controls.** With the solubility mechanism confirmed, it was important to check that the increased solubility was indeed due to DN effects of NO₃⁻ and not another experimental artifact, in particular water contamination. As a first control, the key experiments were repeated with new electrolyte solutions that used lithium nitrate powder that had been dried a second time under vacuum in a heated glove box antechamber at 150°C for 24 hours. All repeated experiments gave consistent results with their original counterparts. As a second control, water levels in the electrolytes were measured via Karl Fischer titration. All electrolytes had less than 70ppm water, although the 1M LiTFSI (0M LiNO₃) and LiBr-containing electrolytes had <10ppm water content. Therefore, a battery employing an electrolyte of 1M LiTFSI in DME with 70ppm of water was discharged at 450 μA/cm² to 2V, analogous to the batteries in Figure 1. As observed in Figure S13, this battery saw an increase in capacity of 40% compared to a battery with 1M LiTFSI in DME, much smaller than the four-fold increase displayed in Figure 1 from the cell employing the 0.3M LiTFSI:0.7M LiNO₃ electrolyte.

**Ising Model for Li⁺ solvation shell.** The Ising model is a mathematical method of using discrete variables, usually called spin, on a graph or lattice to represent interactions in a system. In its most general form, the model allows for the identification of phase transitions in systems exhibiting magnetism, specific adsorption, etc. Although the model is exactly solvable only up to 2 dimensions, problems in higher dimensions can be addressed by modifying the model using concepts from mean field theory.

In order to find the composition and solvation energetics in the first solvation shell of Li⁺ ions, we apply the Ising model within the mean-field approximation. We assume the first solvation shell to be comprised of either the
solvent molecules or the salt anions, which interact with the Li\(^+\) ion and also with each other due to their electron donating/accepting tendency. Owing to their extremely low concentration in the solution phase, we neglect the effect of O\(_2^-\) anions in the Li\(^+\) solvation shell. Additionally, O\(_2^-\) anions have an incomplete shell configuration and are not known to be keen donors of electrons.

The solvation shell of an ion is an interacting system i.e. interactions between different molecules in the solvation shell affects their occupancy in the solvation shell. A solvation shell can be considered as a spherical lattice because it is spatially invariant with respect to Li\(^+\). The Hamiltonian, which describes the total energy of interactions involved in the solvation shell, is constructed by summing over all the interaction energies and the energies associated with a particular species occupying a site in the solvation shell. To describe the occupation of different species in the solvation shell at a given site \(i\), we use the occupation (spin) variables given as species \(\sigma_i = \{l, m, n\}\), for each kind of species. The occupation variables ‘\(n\)’, ‘\(m\)’ and ‘\(l\)’ represent the occupancy of a site by the solvent, the NO\(_3^-\) anions and the TFSI\(^-\) anions respectively. For any site ‘\(i\)’ occupied by the solvent, the occupation variables will have the value \(n_i = 1\), \(m_i = 0\) and \(l_i = 0\) and so on. Thus at any given site, we have \(n_i + m_i + l_i = 1\).

The key energetic contributions for each of the species are dependent on the kind interaction they have with the Li\(^+\) cation, with other molecules in the solvation shell and the entropy loss associated with the species being configurationally pinned in the solvation shell as compared to its mobile state in the bulk. We limit the expansion of the Ising model to nearest neighbor interactions in the imagined spherical lattice that comprises the first solvation shell because only these interactions have a dominant contribution to the total energy. The energetic interactions in the solvation shell of Li\(^+\) can thus be described by a model Hamiltonian, \(H\), given by:

\[
H = h_1\sum_{i=1}^{N} n_i + h_2\sum_{i=1}^{N} m_i + h_3\sum_{i=1}^{N} l_i + J_{11}\sum_{\langle i,j \rangle} n_i n_j + J_{22}\sum_{\langle i,j \rangle} m_i m_j + J_{33}\sum_{\langle i,j \rangle} l_i l_j + J_{12}\sum_{\langle i,j \rangle} n_i m_j + J_{21}\sum_{\langle i,j \rangle} m_i n_j + J_{13}\sum_{\langle i,j \rangle} n_i l_j + J_{31}\sum_{\langle i,j \rangle} l_i n_j + J_{23}\sum_{\langle i,j \rangle} m_i l_j + J_{32}\sum_{\langle i,j \rangle} l_i m_j
\]  

(S1)
In our model, \( h_1 \) represents the interaction energy between a Li\(^+\) ion and a solvent, \( h_2 \) represents the interaction energy between a NO\(^-\) anion and Li\(^+\) and \( h_3 \) represents the interaction energy between a TFSI\(^-\) anion and Li\(^+\). The coupling constant \( J_{11} \) represents the interaction between neighboring solvent molecules in the Li\(^+\) solvation shell. Likewise \( J_{22} \) and \( J_{33} \) represent the interaction between neighboring NO\(^-\) and neighbouring TFSI\(^-\) anions respectively. Owing to symmetry, \( J_{12} = J_{21} \), \( J_{13} = J_{31} \), \( J_{23} = J_{32} \). The cross-coupling terms, \( J_{12} \), \( J_{13} \) and \( J_{23} \), represent interactions between neighboring NO\(^-\) and solvent molecules, neighboring TFSI\(^-\) and solvent molecules and neighboring TFSI\(^-\) and NO\(^-\) anions, respectively.

The Ising model developed here is modified within the framework of a mean field approximation in order to make it solvable, and thus determine the composition of the solvation shell and also the free energy of solvation of Li\(^+\) cation. In the mean field approximation the nearest neighbor interaction terms of the kind \( \{\sigma_i\sigma_j\} \) between two species at sites \( i \) and \( j \) can be replaced by the average interaction \( \{\sigma_i<\sigma>\} \) where \( <\sigma> \) stands for the average occupation for the species in the shell and is defined as \( <\sigma> = \frac{1}{N} \sum_{i=1}^{N} \sigma_i \). It is important to note that this quantity is spatially invariant, \( <\sigma> = \langle \sigma_i \rangle \) which implies \( J_{ij} \sum_{(i,j)} \sigma_i \sigma_j \approx J_{ij} z <\sigma> \sum_{i} \sigma_{i} \), where \( z \) is the coordination number. For the small sized Li\(^+\) cation, we assume that the first solvation shell has \( N = 4 \) sites and hence the coordination number \( z = N/2 = 2 \) (to avoid double counting). We assume that \( z \) is independent of the occupying species in the solvation shell.

Hence, the Hamiltonian, \( H \), under the mean-field approximation is then given by:

\[
H = h_1 \sum_{i=1}^{N} n_i + h_2 \sum_{i=1}^{N} m_i + h_3 \sum_{i=1}^{N} l_i + J_{11} z <n> \sum_{i=1}^{N} n_i + J_{22} z <m> \sum_{i=1}^{N} m_i + J_{33} z <l> \sum_{i=1}^{N} l_i + J_{12} \frac{z}{2} <m> \sum_{i=1}^{N} n_i + J_{21} \frac{z}{2} <n> \sum_{i=1}^{N} m_i + J_{13} \frac{z}{2} <l> \sum_{i=1}^{N} l_i \sum_{i=1}^{N} \sigma_i + J_{31} \frac{z}{2} <n> \sum_{i=1}^{N} l_i \sum_{i=1}^{N} \sigma_i + J_{23} \frac{z}{2} <l> \sum_{i=1}^{N} m_i + J_{32} \frac{z}{2} <m> \sum_{i=1}^{N} l_i \sum_{i=1}^{N} \sigma_i \quad \text{(S2)}
\]
The average occupation for a given species at any site in the solvation sphere can be found by performing an average on each occupation variable using the mean field site energy in the Boltzmann weights as its probabilities, given by:

\[
\langle n \rangle = \frac{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} n \exp \left( \frac{-H}{kT} \right)}{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} \exp \left( \frac{-H}{kT} \right)} \quad (S3. a)
\]

\[
\langle m \rangle = \frac{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} m \exp \left( \frac{-H}{kT} \right)}{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} \exp \left( \frac{-H}{kT} \right)} \quad (S3. b)
\]

\[
\langle l \rangle = \frac{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} l \exp \left( \frac{-H}{kT} \right)}{\sum_{n=0,1} \sum_{m=0,1} \sum_{l=0,1} \exp \left( \frac{-H}{kT} \right)} \quad (S3. c)
\]

On expanding these expressions, we get the average occupation of solvent and salt anions at a site in the Li⁺ solvation shell as given below:

\[
\langle n \rangle = \frac{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right)}{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right) + \exp \left( \frac{-h_2 - I_{22z}(n) - I_{21z}(m) - I_{23z}(0)}{kT} \right) + \exp \left( \frac{-h_3 - I_{33z}(n) - I_{31z}(m) - I_{32z}(0)}{kT} \right)} \quad (S4. a)
\]

\[
\langle m \rangle = \frac{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right)}{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right) + \exp \left( \frac{-h_2 - I_{22z}(n) - I_{21z}(m) - I_{23z}(0)}{kT} \right) + \exp \left( \frac{-h_3 - I_{33z}(n) - I_{31z}(m) - I_{32z}(0)}{kT} \right)} \quad (S4. b)
\]

\[
\langle l \rangle = \frac{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right)}{\exp \left( \frac{-h_1 - I_{11z}(n) - I_{12z}(m) - I_{13z}(0)}{kT} \right) + \exp \left( \frac{-h_2 - I_{22z}(n) - I_{21z}(m) - I_{23z}(0)}{kT} \right) + \exp \left( \frac{-h_3 - I_{33z}(n) - I_{31z}(m) - I_{32z}(0)}{kT} \right)} \quad (S4. c)
\]

Finally, to obtain the values for average occupation, we need to assign the appropriate mathematical functions for all of the energetic interaction terms. The interaction term \(h_1\) is dependent on the donating tendency of the solvent molecule.
to the Li\(^+\) ions in solution. This can be attributed to the free energy of Li\(^+\) ions in a particular solvent. The free energy of Li\(^+\) ions in solvent HA can be determined from the equilibrium between solvated Li\(^+\) ions and metallic Li in a solvent HA, given by

$$\text{Li}_\text{(s)} \rightleftharpoons \text{Li}^+\text{HA} + e^- \quad (S5)$$

The free energy of Li\(^+\) ions, \(G_{\text{Li}^+/\text{HA}}\), can thus be expressed in terms of the half wave potential of Li/Li\(^+\) couple in that solvent, \(U_{\text{Li/Li}^+}\), and the free energy of metallic lithium, \(G_{\text{Li}(s)}\), as:

$$G_{\text{Li}^+/\text{HA}} = G_{\text{Li}(s)} + eU_{\text{Li/Li}^+} \quad (S6)$$

It has been shown experimentally that the half wave potential of Li/Li\(^+\) redox couple varies with the DN of the solvent.(4) As described in our previous work,(5) the free energy of the Li\(^+\) ion, and thus the interaction term \(h_1\) between solvent HA and Li\(^+\), can be given as \(h_1 = 0.001844 \times DN_{\text{HA}}^2 - 0.11314 \times DN_{\text{HA}}\). While similar experiments have not been performed for anions, we expect a similar relationship to hold for the interaction terms \(h_2\) and \(h_3\) between the Li\(^+\) cation and the anions, given that the DN of the anions are measured on a scale similar to that of the solvents. Thus, the interaction terms of the anions with Li\(^+\) (\(h_2\) and \(h_3\)) can be expressed as a function of their respective DNs. However, for the case of anions, there is a loss in entropy of the free ions as they join the solvation shell of Li\(^+\) ions. The contribution per ion is given as \(k_B T \ln(c_{\text{anion}})\), where \(c_{\text{anion}}\) is the concentration of the anion. The interactions \(h_2\) and \(h_3\) can thus be expressed as:

\[h_2 = 0.001844 \times DN_{\text{NO}_3}^2 - 0.11314 \times DN_{\text{NO}_3} - k_B T \ln c_{\text{NO}_3^-}, \quad h_3 = 0.001844 \times DN_{\text{FSI}^-}^2 - 0.11314 \times DN_{\text{FSI}^-} - k_B T \ln c_{\text{FSI}^-}\]

The solvent-anion interactions terms represented by \(\{J_{12}, J_{21}, J_{13}, J_{31}\}\) can be modelled in a similar way in terms of the AN of the solvent. We approximate the solvent-anion interactions by assuming that all anions behave similar to the \(O_2^-\) anion. The free energy of \(O_2^-\) ions, \(G_{O_2^-/HA}\), can be expressed in terms of the half-wave potential of \(O_2/O_2^-\) couple in that solvent, \(U_{O_2^-/O_2^-}\), and then free energy of gas phase oxygen, \(G_{O_2^-}(g)\), as:

$$G_{O_2^-/HA} = G_{O_2^-(g)} + eU_{O_2^-/O_2^-} \quad (S7)$$
It has been shown experimentally that the half wave potential $O_2/O_2^-$ varies as function of the AN of the solvent. As described in our previous work, the free energy of the anions can be expressed as a function of the solvent’s acceptor number to describe the solvent-anion interactions ($J_{12}$, $J_{21}$, $J_{13}$, $J_{31}$) in our model, and is given as: $J_{12} = -0.00024 AN_H^2 + 0.029 AN_{HA}$. The solvent-solvent interaction term ($J_{11}$) represents the weak van der Waal’s forces between the solvent molecules, and is chosen to be -0.01 eV, which lies within the range of values expected for the organic solvents used. The anion-anion coupling term stands for the strong repulsion interactions ($J_{22}$, $J_{23}$, $J_{32}$, $J_{33}$), and we choose this value to be an order of magnitude higher at 0.1 eV.
Figure S1. Scanning electron microscope images of carbon cathodes from cells employing 0.5M LiNO₃:0.5M LiTFSI in DME discharged to 1mAh capacity at currents of 10µA (a), 25µA (b), 50µA (c), and 100µA (d). Total electrode area was 1.1 cm² (12 mm diameter) and typical Vulcan XC72 carbon loading was 1.5-2.0 mg/cm².
Figures S2(a) and S2(d) present galvanostatic discharge-charge profiles for cells employing 1M LiTFSI and 0.5M LiNO₃:0.5M LiTFSI. Discharge, or ORR, overpotentials are similar between the two electrolytes. The cell employing LiNO₃ salt, however, exhibited a higher initial charge overpotential, which likely arises from an electronic transport limitation to toroid decomposition, although further studies are necessary to confirm this hypothesis. Figure S6 shows that for cells charged from the same discharge capacity, this initial charge overpotential does increase with increasing LiNO₃ concentration. The cause of this trend is currently under investigation.

Figures S2(b) and S2(e) show oxygen consumption as a function of capacity during discharge and charge for these two cells. On both discharge and charge, both cells show nearly identical e⁻/O₂, indicating nearly equivalent degrees of
reversibility. Figure S2(c) and S2(f) display gas evolution on charge from DEMS. Oxygen was clearly the dominant gas evolved for both cells, and in nearly identical quantities, with oxygen accounting for 92% of the gases evolved from the 0M LiNO$_3$ (1M LiTFSI) cell, and 93% of the gases from the 0.5M LiNO$_3$ (0.5M LiTFSI) cell. Small quantities of carbon dioxide and hydrogen were evolved from each cell toward the end of charging, with the 0M LiNO$_3$ evolving slightly more carbon dioxide, and the 0.5M LiNO$_3$ cell evolving slightly more hydrogen.
Figure S3. The change in occupation of the solvent DMSO (red line), TFSI$^-$ (green line) and NO$_3^-$ (blue line) in the Li$^+$ solvation shell as we change the concentration of the NO$_3^-$ anion. TFSI$^-$ and NO$_3^-$ both have lower DNs (11.2 and 22.2 kcal/mol) compared to the solvent DMSO (29.8 kcal/mol). Hence they cannot replace DMSO in the solvation shell. Hence even with increasing NO$_3^-$ concentration, DMSO completely occupies the solvation shell of Li$^+$. The occupation variables derived from the model for an electrolyte using DMSO as a solvent is shown in Figure S3. This shows that in DMSO, which is a high-DN solvent, NO$_3^-$ anion is unable to replace DMSO from the solvation shell. The accompanied change in free energy of Li$^+$ as a function of NO$_3^-$ anion concentration is shown in Figure S4. This shows that there should be almost no change in discharge capacity, consistent with the experiments reported here.
Figure S4. The Li$^+$ solvation energy (eV) as a function of the concentration of the NO$_3^-$ anion. The solvent used is DMSO and the salt is mixture with different concentrations of LiNO$_3$ and LiTFSI such that the Li$^+$ concentration is maintained at 1M. The Li$^+$ free energy of Li$^+$, calculated relative to DME and 1M LiTFSI, is independent of the NO$_3^-$ concentration when the solvent is DMSO. As a result, the solution rate enhancement is solely due to the high DN solvent DMSO.
Figure S5. Contour plot showing the occupation in Li⁺ solvation shell of the solvent for varying DN (in kcal/mol) of the solvent and salt anion. The salt anions shown are such that they have DN between 10 and 30 while the solvents shown have DN between 15-30. The electrolyte is considered to be a 50:50 mixture of LiTFSI and a salt consisting of Li⁺ and the salt anion in the corresponding solvent. The blue region represents high solvent occupation in the Li⁺ solvation shell while the red region shows high anion occupation.

Generalized Electrolyte Design

A generalized electrolyte design model is developed based on the Ising model discussed above. A contour map of the occupation of the solvent as a function of varying DN of solvent and anion is shown in Figure S5. This generalized analysis assumes a constant AN chosen to be the average of DME and DMSO and a 50:50 salt blend of LiTFSI and a varying electrolyte anion. The contour map shows that in a low-DN solvent, utilizing a high-DN anion leads to replacement of the solvent by the anion in the solvation shell. For a solvent DN of 20.2 kcal/mol, which corresponds to DME, an anion DN of ~23 kcal/mol leads to an equal amount of solvent and anion in the solvation shell. It is worth highlighting that the occupation is a stronger function of the DN of the solvent than that of the anion. For high-DN (>25 kcal/mol) solvents, the solvation shell is predominantly occupied by the solvent.
Figure S6. Representative discharge-charge profiles of cells of various LiNO₃ concentrations. All cells were discharged at 450 µA/cm² to 0.23 mAh/cm². A 1.0 M Li⁺ concentration was used for all cell electrolytes, while the LiTFSI:LiNO₃ ratio was varied. The LiNO₃ concentration for each cell is provided in the figure legend.
Figure S7. Representative $^7$Li NMR spectrum on 0.5M LiTFSI/0.5M LiNO$_3$ in DME. The chemical shift at 0 ppm corresponds to the Li shift of LiCl in D$_2$O, whereas the chemical shift at -0.40 ppm corresponds to the Li shift in the electrolyte.
Figure S8. Plot showing the linear correlation between the $^7$Li chemical shift (ppm) obtained from experiments and the free energy of solvation of Li$^+$ (eV) derived from the Ising model when DME is used as the solvent and NO$_3^-$ is used as the salt. The individual points in the plot correspond to different concentrations of LiNO$_3$. 
Figure S9. Plot showing the linear correlation between Capacity (mAh) obtained from experiments (from Figure 1a inset) and rate enhancement of the solution process $r_s \sim \exp\left(-\frac{\Delta G_{sol}}{kT}\right)$ as evaluated from the Ising model for various concentrations of LiNO$_3$ in DME. The plot shows that the capacity varies exponentially with the Gibbs free energy of solvation of Li$^+$ in the electrolyte.
Figure S10. (a) $^7$Li chemical shift of DMSO and DME-based electrolytes, versus a 3M LiCl in D$_2$O reference, as a function of LiBr concentration. A less negative chemical shift represents a shift downfield. Analogous to Figure 3a) in the main text, 0.5M Br$^-$ causes a noticeable downfield shift in the $^7$Li in DME, but not in DMSO. (b) Discharge profiles (45µA/cm$^2$, 1.5 atm O$_2$ atmosphere, 2V cutoff), as a function of LiBr concentration for both DMSO and DME-based electrolytes. A 1.0 M Li$^+$ concentration was used for all cell electrolytes, and the LiBr and LiTFSI concentration for each cell is provided in the legend. Analogous to NO$_3^-$ in Figure 3b) in the main text, 0.5M Br$^-$ provides over a three-fold increase in capacity in a DME-based electrolyte, but not in a DMSO-based electrolyte.
**Figure S11.** Plots showing the comparison between (a) occupations of all species in the solvation shell and (b) Li⁺ solvation energy as a function of the varied anion concentration (Br⁻, NO₃⁻) for the two cases: LiBr:LiTFSI and LiNO₃:LiTFSI in DME. The electrostatic repulsion terms between the anions (J₂₂, J₃₃, J₂₃, J₃₂) were chosen to be 4 times for the case with Br⁻ ion compared to the case with NO₃⁻ ion because Br⁻ is smaller and has a higher charge density.
**Figure S12.** Plots showing the **(a)** occupations of all species in the solvation shell and **(b)** the solvation energy of Li$^+$ as a function of the Br$^-$ anion concentration for LiBr:LiTFSI as the salt mixture in the solvent DMSO. The Li$^+$ free energy of Li$^+$, calculated relative to DME and 1M LiTFSI.
Figure S13. Galvanostatic discharge of a cell employing nominally anhydrous (<10 ppm H$_2$O, purple curve) and 70 ppm H$_2$O added (red curve) to 1 M LiTFSI in DME. A small water impurity in the LiNO$_3$ salt led to a linear increase in H$_2$O content with LiNO$_3$ concentration, with a maximum water content of 70 ppm H$_2$O in the 0.7N LiNO$_3$ cell. A 40% increase in capacity is observed when 70 ppm H$_2$O is added to a 1N LiTFSI cell. A greater than 400% increase was observed in the 0.7N LiNO$_3$ cell compared to the anhydrous 1N LiTFSI cell (Figure 1a in the main text).
References


