Experimental and Computational Analysis of the Solvent-Dependent $O_2$/Li$^+$-$O_2^{2-}$ Redox Couple: Standard Potentials, Coupling Strength,
Experimental and Computational Analysis of the Solvent-Dependent O$_2$/Li$^+$/O$_2^-$ Redox Couple: Standard Potentials, Coupling Strength, and Implications for Lithium–Oxygen Batteries

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Abstract: Understanding and controlling the kinetics of O$_2$ reduction in the presence of Li$^+$-containing aprotic solvents, to either Li$^+$/O$_2^-$ by one-electron reduction or Li$_2$O$_2$ by two-electron reduction, is instrumental to enhance the discharge voltage and capacity of aprotic Li-O$_2$ batteries. Standard potentials of O$_2$/Li$^+$/O$_2^-$ and O$_2$/O$_2^-$ were experimentally measured and computed using a mixed cluster-continuum model of ion solvation. Increasing combined solvation of Li$^+$ and O$_2$ was found to lower the coupling of Li$^+$ and O$_2^-$, and the difference between O$_2$/Li$^+$/O$_2^-$ and O$_2$/O$_2^-$ potentials. The solvation energy of Li$^+$ trended with donor number (DN), and varied greater than that of O$_2^-$ ions, which correlated with acceptor number (AN), explaining a previously reported correlation between Li$^-$-O$_2^-$ solubility and DN. These results highlight the importance of the interplay between ion–solvent and ion–ion interactions for manipulating the energetics of intermediate species produced in aprotic metal–oxygen batteries.

Activating O$_2$ is central to transforming energy storage by providing high gravimetric energy in devices such as rechargeable Li-O$_2$ and Na-O$_2$ batteries and reversible fuel cells. Non-aqueous Li$_2$O$_2$ batteries operate by reducing molecular O$_2$ in the presence of Li$^+$ to form Li$_2$O$_2$ at the positive electrode on discharge and releasing O$_2$ by oxidizing Li$_2$O$_2$ on charge. There are, however, significant challenges to practical implementation, including poor voltage efficiency, cycle life, and power capability. These are due primarily to the lack of fundamental understanding of O$_2$ reduction and evolution reaction kinetics and parasitic reactions in Li-O$_2$ batteries. The kinetics of O$_2$ reduction in the presence of strongly coordinating Li$^+$ are sluggish (Supporting Information, Figure S1), and its elementary steps are not well understood. O$_2$ reduction proceeds first by the formation of superoxide (O$_2^-$)[8,10] and then lithium superoxide (Li$^+$ + O$_2^-$ → Li$^+$-O$_2^-$)[11–14] Li$_2$O$_2$ is then formed by disproportionation of Li$^+$-O$_2^-$ (2Li$^+$-O$_2^-$ → Li$_2$O$_2$ + O$_2$) and/or a second electron reduction of Li$^+$-O$_2^-$ to solid Li$_2$O$_2$.[14,15] A number of studies have attributed the formation of large Li$_2$O$_2$ particles and high discharge capacities observed at low rates (< 10 μA cm$^{-2}$ in ethers[16,17]), to high availability of soluble Li$^+$-O$_2^-$.[18,19] Abraham and co-workers[15,14,18] have suggested that the stability of Li$^+$-O$_2^-$ increases with solvent donor number (DN), which is a measure of the solvation enthalpy of the Lewis acid SbCl$_5$ in a given solvent[19]. This concept is supported by recent work,[20] which reports that increasing solvent DN leads to increased Li$^+$-O$_2^-$ solubility and capacities upon discharge. Understanding how standard potentials of O$_2$/Li$^+$/O$_2^-$ change in different solvents and correlating the changes with that of O$_2$/O$_2^-$ and Li$^+$-O$_2^-$ solubility can help control the kinetics and discharge product characteristics of Li$_2$O$_2$ batteries. Unfortunately, the standard potentials and kinetics of the O$_2$/Li$^+$/O$_2^-$ couple in aprotic solvents are not known, in contrast to extensive study of O$_2$ reduction to O$_2^-$ in the presence of weakly coordinating tetrabutylammonium (TBA$^+$), which forms a stable TBA$^+$-O$_2^-$ complex[13,14] (TBA$^+$ + O$_2$ + e$^-$ → TBA$^+$-O$_2^-$ in Figure 1a). Greater O$_2^-$ ion solvation was expected to stabilize TBA$^+$-O$_2^-$ and increase the O$_2$/TBA$^+$-O$_2^-$ redox potential,[20] while the Li$^+$/Li potential decreases with increasing Li$^+$ solvation (Figure 1b). These trends are consistent with reports that the reversible potential of O$_2$/TBA$^+$-O$_2^-$ increases with solvent acceptor number (AN),[21] (a measure of solvent Lewis basicity), while that of Li$^+$/Li decreases with greater solvent DN.[21] It is not straightforward, however, to estimate the O$_2$/Li$^+$/O$_2^-$ potential and its solvent dependence from AN-dependent O$_2$/TBA$^+$-O$_2^-$ and DN-dependent Li$^+$/Li potentials. Not only are DN and AN different units, they also do not provide quantitative solvation energies for Li$^+$ and O$_2^-$ ions. Moreover, the O$_2$/Li$^+$-O$_2^-$ potential is greatly affected by the acid–base coupling between Li$^+$ and O$_2^-$, which is not directly reflected by O$_2$/TBA$^+$-O$_2^-$ and Li$^+/$
Li potentials, and cannot be inferred from hard–soft acid–base theory.[24]

Herein we report for the first time increasing standard O2\/-TBA\^-\^-O2\^- potentials with greater AN and decreasing Li^+\/-Li redox potentials with DN for a series of aprotic solvents, referenced to the solvent-independent decamethylferrocenium/decamethylferrocene (Me$_{10}$Fc/Me$_{10}$Fc$^+$) redox couple, which is stable against O$_2^-$, unlike ferrocenium (Fc$^+$) in the Fc\^-/Fc couple.[25] The measured redox potentials of O2/TBA^-\^-O2^- and Li^+\/-Li are in agreement with standard potentials computed using a mixed cluster-continuum model, which increase and decrease with greater computed solvation energy of O$_2^-$ and Li^+, respectively. Of significance, we show that greater Li^+ and O2^- solvation correlates with weakened coupling strength of Li^+\/-O2^- as evidenced by decreasing differences between measured O2/Li^+\/-O2^- and O2/TBA^-\^-O2^- standard potentials.

We first show that measured standard potentials of O2/TBA^-\^-O2^- and Li^+\/-Li scale with computed solvation energy of O$_2^-$ and Li^+. The use of higher AN solvents led to higher O2/TBA^-\^-O2^- redox potentials, as indicated in Figure 1b and previous work.[20,21]

Figure 2a shows cyclic voltammograms (CVs) obtained in O2-saturated dimethylsulfoxide (DMSO), 1,2-dimethoxyethane (DME), acetonitrile (MeCN), and dimethyl acetamide (DMA)-based electrolytes, which contained TBA$^+$ ethane (DME), acetonitrile (MeCN), and dimethyl acetamide (DMA) as solvent AN and O2/TBA^-\^-O2^- redox potentials measured using an Ag/Ag$^+$ reference electrode and Me$_{10}$Fc/Me$_{10}$Fc as a solvent independent redox reference.

Li^-/Li redox potentials were found to decrease with greater DN (Figure 2b) in accordance with the trend suggested in Figure 1b, and had values vs. Me$_{10}$Fc$^+$/Me$_{10}$Fc consistent with other ferrocene derivatives.[20] Li^+\/-Li potentials were obtained from Li plating/striping CV measurements vs. Ag$^+$/Ag, which were then referenced to the Me$_{10}$Fc$^+$/Me$_{10}$Fc potential using the scaling factor between Me$_{10}$Fc$^+$/Me$_{10}$Fc and Ag$^+$/Ag. The CVs in 0.1M LiClO$_4$ in DMSO, DMA, MeCN and DMA are shown in the Supporting Information, Figure S5a. The redox potential of Li^+\/-Li (Li^+\/-Li) was defined from the potential at zero current (that is, where neither Li plating nor removal occurs) during the anodic scan. Decreasing Li^-/Li redox potentials with greater DN obtained from this method is in accordance with the trend obtained using open-circuit voltage measurements (Supporting Information, Figure S5b and Table S1).

Figure 2b shows steady-state voltammograms (CVs) of O2/TBA^-\^-O2^- and Me$_{10}$Fc$^+$/Me$_{10}$Fc redox reactions collected at 20 mV s$^{-1}$ in O2-saturated electrolytes containing 2 mm Me$_{10}$Fc in 0.5 M TBACIO$_4$ in DME, 0.1 M TBACIO$_4$ in DMA, and DMSO, obtained with an Ag/Ag$^+$ reference electrode and Ni foam counter electrode. b) Experimental standard O2/TBA^-\^-O2^- and Li^-/Li redox potentials vs. Me$_{10}$Fc/Me$_{10}$Fc plotted against acceptor and donor numbers of each solvent.

These references are much improved in comparison to the trend obtained using the solvent-dependent Ag/Ag$^+$ reference reported by Sawyer et al.[20] (Supporting Information, Figure S4b, $R^2$ = 0.75).

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MeCN and DMA (Figure 3) using a mixed cluster-continuum model. These solvation free energies \( \text{O}_2^- \) and \( \text{Li}^+ \) were referenced to the ion free energy in the gas phase and computed according to Figure 3a. The most stable ion-solvent clusters for \( \text{O}_2^- \) in DMSO and DME are shown in Figure 3b as examples, from which single-ion solvation free energies were obtained (Supporting Information, Table S2). The computed solvation free energy, \( \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-) \), was found to increase with greater AN (R² = 0.81), from \(-259 \text{ kJ mol}^{-1} \) in DME to \(-215 \text{ kJ mol}^{-1} \) in DMSO, as shown in the Supporting Information, Table S2. The absolute \( \text{O}_2^- \) reduction potential (\( \text{O}_2^-/\text{O}_2 \)) was computed with respect to electron energy in a vacuum, using:

\[
-\text{FE}^*_{\text{an}} = \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-) + \Delta G^\text{red} - \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-)
\]

where \( \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-) \) and \( \Delta G^\text{red} \) are solvent-independent parameters related to gas-phase ionization and standard state correction, respectively (see details in Supporting information). Computed \( \text{O}_2^-/\text{O}_2 \) redox potentials referenced to DME show a good agreement with, but are consistently higher than experimental measurements.

Remarkably, computed solvent-dependent changes in the \( \text{Li}^+/-\text{Li} \) redox potential referenced to MeCN showed an excellent agreement compared with measured differences, as shown in Figure 3c. The most stable \( \text{Li}^+/-\text{Li} \)-solvent clusters with cluster size \( n = 4 \) for DMSO and \( n = 3 \) for DME are shown in Figure 3b, from which single ion solvation free energies were obtained (Supporting Information, Table S3). As greater \( \text{Li}^+/-\text{Li} \) solvation lowers the \( \text{Li}^+/-\text{Li} \) potential while greater \( \text{O}_2^-/-\text{O}_2 \) solvation increases the \( \text{O}_2^-/-\text{O}_2 \) potential, solvents that strongly solvate both \( \text{Li}^+/-\text{Li} \) and \( \text{O}_2^-/-\text{O}_2 \) have high \( \text{O}_2^-/-\text{O}_2 \) potentials vs. \( \text{Li}^+/-\text{Li} \) potentials. Indeed, the \( \text{O}_2^-/-\text{O}_2 \) redox potentials referenced to the \( \text{Li}^+/-\text{Li} \) scale increased with greater combined solvation of \( \text{O}_2^-/-\text{O}_2 \) and \( \text{Li}^+/-\text{Li} \) (Figure 3d), and were in close agreement with computed standard \( \text{O}_2 \) reduction potential of \( \text{O}_2^-/-\text{O}_2 \) vs. \( \text{Li}^+/-\text{Li} \) (Supporting Information, Tables S4-S5), and previous experimental findings reporting higher \( \text{O}_2^-/-\text{O}_2 \) potentials vs. \( \text{Li}^+/-\text{Li} \) of 2.25[14] and 2.37[14] V in DMSO, compared to about 2.0 V for DME, MeCN[14] and ionic liquids[35].

Solvation-dependent \( \text{O}_2^-/-\text{O}_2 \) redox potentials in \( \text{Li}^+/-\text{Li} \)-containing DMSO, DME, DMA, and DMF were estimated using chronoamperometric rotating ring-disk electrode (RRDE) measurements. The disk was held at a potential to reduce \( \text{O}_2 \) under rotation at 900 rpm while the ring was held at discrete potentials to oxidize soluble intermediate species that diffused from the disk (Supporting Information, Figure S7). Ring current transients measured from 3.50 to 2.76 V vs. \( \text{Li}^+/-\text{Li} \) (Figure 4a) with the disk potential kept at 2.6 V vs. \( \text{Li}^+/-\text{Li} \) (Figure 4b) in DMSO are shown as an example (for those for other solvents, see the Supporting Information, Figure S8). Ring currents were found to decrease with reducing potentials from 3.7 V to 2.7 V vs. \( \text{Li}^+/-\text{Li} \) for all solvents examined, which can be attributed to the ring potential approaching the equilibrium potential for soluble intermediate oxidation. We hypothesize that soluble ORR intermediates oxidized on the ring are \( \text{Li}_n\text{O}_m \) like species. This is supported by previous in situ electrochemical quartz microbalance[36].

Figure 3. a) Thermodynamic cycle for the calculation of \( \text{Li}^+/-\text{Li} \) or \( \text{O}_2^-/-\text{O}_2 \) ion solvation. b) Structures of the most stable X(solvent) clusters (solvent = DMSO, DME, X = Li, \( \text{O}_2^- \), n = 3–6) obtained at the M06-L/6-311++G**/B3LYP/6-31G** level. c) Comparison of standard experimental (open hexagons) and calculated (open squares) \( \text{O}_2^-/-\text{O}_2 \) and \( \text{O}_2^-/-\text{Li}^+ \) solvation energies of each solvent. All \( \text{Li}^+/-\text{Li} \) and \( \text{O}_2^-/-\text{O}_2 \) potentials are plotted with respect to MeCN and DME, respectively. d) Standard experimental redox potentials of \( \text{O}_2^-/-\text{O}_2 \) and \( \text{Li}^+/-\text{Li} \) against combined \( \text{Li}^+/-\text{Li} \) and \( \text{O}_2^-/-\text{O}_2 \) solvation energy.

\[ \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-) + \Delta G^\text{red} + \Delta G^\text{solv}_{\text{an}}(\text{O}_2^-) \]

(2)
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energies of Li⁺ and Na⁺ in 27 organic solvents,[42] which found that Na⁺ de-solvation energies were on average 20% less than Li⁺, implying weaker Na⁺ solvation in non-aqueous solvents. Similarly, computed gas-phase binding energies of Na⁺ and K⁺ to tetrahydrofuran have been reported to be much less than that for Li⁺,[43] and comparable to the computed solvation energies of O₂⁻, $\Delta G^{\text{bulk}}(\text{O}_2^{-})$, as found in this study.

Understanding and controlling the solvation and coupling of O₂⁻ and Li⁺ ions has far-reaching implications for developing reversible Li-O₂ battery electrochemistry. Increasing Li⁺-O₂⁻ solubility can suppress surface nucleation rates[44] or trigger solution-phase growth of Li₂O₂,[12,16] resulting in high discharge capacities by increased pore filling with large, solid Li₂O₂ agglomerates.[17,45,46] However, solvents with high Li⁺-O₂⁻ solubilities such as DMSO can be more subject to superoxide attack and decrease solvent stability in Li-O₂ batteries.[47,49] This argument is supported by increasing computed $\Delta G^{\text{bulk}}(\text{O}_2^{-})$ with decreasing computed $pK_a$ of solvents (in DMSO: Supporting Information, Table S2), and previous findings which established a correlation between solvent AN and DN, and $pK_a$, where solvents with higher Li⁺-O₂⁻ solubility were more susceptible to proton abstraction by O₂⁻.[50] As Li⁺ solvation structures can vary greatly among similar solvents (for example, glymes)[51,52] and across different classes of solvents such as ionic liquids,[53] caution should be exercised and further studies are needed to examine the influence of solvation and coupling of O₂⁻ and Li⁺ ions on solvent stability.

In summary, we have shown that standard potentials of the O₂/Li⁻-O₂⁻ redox reaction becomes comparable to those of O₂/TBA⁻-O₂⁻ with increasing combined solvation energy of Li⁺ and O₂⁻ ions, owing to reduced coupling energy of Li⁺-O₂⁻. Furthermore, we have shown that Li⁺-O₂⁻ solubility increases with greater combined solvation energy of O₂⁻ and Li⁺, which can be correlated with experimental standard O₂/TBA⁻-O₂⁻ potentials. These results highlight the importance of the interplay between ion-solvent and ion-ion interactions in understanding and controlling the intermediate species energetics, reaction product morphology, discharge capacity, and solvent stability in aprotic metal-O₂ batteries.

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Figure 5. Comparison between a) combined computed solvation energy of Li⁺ and O₂⁻ ions in DMSO, DME, and DMA and computed (diamonds) and experimental (circles) Li⁺-O₂⁻ coupling energies and b) O₂/TBA⁻-O₂⁻ vs. Li⁺/Li redox potentials with the logarithm of ring-to-disk charge during Li-ORR (circles) and combined computed solvation energy of Li⁺ and O₂⁻ ions in DMSO, DME, DMA, and DMF (diamonds). Dotted line shows linear regression through experimental data, $R^2 = 0.98$.

in Figure 5b. Li⁺-O₂⁻ solubility was assessed using the logarithm of the ring-to-disk charge ratio obtained during ORR from RRDE measurements with the ring kept at 3.5 V vs. Li⁺/Li (Supporting Information, Figures S9 and S11). Li⁺-O₂⁻ solubility was found to increase linearly (DME < DMA < DMF < DMSO) with combined computed solvation energies of Li⁺ and O₂⁻ ions, and measured (Figure 5b) and computed (Supporting Information, Figure S12a) O₂/TBA⁻-O₂⁻ redox potentials vs. Li⁺/Li.

A previously reported correlation between Li⁺-O₂⁻ solubility and DN[52] (Supporting Information, Figure S12b) can be attributed to the fact that the combined computed solvation energy is dominated by computed Li⁺ solvation energies (which scales with DN), as computed Li⁺ solvation energies are considerably higher than those of O₂⁻ ions. However, considering Li⁺ solvation (or DN) alone cannot explain trends in the Li⁺-O₂⁻ solubility for solvents with similar DN but different ANs such as DMSO (DN = 26.6 and AN = 16.0) and DMA (DN = 27.8 and 13.6), where greater Li⁺-O₂⁻ solubility observed for DMSO than DMA cannot be explained by DN (Supporting Information, Figure S12c). Extending this understanding to non-aqueous Na-O₂ and K-O₂ electrochemistry, it would be expected that the solubility of Na⁺-O₂⁻ and K⁺-O₂⁻ would not scale with DN as well, as Na⁺ and K⁺ are weaker Lewis acids than Li⁺ and will be solvated less strongly. This is supported by a recent computational study of de-solvation...
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Communications

Oxygen Electrochemistry

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Experimental and Computational Analysis of the Solvent-Dependent O₂/Li⁺⁻O₂/C₀ Redox Couple: Standard Potentials, Coupling Strength, and Implications for Lithium–Oxygen Batteries

The free-energy landscape of reactions involved in the Li oxygen reduction reaction (ORR) were obtained by rotating ring disk (RRD) measurements and calculations. Differences in redox potentials of O₂/O₂⁻ and O₂/Li⁺⁻O₂⁻ couples vs. Li⁺/Li in dimethoxyethane (DME) and dimethylsulfoxide (DMSO) reflect the influence of increasing solvation on the free energy of O₂⁻ formation vs. Li⁺/Li and Li⁺⁻O₂⁻ coupling.