

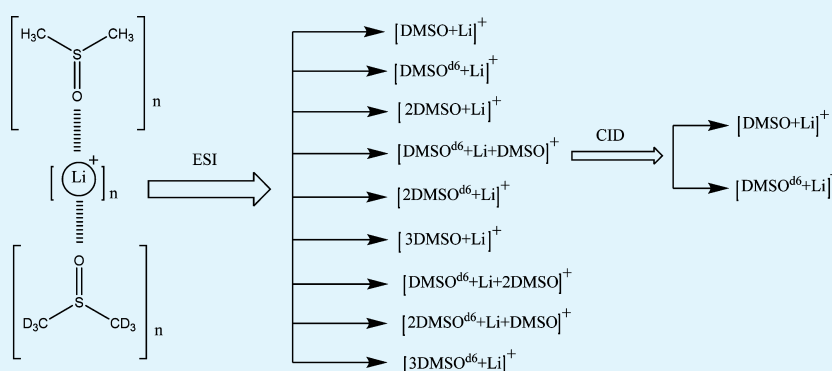
Preferential Solvation of Lithium Cations and Impacts on Oxygen Reduction in Lithium–Air Batteries

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ABSTRACT: The solvation of Li^+ with 11 nonaqueous solvents commonly used as electrolytes for lithium batteries was studied. The solvation preferences of different solvents were compared by means of electrospray mass spectrometry and collision-induced dissociation. The relative strength of the solvent for the solvation of Li^+ was determined. The Lewis acidity of the solvated Li^+ cations was determined by the preferential solvation of the solvent in the solvation shell. The kinetics of the catalytic disproportionation of the $\text{O}_2^{\bullet-}$ depends on the relative Lewis acidity of the solvated Li^+ ion. The impact of the solvated Li^+ cation on the O_2 redox reaction was also investigated.

KEYWORDS: superoxide, solvation, lithium ion, ESI-MS, oxygen reduction

INTRODUCTION

Due to their high theoretical energy density, rechargeable Li– O_2 batteries are particularly attractive for replacing the state-of-art Li-ion batteries in electric vehicles for longer distance travel. Therefore, Li– O_2 has attracted much research attention in recent years. Besides the long-time challenges for the rechargeable metallic Li anode, the rechargeable O_2 cathode in nonaqueous electrolytes is still away from practicality. The detailed mechanism of O_2 reduction in nonaqueous electrolytes is still not fully understood. It is well-known that O_2 reduction in a nonaqueous electrolyte is a 1-e reaction and that superoxide ($\text{O}_2^{\bullet-}$) is the reduction product.¹ The redox reaction is very reversible. Most of the early studies for O_2 reduction in nonaqueous electrolyte were done in the electrolyte without Li salt.² In our early papers,^{3,4} a Lewis acid was found to facilitate the catalytic disproportionation of $\text{O}_2^{\bullet-}$, and the catalytic activity seemed to be related to the acidity of the Lewis acid. The Li^+ cation is a Lewis acid and was proven to catalyze the disproportionation of $\text{O}_2^{\bullet-}$.

Recently, the mechanism for the O_2 redox reaction in nonaqueous electrolyte was reported to be greatly influenced by the solvated Li^+ cations in the electrolyte solution with

different solvents, a conclusion that is consistent with Pearson's hard–soft acid–base (HSAB) theory.^{5,6} Indeed, decent rechargeability of the O_2 cathode was demonstrated in the Li– O_2 battery with a LiClO_4 dimethyl sulfoxide (DMSO) electrolyte.⁷ Those studies suggested that the electrolytes and the solvation properties of the solvents could have a great impact on the O_2 redox reaction.

To investigate the solvation of Li^+ in different organic solvents, two analytical methods have been employed to determine Li^+ solvation numbers: Raman spectroscopy^{8–11} and electrospray ionization mass spectrometry (ESI-MS).^{12–14} As the Li^+ cations are solvated by solvent molecules, the vibrational band of the solvent molecules will shift in Raman spectroscopy. Through comparison of the intensities of the bands from coordinated and uncoordinated solvent molecules, the average solvation number of solvents to Li^+ cations could be estimated. However, due to the peak overlap of the coordinated and uncoordinated vibrational bands, the quantitative inter-

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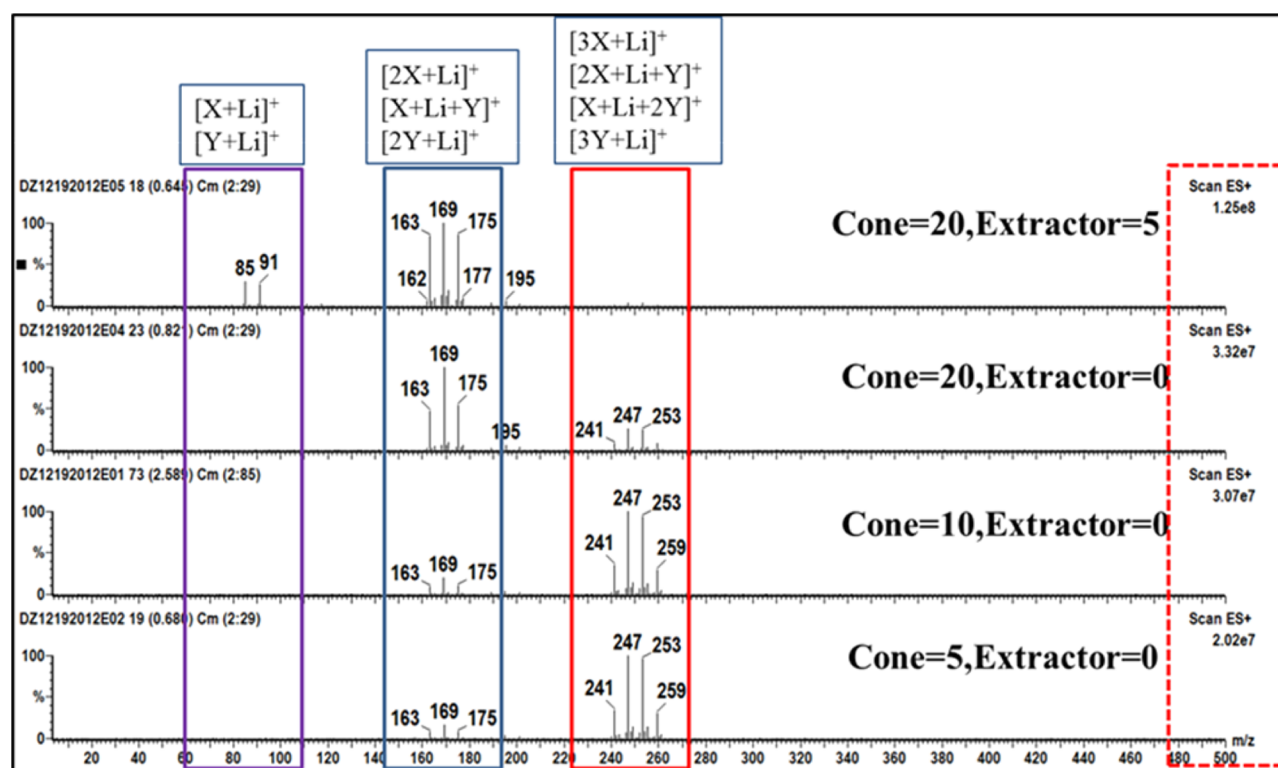


Figure 1. ESI-MS spectra of DMSO and DMSO- d_6 (1:1) mixture with 5 mM LiBF₄ under different ESI-MS conditions (different cone and extractor voltages). X = DMSO (MW = 78), Y = DMSO- d_6 (MW = 84); for adduct [X + Li]⁺ m/z 85, for adduct [Y + Li]⁺ m/z 91, for adduct [2X + Li]⁺ m/z 163, for adduct [X + Li + Y]⁺ m/z 169, for adduct [2Y + Li]⁺ m/z 175, for adduct [3X + Li]⁺ m/z 241, for adduct [2X + Li + Y]⁺ m/z 247, for adduct [X + Li + 2Y]⁺ m/z 253, and for adduct [3Y + Li]⁺ m/z 259. The absolute intensities of the most abundant adduct for each MS spectrum under different ESI condition are listed to the right of each spectrum.

pretation of the obtained Raman spectra is a challenge. In the ESI-MS measurement, however, the Li⁺ cations solvated by solvents will form gas-phase adducts through the ESI process, and the lithiated adducts [Li + (solvent)_n]⁺ with different solvation number will be recorded in the MS spectra at different mass/charge (m/z) ratios. The solvent molecules in the primary solvation shell of Li⁺ cations were believed to survive in the ionization process and remain intact. Therefore, the distribution of different adducts with different solvent numbers can be reliably obtained by comparing the intensities of corresponding m/z ratios of different lithiated adducts, because each m/z ratio represents one intact solvated Li⁺ ion.¹⁴

In this work, ESI-MS was used to investigate the Li⁺ solvation with 11 of the most common solvents used in Li batteries. The collision-induced dissociation (CID) spectra of the lithiated adduct [X + Li + Y]⁺ were also studied. In addition, the impact of the solvated Li⁺ with different solvents on the O₂ redox reaction was demonstrated and discussed.

EXPERIMENTAL SECTION

Twelve anhydrous solvents (from Sigma-Aldrich) were purchased and used without further treatment, including acetonitrile (ACN), diethylene glycol dimethyl ether (DEDME), dimethoxyethane (DME), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), deuterated dimethyl sulfoxide (DMSO- d_6), γ -butyrolactone (GBL), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), propylene carbonate (PC), and pyridine (Py). Eleven binary electrolyte mixtures were made by mixing DMSO with other solvents in a 1:1 molar ratio; lithium tetrafluoroborate (LiBF₄, battery grade from FERRO) was used as the lithium salt at a

concentration of 5 mM. All electrolytes were prepared in an Ar-filled glovebox (O₂ and moisture <5 ppm) and sealed in airtight sample vials before being introduced into the ESI-MS.

A Quattro LC mass spectrometer (triple quadrupole, controlled by Masslynx 4.0 from Micromass-Waters) with ESI source was operated under positive mode. The typical source parameters were set as follows: capillary, 2.60 kV; cone, 20 V; extractor, 0 V; RF lens, 0.5 V; source temperature, 100 °C; desolvation temperature, 250 °C; N₂ gas flow, 50 L/h for nebulizer and 600 L/h for desolvation. For ESI-MS scan, the m/z ratio from 10 to 500 was recorded; for CID scan (or daughter ion scan), the m/z ratio from 10 to 500 was recorded, collision voltage was set at 20, and argon was used as the collision gas. The 1:1 binary solvent electrolyte with 5 mM LiBF₄ was introduced into the mass spectrometer through a syringe pump at a flow rate of 40 μ L/min. It is worth emphasizing that the “direct injection” method was used to introduce the electrolyte directly into the nebulizer without further dilution, so any competing interference from the diluting solvent could be avoided.

Electrochemical investigation was carried out using an AutoLab PGSTAT30 potentiostat in a typical three-electrode system. A glassy carbon electrode (0.01 cm²) was used as the working electrode. A Pt wire electrode and a Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively.

RESULTS AND DISCUSSION

One of the remaining arguments regarding using the ESI-MS technique to determine the solvation numbers is whether the number of solvent molecules in the solvation shell changes after vaporization during the ESI process. Figure 1 shows typical ESI-MS spectra for the 5 mM LiBF₄/DMSO/DMSO- d_6 electrolyte. Normally the lithiated adducts solvated with one to three solvent molecules are readily observed in ESI-MS spectra, whereas the lithiated adducts with four or more solvent

Table 1. Comparison of the Relative Abundance of 5 mM LiBF₄/DMSO/DMSO-*d*₆ Electrolyte under Different ESI-MS Conditions with Theoretical Nonselective Solvation^a

solvation no.	Li ⁺ adduct	relative abundance				nonselective solvation
		C = 20 V E = 5 V	C = 20 V E = 0 V	C = 10 V E = 0 V	C = 5 V E = 0 V	
1	[DMSO + Li] ⁺	100	100	100	87.5	100
	[DMSO- <i>d</i> ₆ + Li] ⁺	88.5	86.7	91.1	100	100
2	[2DMSO + Li] ⁺	84.2	47.0	48.6	53.5	50
	[DMSO + DMSO- <i>d</i> ₆ + Li] ⁺	100	100	100	100	100
	[2DMSO- <i>d</i> ₆ + Li] ⁺	85.8	54.5	54.3	54.1	50
3	[3DMSO + Li] ⁺	35.7	33.8	35.0	34.2	33.3
	[2DMSO + DMSO- <i>d</i> ₆ + Li] ⁺	100	100	100	100	100
	[DMSO + 2DMSO- <i>d</i> ₆ + Li] ⁺	96.1	99.4	93.9	95.9	100
	[3DMSO- <i>d</i> ₆ + Li] ⁺	30.1	32.6	29.5	30.7	33.3

^aC is the cone voltage, and E is the extractor voltage; both are parameters in the ESI source. The relative abundance for each lithiated adduct is normalized to the highest abundance species (which is 100%). A smaller number means lower relative abundance. The relative abundance of nonselective solvation is obtained by statistical calculation: when the DMSO and DMSO-*d*₆ are in a 1:1 ratio mixture, the relative abundance for lithiated monomers should be 1:1 (or 100:100); the relative abundance for lithiated dimers should be 1:2:1 (or 50:100:50); the relative abundance for lithiated trimers should be 1:3:3:1 (or 33.3:100:100:33.3).

molecules are seldom observed (or in extremely low abundance).^{12–14} Although the ideal solvation number (for a closed sheath) for Li⁺ is 4, the average solvation number from the Raman spectroscopic method is from 1 to 3, which is also observed in ESI-MS spectra.

By comparing the ESI-MS spectra in Figure 1 obtained under different ESI-MS conditions, one can observe that the intensities of lithiated adducts in ESI-MS spectra are greatly influenced by the ESI conditions. With an increase in the cone and extractor voltages, which are used to extract ions into the mass analyzer, the absolute intensities of the most abundant lithiated adducts increased from 2.02×10^7 to 1.25×10^8 (as marked with the dashed line in Figure 1). In addition, the relative distributions of each lithiated adduct in the ESI-MS spectra were also influenced by the ESI conditions. At low cone voltages (5 or 10 V), the majority of species in the ESI-MS spectra are Li⁺ cations coordinated with three solvent molecules and with the minor species of Li⁺ cations coordinated with two solvent molecules. However, at high cone voltage (20 V), the majority of species in ESI-MS spectra are Li⁺ cations coordinated with two solvent molecules with the minor species of Li⁺ cations coordinated with three solvent molecules. When the extractor voltage increases from 0 to 5 V (cone = 20 V), the majority of species in ESI-MS spectra were Li⁺ cations coordinated with two solvent molecules and with the minor species of Li⁺ cation coordinated with just one solvent molecule. Obviously, the number of solvent molecules remaining in the solvated Li⁺ ions in the gas-phase is the influenced by the ESI conditions due to the in-source fragmentation of lithiated adducts in ESI source.

To quantitatively calculate the statistical distribution of different carbonate molecules in the lithiated adducts obtained by ESI-MS, Xu et al.¹⁴ proposed a method that compares the total relative molar ratio of different solvents in the lithiated adducts with different coordination numbers. It was assumed that if the different solvents can coordinate with the Li⁺ cations nonselectively, then the relative ratio of different solvents in the adducts should solely depend on the relative ratio of the different solvents in the electrolyte. Because the substitution of hydrogen with deuterium in DMSO has little influence on

solvation, the DMSO and DMSO-*d*₆ solvents were used as the nonselective solvent to further validate the method proposed by von Cresce and Xu.¹⁴ The ESI-MS spectra of the 5 mM LiBF₄/DMSO/DMSO-*d*₆ electrolyte under different ESI-MS conditions are shown in Figure 1, and the relative ratios of different lithiated adducts are summarized in Table 1. It is evident that the relative ratios obtained experimentally coincided well with the prediction based on the nonselective solvation of DMSO/DMSO-*d*₆. The more important conclusion is that the relative distributions of different solvents in the lithiated adducts are independent of the experimental conditions. Therefore, ESI-MS is proven to be a valid technique to investigate Li⁺ solvation.

Table 2 provides the relative distributions of solvent molecules in the solvated Li⁺ ion obtained from the ESI-MS spectra for the 11 binary electrolytes. Again, in the electrolyte containing the mixture of 1:1 (mole ratio) DMSO and DMSO-*d*₆, the relative distribution of DMSO and DMSO-*d*₆ in the solvated Li⁺ ion was close to 1:1. For the binary electrolytes with DMSO mixed with other solvents at a 1:1 ratio, the mole

Table 2. Relative Molar Ratio of Different Solvents in the Li⁺ Solvation Adducts Obtained from ESI-MS Spectra of 5 mM LiBF₄ DMSO and Other Solvent (1:1) Mixtures^a

solvent X =	mol % of solvent X in Li ⁺ solvation shell	solvent Y =	mol % of solvent Y in Li ⁺ solvation shell
DMSO	98.2	Py	1.8
DMSO	97.1	ACN	2.9
DMSO	69.9	DME	30.1
DMSO	43.1	DEDME	56.9
DMSO	98.6	EC	1.4
DMSO	91.8	PC	8.2
DMSO	99.4	DMC	0.6
DMSO	98.6	DEC	1.4
DMSO	69.2	DMF	30.8
DMSO	97.7	GBL	2.3
DMSO	48.9	DMSO- <i>d</i> ₆	51.1

^aThe voltages of cone and extractor are 20 and 0 V, respectively, for ESI-MS.

percent of DMSO in the solvation shell varies from 43 to 98%. The results clearly demonstrated the preferential solvation of Li^+ cations for different solvents, because the distribution of solvents in the solvated Li^+ ion diverged from that in the electrolyte solutions.

The solvation preference of a solvent was reported to be related to its donor number (DN). The solvent with the higher DN would be preferentially solvated with cations in the solution of mixed solvents.^{15,16} Table 3 summarizes the DNs

Table 3. Lewis Basicity of Different Solvents Summarized from the Published Literature^{6,17}

solvent	DN (kJ mol^{-1}) (SbCl_5 affinity)	BF_3 affinity (kJ mol^{-1})
Py	142.3	128.1
ACN	61.1	60.4
DME	83.8	74.7
DEDME	69.5	n/a
EC	68.6	66.4
PC	62.4	64.2
DMC	63.5	67.6
DEC	66.9	71.0
DMF	111.3	110.5
GBL	73.2	75.1
DMSO	124.7	105.3

and BF_3 affinities as reported in the literature, both of which have been used to indicate solvent basicity.^{6,17} By comparison of the DNs provided in Table 3 with the experimental data in Table 2, that hypothesis was not supported by our results. The inconsistency can easily be found: pyridine, which had the highest DN value, shows the least mole percent in the solvation sheath, whereas diethylene glycol dimethyl ether (DEDME), which has a moderate DN value, shows the highest mole percent in the solvation shell. Similar inconsistencies were also observed in other publications, which indicates the limitation of evaluating the solvation preference using DNs.¹³ Because the DN values were obtained by using SbCl_5 as the reference Lewis

acid,¹⁷ the limitation of applying DNs to the solvation of Li^+ would not be surprising.

To understand the relative strength of the interaction between the solvent molecules and the Li^+ in a solvation shell, the CID spectra were used. The lithiated adducts $[\text{DMSO} + \text{Li} + \text{Y}]^+$ (Y stands for another solvent in the binary solution) formed in the ESI source are selected and accelerated by a potential and then collided with Ar molecules to form fragment ions (or daughter ions): $[\text{DMSO} + \text{Li}]^+$ and $[\text{Y} + \text{Li}]^+$. The scheme is shown in Figure 2. Because the formation of $[\text{DMSO} + \text{Li}]^+$ or $[\text{Y} + \text{Li}]^+$ needs to overcome the interaction between Li^+ and Y or Li^+ and DMSO, by comparing the relative abundances of $[\text{DMSO} + \text{Li}]^+$ and $[\text{Y} + \text{Li}]^+$ in the CID spectra, the relative strength of the interaction between the solvents and the Li^+ in the solvation shell can be estimated. If DMSO has a stronger interaction with Li^+ , then the abundance of $[\text{Y} + \text{Li}]^+$ in the CID spectra would be lower. Conversely, if DMSO has a weaker interaction with Li^+ , then the abundance of $[\text{DMSO} + \text{Li}]^+$ in the CID spectra would be lower. Figure 2 shows the CID spectrum of $[\text{DMSO} + \text{Li} + \text{DMSO-}d_6]^+$. Due to the fact that DMSO and $\text{DMSO-}d_6$ have the same strengths of interaction with Li^+ , the relative abundances of $[\text{DMSO} + \text{Li}]^+$ and $[\text{DMSO-}d_6 + \text{Li}]^+$ in the CID spectrum are almost the same. The relative abundances of the daughter ions in the CID spectra for the different $[\text{DMSO} + \text{Li} + \text{Y}]^+$ parent ions are summarized in Table 4. The data in Table 4 are consistent with those shown in Table 2: the solvent that had a stronger interaction with Li in the solvation shell showed a higher mole percent in the solvation sheath. The only exception is DME, which showed a higher relative abundance in the CID spectrum but a lower mole percent in the Li^+ solvation shell than DMSO. This phenomenon could be attributed to the bidentate interaction between DME and Li^+ in the $[\text{DMSO} + \text{Li} + \text{Y}]^+$ parent ions.

The local structure of solvation around a Li^+ cation in a mixed-solvent electrolyte plays an important role in the properties of an electrolyte (e.g., the conductivity and viscosity of the electrolyte). Using ESI-MS and CID, we indeed observed the selective solvation of a Li^+ cation. Such selective solvation

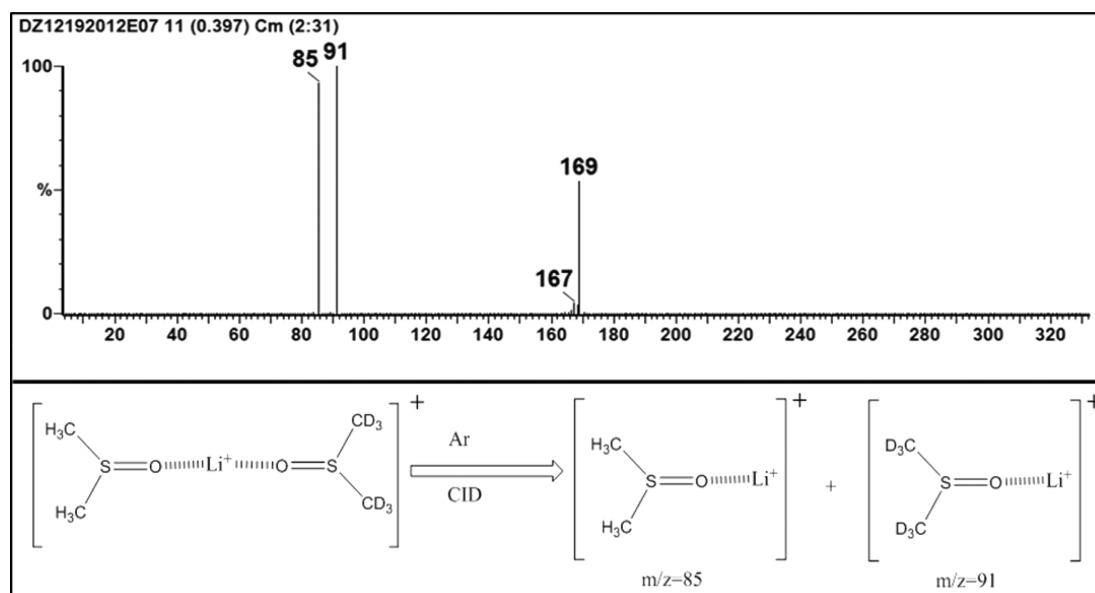


Figure 2. CID spectra of $[\text{DMSO} + \text{Li} + \text{DMSO-}d_6]^+$ obtained at collision voltage = 20 V and the scheme of the CID procedure.

Table 4. Relative Abundance of Daughter Ions for the CID Spectra of [DMSO + Li + Y]⁺

daughter ion	relative abundance	daughter ion	relative abundance
[DMSO + Li] ⁺	100	[Py + Li] ⁺	3.6
[DMSO + Li] ⁺	100	[ACN + Li] ⁺	2.3
[DMSO + Li] ⁺	30.1	[DME + Li] ⁺	100
[DMSO + Li] ⁺	0.1	[DMDME + Li] ⁺	100
[DMSO + Li] ⁺	100	[EC + Li] ⁺	6.2
[DMSO + Li] ⁺	100	[PC + Li] ⁺	5.7
[DMSO + Li] ⁺	100	[DMC + Li] ⁺	6.2
[DMSO + Li] ⁺	100	[DEC + Li] ⁺	9.6
[DMSO + Li] ⁺	100	[DMF + Li] ⁺	51.6
[DMSO + Li] ⁺	100	[GBL + Li] ⁺	8.0
[DMSO + Li] ⁺	94	[DMSO- <i>d</i> ₆ + Li] ⁺	100

was proven to be related to the relative strength of the interaction between the solvent and Li⁺. The electrochemical behaviors of a Li–air battery are dramatically affected by the kind of solvent used in the electrolytes, which was attributed, at least partially, to the manner in which Li⁺ cations were solvated.^{5,6} The solvent effects on the O₂ redox reaction were attributed to the alteration of the acidity of the solvated Li⁺ cation. The superoxide (O₂^{•−}), which is the product of O₂ reduction, is a Lewis base and can be catalytically disproportionated by a Lewis acid. The inclination is that the Lewis acidity of a solvated Li⁺ ion decreases if solvated with a solvent that strongly interacts with it. Figure 3 shows the cyclic voltammograms at various scan rates for a glassy carbon electrode in the O₂ saturated DMSO solution containing 1 M tetraethylammonium tetrafluoroborate (TEABF₄) and 1 M LiBF₄, panels A and B, respectively.

A pair of very symmetric O₂ reduction (−0.95 vs Ag/AgCl) and O₂^{•−} oxidation (−0.79 vs Ag/AgCl) peaks are clearly shown in Figure 3A. The ratio between the anodic and cathodic peak area, which is close to 1, remained the same at various scan rates. Because TEABF₄ has little Lewis acidity, O₂^{•−} anions formed during the reduction were stable in DMSO and eventually became oxidized during the positive scan. A ratio of slightly lower than 1 at lower scan rate resulted from the loss of O₂^{•−} species because they had a longer time to diffuse away from the electrode surface. Figure 3B shows the cyclic voltammograms for the same electrode in the O₂-saturated DMSO solution, except TEABF₄ was replaced with LiBF₄. As a Lewis acid, the Li⁺ cation is able to catalyze the disproportionation of O₂^{•−} anions.⁴ Thus, O₂^{•−} anions formed on the surface of the glassy carbon electrode during the reduction of O₂ were catalytically disproportionated by Li⁺, and the remaining O₂^{•−} anions were oxidized on the electrode surface during the oxidation scan. Therefore, the ratio between the anodic and cathodic peak areas was determined by both the scan rate and the kinetics of the disproportionation reaction. A fast scan rate and a low catalytic disproportionation rate would result in a high ratio between the anodic and cathodic peak areas, because more O₂^{•−} species survived from disproportionation. However, when there is sufficient time allowed at a low scan rate, O₂^{•−} on the electrode surface could be completely consumed by the catalytic disproportionation, and then little oxidation current would be detected during the reverse anodic scan because no O₂^{•−} remains to be oxidized. The trend is clearly demonstrated in Figure 3B.

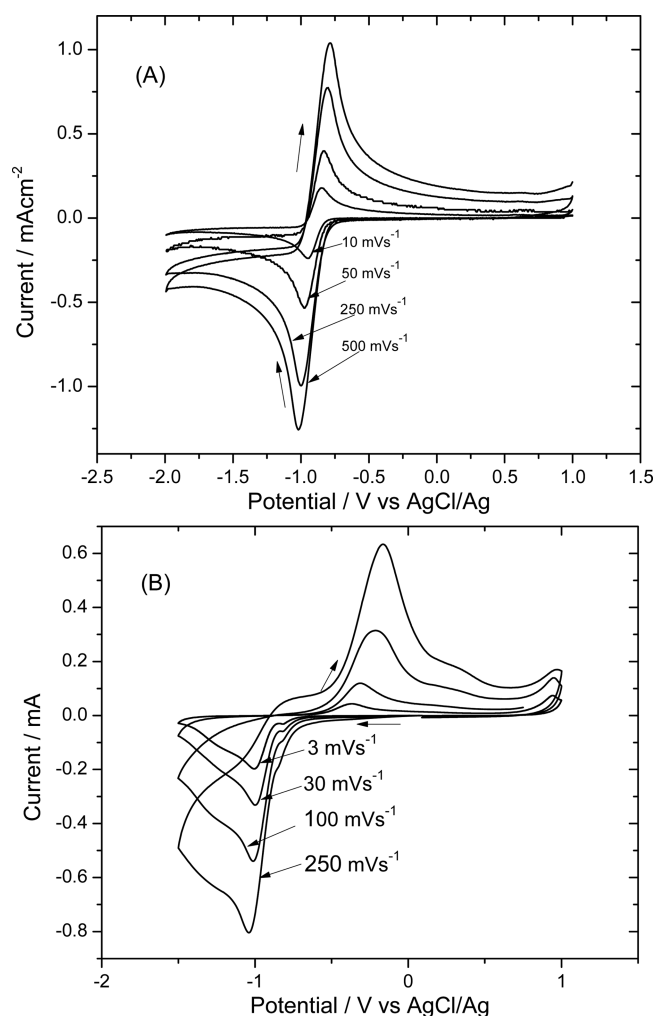


Figure 3. Cyclic voltammograms at various scan rates in 1 M TEABF₄ DMSO electrolyte (A) and 1 M LiBF₄ DMSO electrolyte (B) saturated with O₂ on a glassy carbon-disk electrode.

Figure 4 shows the change in the ratio between the anodic and cathodic peak areas with the scan rate in various

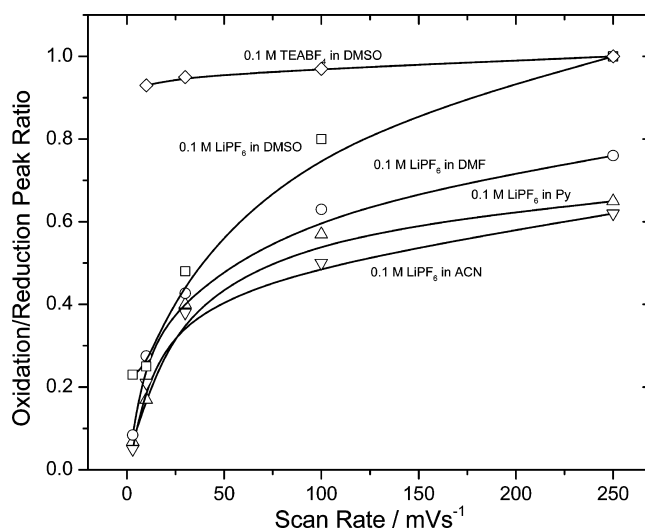
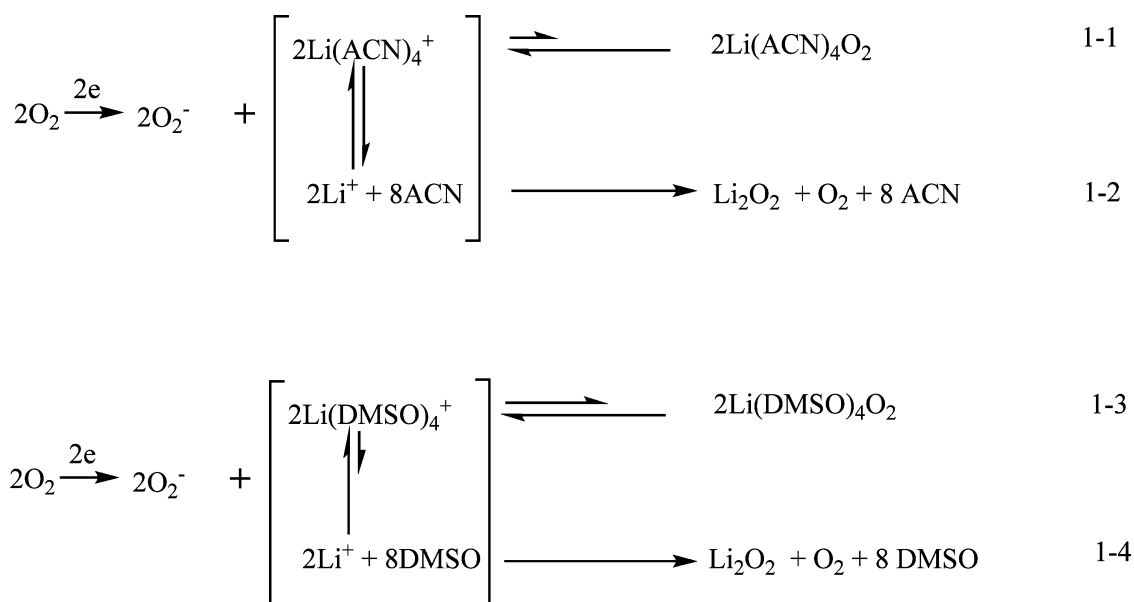


Figure 4. Comparison of the ratio between the anodic and cathodic peak areas for the O₂ redox reaction in various electrolytes.

Scheme 1. Proposed Mechanism: Impact of the Strength of the Solvent for the Solvation of Li^+ on the Disproportionation of the Electrochemically Generated $\text{O}_2^{\bullet-}$ ^a



^aAcetonitrile (ACN) and dimethyl sulfoxide (DMSO) are used as examples.

electrolytes. The solvents chosen to be shown in the figure do not react with $\text{O}_2^{\bullet-}$. Clearly, the anodic and cathodic peak area ratio for the O_2 redox reaction in TEABF₄ DMSO is close to 1. At a 3 mV s⁻¹ scan rate, the ratios for the O_2 redox reaction in LiBF₄ with various solvents were close to 0, and almost all $\text{O}_2^{\bullet-}$ ions were disproportionated. As the scan rate was increased, the ratio also increased. The ratio between the anodic and cathodic peak areas was also solvent related as shown in Figure 4. Comparing Figure 4 and Table 2, one can conclude that more $\text{O}_2^{\bullet-}$ survived the catalytic disproportionation in the electrolyte in which the solvent has a stronger affiliation with Li^+ cations. The observations support the hypothesis that the catalytic activity of the solvated Li^+ ions toward the disproportionation of $\text{O}_2^{\bullet-}$ is related to the Lewis acidity of the solvated ion and that the Lewis acidity of a Li^+ ion is reduced when solvated with a solvent that strongly interacts with Li^+ as shown in Scheme 1.

One could argue that the interaction between $\text{O}_2^{\bullet-}$ and the electrolyte would also contribute to the change of the oxidation/reduction peak ratio shown in Figure 4. Indeed, in our previous publication,³ the influence of electrolyte on the oxidation/reduction peak ratio for the O_2 reduction was studied in detail. The oxidation/reduction peak ratio was found dependent on the CV scan rate in the tetraethylammonium/PC electrolyte because $\text{O}_2^{\bullet-}$ was consumed by its reaction with PC. The instability of many solvents against $\text{O}_2^{\bullet-}$ was found,^{18–23} including DMSO and glyme. However, the instability of solvent had little influence on the observation in Figure 4, because the five solvents shown in Figure 4 were very stable during the time scale of the experiments, which was <1 h. For example, no changes can be observed when DMSO was mixed with KO₂ for 24 h; the instability of DMSO is evident only after after mixing with KO₂ for 2 months.²² Of course, DMSO was reported not stable at a carbon fiber electrode.²⁴ It is worth pointing out that $\text{O}_2^{\bullet-}$ would survive longer in a solvent with stronger solvation of Li^+ , which could consequently increase the instability of the electrolyte.

Although the impacts of solvation on the alteration of Lewis acidity and the catalysis superoxide disproportionation were the focus of the study, it is also worth emphasizing that the solvation may be also important to the formation of surface layers, for example, on a Li-ion anode, because the affinity of solvents with Li cations may alter their reaction on the electrode surface. The importance of solvent in Li–air batteries is well documented.²⁵

CONCLUSION

Using ESI-MS and CID, the preferential solvation of Li^+ cations and the relative strength of interaction were determined. Not only does the solvation preference of Li^+ vary with different solvents, but also the solvent molecules in the solvation shell alter the Lewis acidity of the solvated Li^+ ions. Low acidity is exhibited by the Li^+ that is solvated with the solvent molecules that have a high strength of interaction with Li^+ . The difference in the acidity for the solvated Li^+ ions was demonstrated through the catalytic disproportionation of the $\text{O}_2^{\bullet-}$ formed during the reduction of O_2 in the corresponding electrolyte.

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Notes

The authors declare no competing financial interest.

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