BNL-108382-2015-JA

Preferential Solvation of Lithium Cations and the Impacts on the Oxygen Reduction in Li-Air Batteries

Dong Zheng[†], *Deyu Qu*[§], *Xiao-Qing Yang*[‡], *Hung-Sui Lee*[‡], *Deyang Qu*[*†]

† Department of Mechanical Engineering, College of Engineering and Applied Science, University of Wisconsin Milwaukee, Milwaukee, WI 53211,USA

§Department of Chemistry, School of Chemistry, Chemical Engineering and Life Science, Wuhan University of Technology, Wuhan 430070, Hubei, P.R. China

‡ Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973,USA

*****qud@uwm.edu

ABSTRACT

The solvation of Li^+ with eleven non-aqueous solvents commonly used as the electrolytes for Li batteries were 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 $O_2^{\cdot -}$ 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

1. 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. So Li-O_2 has attracted much research attentions of research in the recent years. Besides the long-time challenges for the rechargeable metallic Li anode, the rechargeable O_2 cathode in non-aqueous electrolytes is still a ways from practicality. The detail mechanisms of O_2 reduction in non-aqueous electrolytes are still not fully understood. It is well know that O_2 reduction in a non-aqueous electrolyte is a 1-e reaction and superoxide ($O_2^{\cdot -}$) is the reduction product.[1] The redox reaction is very reversible. Most of the early studies for O_2 reduction in non-aqueous electrolyte were done in the electrolyte without Li salt.[2] In our early reports,[3,4] a Lewis acid was found to facilitate the catalytic disproportionation of $O_2^{\cdot -}$ and the catalytic activity seemed to related to the acidity of the Lewis acid. The Li^+ cation is a Lewis acid and was proven to catalyze the disproportionation of $O_2^{\cdot -}$.

Recently, the mechanism for the O_2 redox reaction in non-aqueous 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 the Pearson's hard soft acid base (HSAB) theory.[5,6] Indeed, decent rechargeabilty 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 a Roman spectroscopy. Through comparing 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 interpretation of the obtained Roman 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 have survived the ionization process and remained 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, since each m/z ratio represents one intact solvated Li^+ ion.[14]

In this work, ESI-MS was used to investigate the Li^+ solvation with eleven of the most common solvents used in Li batteries. The collision-induced dissociation (CID) spectra of the lithiated adduct $[X+Li+Y]^+$ was also investigated. In addition, the impact of the solvated Li^+ with different solvents on the O_2 redox reaction was investigated.

2. 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 ($DMSO^{d6}$), 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 1:1 molar ratio, lithium tetrafluoroborate ($LiBF_4$, battery grade from FERRO) was used as the lithium salt at a concentration of 5mM. All electrolytes were prepared in Ar filled glove box (O_2 and moisture <5 ppm) and sealed in air-tight 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 following: Capillary 2.60kV, Cone 20V, Extractor 0V, RF lens 0.5V, Source temperature 100°C, Desolvation temperature 250°C, N_2 gas flow is 50L/hr for Nebuliser and 600L/hr 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, and collision voltage was set at 20, and argon as the collision gas. The 1:1 binary solvent electrolyte with 5mM $LiBF_4$ was introduced into the mass spectrometer through a syringe pump at flow rate of 40µL/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 cm^2) was used as the working electrode. Pt wire electrode and Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively.

3. RESULTS AND DISCUSSION

One of the remaining arguments regarding using the ESI-MS technique to determine the solvation numbers is whether the number of the solvent molecules in the solvation shell changes

after vaporization during the ESI process. Figure 1 shows typical ESI-MS spectra for the 5mM $LiBF_4$/DMSO/DMSO^{d6} electrolyte. Normally the lithiated adducts solvated with 1 to 3 solvent molecules are readily observed in ESI-MS spectra while the lithiated adducts with 4 and more solvent 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.

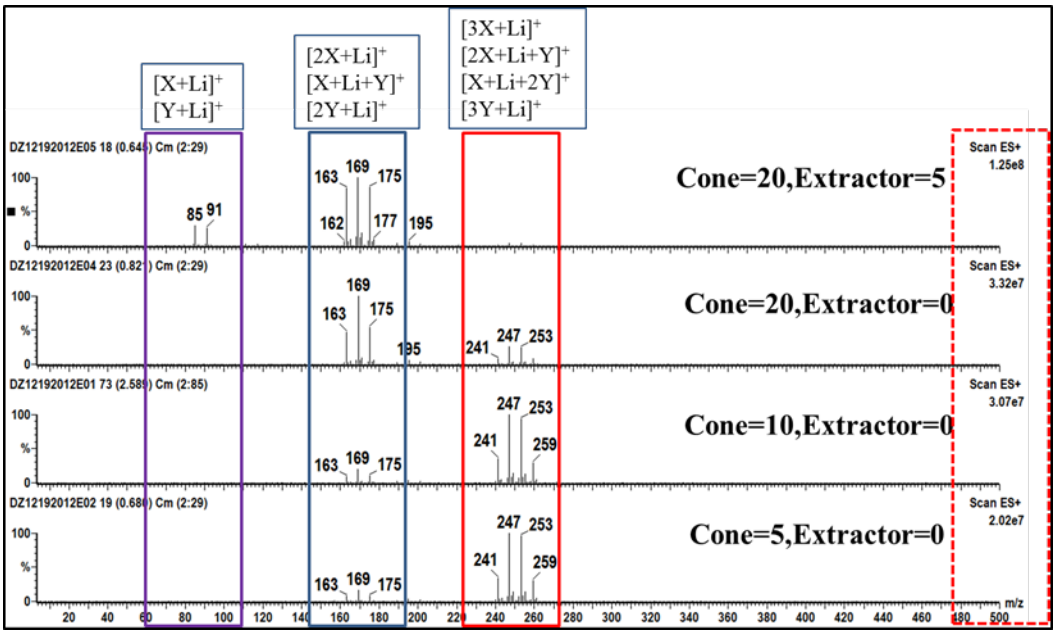


Figure 1. The ESI-MS spectra of DMSO and DMSO^{d6} (1:1) mixture with 5mM $LiBF_4$ under different ESI-MS conditions (different Cone and Extractor voltages). X=DMSO (M.W.=78), Y= DMSO^{d6} (M.W.=84); for adduct $[X+Li]^+$ m/z=85, for adduct $[Y+Li]^+$ m/z=91, for adduct $[2X+Li]^+$ m/z=163, for adduct $[X+Li+Y]^+$ 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, for adduct $[3Y+Li]^+$ m/z=259. The absolute intensities of the most abundant adduct for each MS spectra under different ESI condition were listed on the right of each 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 dash 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 or10 V), the majority species in the ESI-MS spectra are Li^{+} cations coordinated with 3 solvent molecules and with the minor species of Li^{+} cations coordinated with 2 solvent molecules. However, at high Cone voltage (20V), the majority species in ESI-MS spectra are Li^{+} cations coordinated with 2 solvent molecules with the minor species of Li^{+} cations coordinated with 3 solvent molecules. When the Extractor voltage increases from 0 to 5 V (Cone= 20 V), the majority species in ESI-MS spectra were Li^{+} cations coordinated with 2 solvent molecules and with the minor species of Li^{+} cation coordinated with just 1 solvent molecule. Obviously, the number of the solvent molecules remained in the solvated Li^{+} ions in the gas is the influenced by the ESI conditions due to the in-source fragmentation of lithiated adducts in ESI source.

In order to quantitatively calculate the statistic 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 non-selectively, then the relative ratio of different solvents in the adducts should solely depend on the relative ratio of the different solvents in the electrolyte. Since the substitution of hydrogen with deuterium in DMSO has little influence on solvation, the DMSO and $DMSO^{d6}$ solvents were used as the non-selective solvent to further validate the method proposed by Xu.[14] The ESI-MS spectra of the 5mM $LiBF_4$/DMSO/$DMSO^{d6}$ 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 non-selective solvation of DMSO/DMSO^{d6}. 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 1. The comparison of the relative abundance of 5mM $LiBF_4$/DMSO/DMSO^{d6} electrolyte under different ESI-MS conditions with theoretical non-selective solvation. C is the Cone voltage and E is the Extractor voltage, both are parameters in the ESI source. The relative abundance for each lithiated adducts is normalized to the highest abundance species (which is the 100 percent). Smaller number means lower relative abundance. The relative abundance of non-selective solvation is obtained by statistical calculation: when the DMSO and DMSO^{d6} are in the 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).

Solvation number	Li^+ adducts	Relative Abundance				
		C=20V E=5V	C=20V E=0V	C=10V E=0V	C=5V E=0V	Non-selective solvation
1	$[DMSO+Li]^+$	100	100	100	87.5	100
	$[DMSO^{d6}+Li]^+$	88.5	86.7	91.1	100	100
2	$[2DMSO+Li]^+$	84.2	47.0	48.6	53.5	50
	$[DMSO+DMSO^{d6}+Li]^+$	100	100	100	100	100
	$[2DMSO^{d6}+Li]^+$	85.8	54.5	54.3	54.1	50
3	$[3DMSO+Li]^+$	35.7	33.8	35.0	34.2	33.3
	$[2DMSO+DM\ SO^{d6}+Li]^+$	100	100	100	100	100
	$[DMSO+2DMSO^{d6}+Li]^+$	96.1	99.4	93.9	95.9	100
	$[3DMSO^{d6}+Li]^+$	30.1	32.6	29.5	30.7	33.3

Table 2 tabulates the relative distributions of solvent molecules in the solvated Li^+ ion obtained from the ESI-MS spectra for the eleven binary electrolytes. Again, in the electrolyte containing the mixture of 1:1 (mole ratio) DMSO and DMSO^{d6}, the relative distribution of DMSO and DMSO^{d6} in the solvated Li^+ ion was close to 1:1. For the binary electrolytes with DMSO mixed

with other solvents at 1:1 ratio, the mol% of DMSO in the solvation shell varies from 43% to 98%. The results clearly demonstrated the preferential solvation of Li^+ cations for different solvents, since the distribution of solvents in the solvated Li^+ ion diverged from that in the electrolyte solutions.

Table 2. Relative molar ratio of different solvents in the Li^+ solvation adducts obtained from ESI-MS spectra of 5mM $LiBF_4$ DMSO and other solvents (1:1) mixture. The voltages of Cone and Extractor are 20 and 0V for ESI-MS.

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	$DMSO^{d6}$	51.1

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 and BF_3 affinities as reported in the literature, both of which have been used to indicate solvent basicity.[6,17] By comparing the DNs tabulated 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 mol% in the solvation sheath, while diethylene glycol dimethyl ether (DEDME), which has a moderate DN value, shows the highest mol% in the solvation shell. Similar inconsistences were also observed in other publications which indicates the limitation of evaluating the solvation

preference using DNs.[13] Since 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.

Table 3. The Lewis basicity of different solvents summarized from published literatures. [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

To understand the relative strength of the interaction between the solvent molecules and the Li^+ in a solvation shell, the collision-induced dissociation spectra (CID) was used. The lithiated adducts $[DMSO+Li+Y]^+$ (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): $[DMSO+Li]^+$ and $[Y+Li]^+$. The scheme is shown in figure 2. Since the formation of $[DMSO+Li]^+$ or $[Y+Li]^+$ needs to overcome the interaction between Li^+ and Y or Li^+ and DMSO, by comparing the relative abundances of $[DMSO+Li]^+$ and $[Y+Li]^+$ 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 $[Y+Li]^+$ in the CID spectra would be lower. Conversely, if DMSO has a weaker interaction with Li^+ then the abundance of $[DMSO+Li]^+$ in the CID spectra would be lower. Figure 2 shows the CID spectra of $[DMSO+Li+DMSO^{d6}]^+$. Due to the fact that DMSO and

DMSO^{d6} have the same strengths of the interaction with Li^+, the relative abundances of $[DMSO+Li]^+$ and $[DMSO^{d6}+Li]^+$ in the CID spectra are almost the same. The relative abundances of the daughter ions in the CID spectra for the different $[DMSO+Li+Y]^+$ parent ions are summarized in table 4. The data in table 4 is consistent with that shown in table 2: the solvent that had a stronger interaction with Li in the solvation shell showed a higher mol% in the solvation sheath. The only exception is DME, which showed a higher relative abundance in CID spectrum but a lower mol% in the Li^+ solvation shell than DMSO. This phenomenon could be attributed to the bidentate interaction between DME and Li^+ in the $[DMSO+Li+Y]^+$ parent ions.

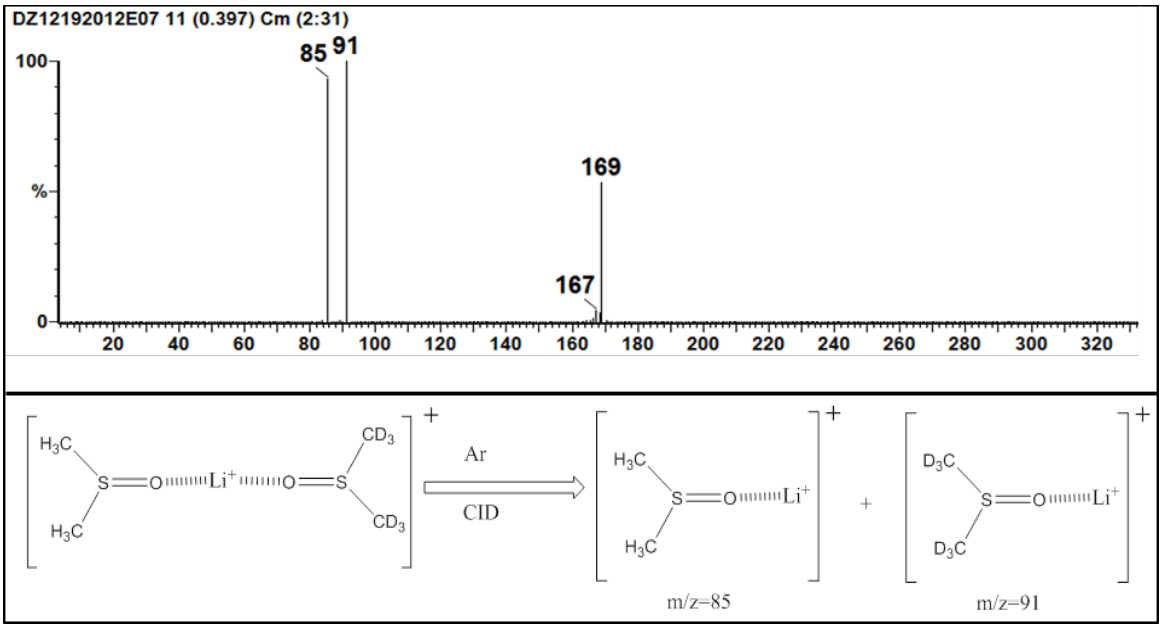


Figure 2. The CID spectra of $[DMSO+Li+DMSO^{d6}]^+$ obtained at collision voltage= 20V, and the scheme of CID procedure.

The local structure of solvation around a Li^+ cation in a mixed solvent electrolyte plays important roles 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 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 O_2 redox reaction were attributed to the alteration of the acidity of the solvated Li^+ cation. The superoxide ($O_2^{\cdot-}$), which is the product of O_2 reduction, is a Lewis base and can be catalytically disproportioned 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. Figures 3A and B show the cyclic voltammetry profiles at various scan rates for a glassy carbon electrode in the O_2 saturated DMSO solution containing 1M tetraethyl ammonium tetrafluoroborate ($TEABF_4$) and 1M $LiBF_4$, respectively.

Table 4. The relative abundance of daughter ions for the CID spectra of $[DMSO+Li+Y]^+$.

CID 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	$[DMSO^{d6}+Li]^+$	100

A pair of very symmetric O_2 reduction (-0.95 *vs.* Ag/AgCl) and O_2^- 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 one, remained the same at various scan rates. Since $TEABF_4$ has little Lewis acidity, $O_2^{\cdot-}$ anions formed during the reduction were stable in DMSO and eventually got oxidized during the positive scan. A ratio of slightly lower than one at lower scan rate resulted

from the loss of $O_2^{\cdot-}$ species since they had longer time to diffuse away from the electrode surface. Figure 3B shows the cyclic voltammetry for the same electrode in the O_2 saturated DMSO solution, except $TEABF_4$ was replaced with $LiBF_4$. As an Lewis acid, the Li^+ cation is able to catalyze the disproportionation of $O_2^{\cdot-}$ anions.[4] Thus, O_2^- anions formed on the surface of the glassy carbon electrode during the reduction of O_2 were catalytically disproportioned by Li^+, and the remaining $O_2^{\cdot-}$ anions were oxidized on the electrode surface during the oxidation scan. Therefore, the ratio between the anodic and cathodic peak area 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 area, since more $O_2^{\cdot-}$ species survived from disproportionation. However, when there is sufficient time allowed at a low scan rate, O_2^- 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 since no O_2^- remains to be oxidized. The trend is clearly demonstrated in figure 3B.

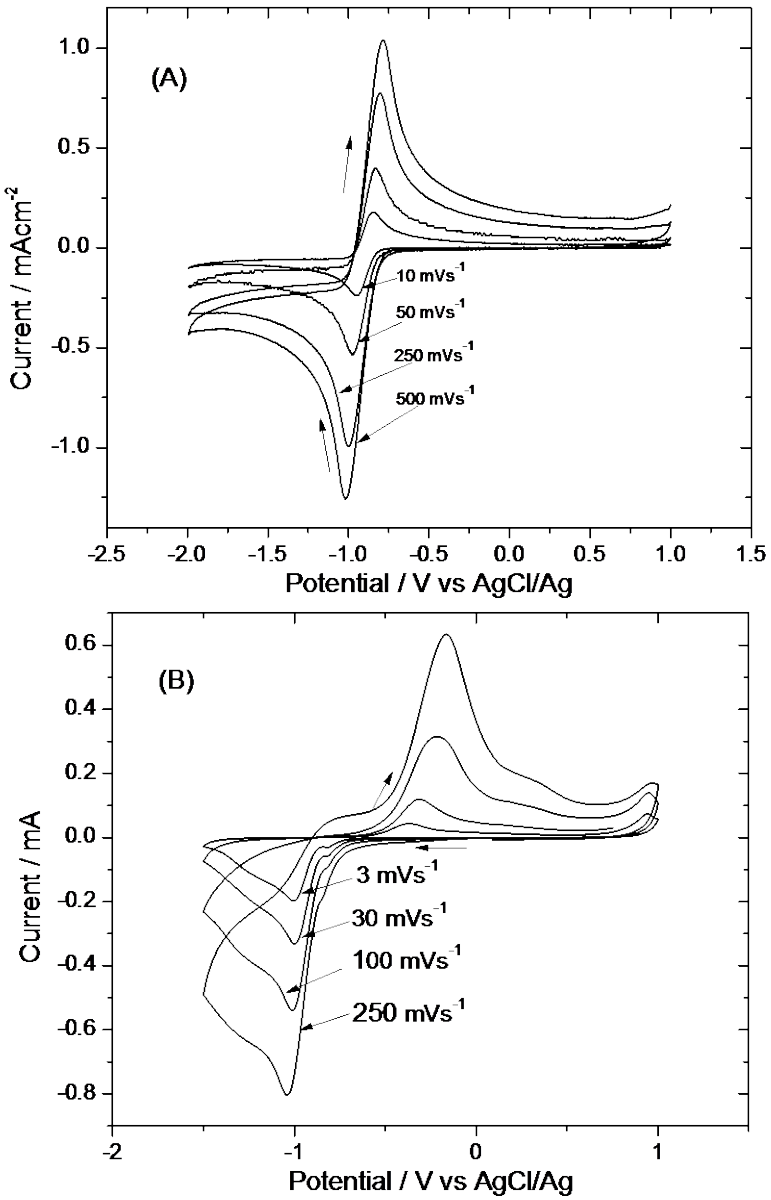


Figure 3. Cyclic voltammograms at various scan rates in 1 M TEABF4 DMSO electrolyte (A) and 1 M $LiBF_4$ DMSO electrolyte (B) saturated with O_2 on a glassy carbon-disc electrode.

Figure 4 shows the change in the ratio between the anodic and cathodic peak area with the scan rate in various electrolytes. The solvents chosen to be shown in the figure don't react with $O_2^{\cdot-}$. Clearly, the anodic and cathodic peak area ratio for the O_2 redox reaction in $TEABF_4$ DMSO is close to one. At a 3 mVs^{-1} scan rate, the ratios for the O_2 redox reaction in $LiBF_4$ with various

solvents were close to zero, almost all $O_2^{\cdot -}$ ions were disproportioned. As the scan rate was increased, the ratio also increased. The ratio between the anodic and cathodic peak area was also solvent related as shown in figure 4. Comparing figure 4 and table 2, one can conclude that more $O_2^{\cdot -}$ 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 towards the disproportionation of $O_2^{\cdot -}$ is related to the Lewis acidity of the solvated ion and that the Lewis acidity of a Li^+ ion is reduced when solvated with the a solvent that strongly interacts strength with Li^+ as shown in scheme 1

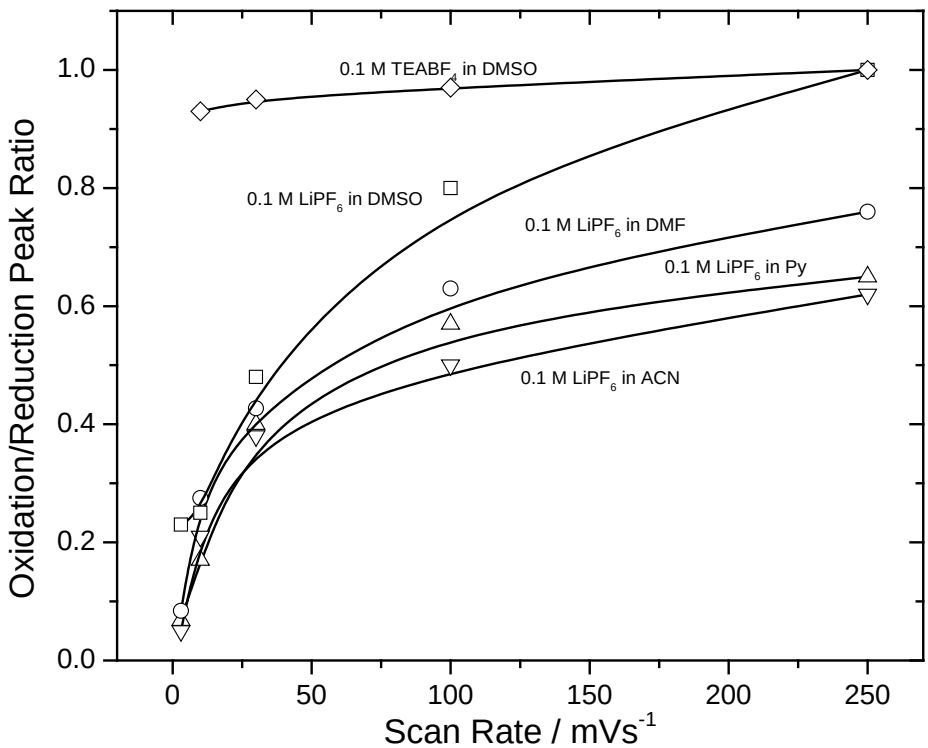
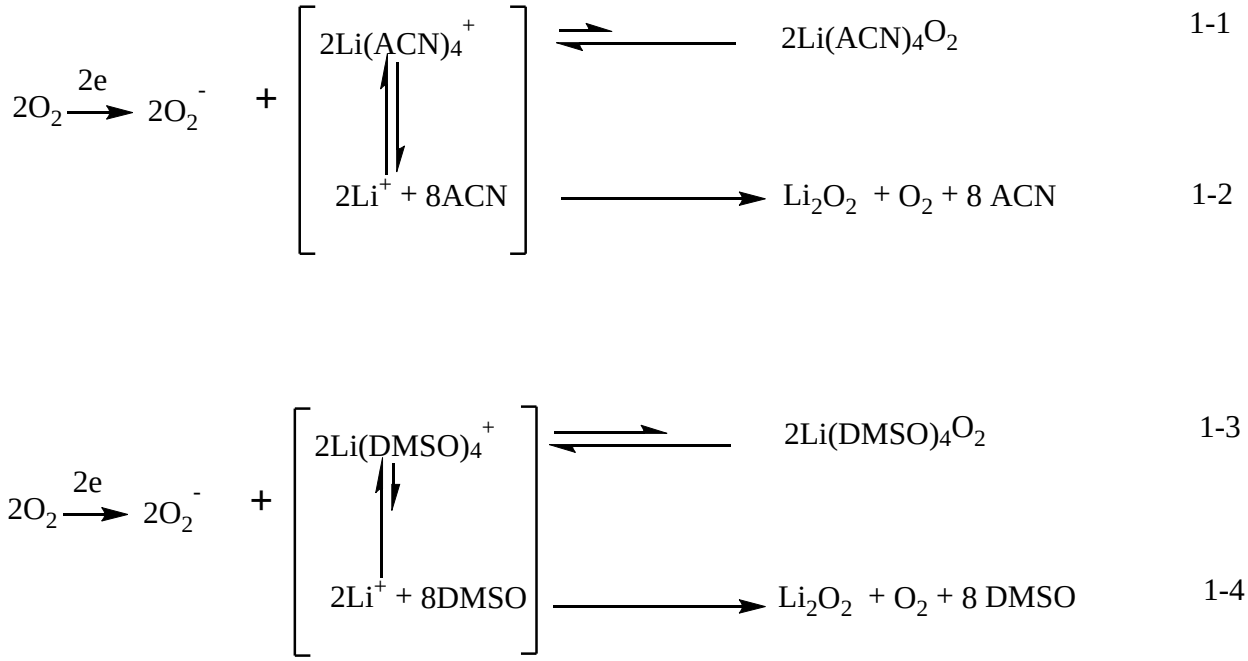


Figure 4. Comparison of the ratio between the anodic and cathodic peak area for the O_2 redox reaction in various electrolytes.



Scheme 1. The proposed mechanism: the impact of the strength of the solvent for the solvation of Li^+ on the disproportionation of the electrochemically generated $O_2^{\cdot-}$. Acetonitrile (ACN) and dimethyl sulfoxide (DMSO) are used as example.

One could argue that the interaction between $O_2^{\cdot-}$ 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 to the oxidation/reduction peak ratio for the O_2 reduction was studied in details. The oxidation/reduction peak ratio was found dependent on the CV scan rate in the tetraethylammonium/PC electrolyte because $O_2^{\cdot-}$ was consumed by its reaction with PC. The instability of many solvents against $O_2^{\cdot-}$ 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 less than an hour. For example, no changes can be observed when DMSO was mixed with KO_2 for 24 hours, the instability of DMSO can only be evident after mixing with KO_2 for two month [22]. Of course, DMSO was reported not stable at carbon fiber electrode[24]. It is worth to pointing out that $O_2^{\cdot-}$ would survive longer in an solvent with stronger solvation of Li^+, which could consequently increase the instability of the electrolyte.

Although the impacts of solvation to the alteration of Lewis acidity and the catalysis superoxide disproportionation were the focus of the report, it is also worth to emphasizing that the solvation may be also important to the formation of surface layers e.g. on Li-ion anode, since affinity of solvents with Li cations may alter their reaction on the electrode surface. The importance of solvent in the Li-air batteries were well documented.[24]

4. 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. The low acidity is exhibited by the Li^+ that is solvated with the solvent molecules that have a high strength of interaction with Li^+. The differences in the acidity for the solvated Li^+ ions was demonstrated through the catalytic disproportionation of the $O_2^{\cdot -}$ formed during the reduction of O_2 in the corresponding electrolyte.

AUTHOR INFORMATION

Corresponding Author

* D.Y. Qu. E-mail: qud@uwm.edu

ACKNOWLEDGMENT

This work was supported by the U.S. Department of Energy, the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies under Contract Number DE-SC0012704.

REFERENCES

(1) Lorenzola, T.A.; Lopz, B.A.; Giordano, M.C. Molecular Oxygen Electroreduction at Pt and Au Electrodes in Acetonitrile Solutions. *J. Electrochem. Soc.*, **1983**, *130*, 1359-1365.

(2) Sawyer, D.T.; Ghierlcato, F.; Angells, C.T.; Nannl, E.J.; Tsuchlya, T. Effects of Media and Electrode Materials on the Electrochemical Reduction of Dioxygen. *Anal. Chem.*, **1982**, *5*, 1720-1724.

(3) Zheng, D.; Wang, Q.; Lee, H-S; Yang, X.Q.; Qu**,** D.Y. Catalytic Disproportionation of the Superoxide Intermediate from Electrochemical O_2 Rreduction in Nonaqueous Electrolytes. *Chem. –Eur. J.*, **2013**, *19*, 8679-8683.

(4) Wang, Q.; Zheng, D.; McKinnon, M.E.; Yang, X.Q.; Qu, D.Y. Kinetic Investigation of Catalytic Disproportionation of Superoxide Ions in the Non-aqueous Electrolyte Used in Li-Air Batteries. *J. Power Sources*, **2015**, *274*, 1005-1008.

(5) Laorie, C.O.; Mukerjee, S.; Abraham, K.M.; Plichta, E.J.; Hendrickson, M.A. Elucidating the Mechanism of Oxygen Reduction for Lithium-Air Battery Applications. *J. Phys. Chem. C*, **2009**, *113*, 20127-20134.

(6) Laorie, C.O.; Mukerjee, S.; Abraham, K.M.; Plichta, E.J.; Hendrickson, M.A. Influence of Nonaqueous Solvents on the Electrochemistry of Oxygen in the Rechargeable Lithium−Air Battery. *J. Phys. Chem. C*, **2010**, *114*, 9178-9186.

(7) Peng, Z.Q.; Freunberger, S.A.; Chen, Y.H.; Bruce, P.G. A Reversible and Higher-rate Li-O_2 Battery. *Science*, **2012**, *337*, 563-566.

(8) Klassen, B.; Aroca, R.; Nazri, M.; Nazri, G.A. Raman Spectra and Transport Properties of Lithium Perchlorate in Ethylene Carbonate Based Binary Solvent Systems for Lithium Batteries. *J. Phys. Chem. B*, **1998**, *102*, 4795-4801.

(9) Brouillette, D.; Irish, D.E.; Taylor, N.J.; Perron, G.; Odziemkowski, M.; Desnoyers, J.E. Stable Solvates in Solution of Lithium Bis(trifluoromethylsulfone)imide in Glymes and Other Aprotic Solvents: Phase Diagrams, Crystallography and Raman Spectroscopy. *Phys. Chem. Chem. Phys.*, **2002**, *4*, 6063-6071.

(10) Seo, D.M.; Borodin, O.; Han, S.D; Ly, Q.; Boyle, P.D.; Henderson, W.A. Electrolyte Solvation and Ionic Association I. Acetonitrile-Lithium Salt Mixtures: Intermediate and Highly Associated Salts. *J. Electrochem. Soc.*, **2012**, *159*, A553-A565.

(11) Seo, D.M.; Borodin, O.; Han, S.D; Ly, Q.; Boyle, P.D.; Henderson, W.A. Electrolyte Solvation and Ionic Association II. Acetonitrile-Lithium Salt Mixtures: Highly Associated Salts. *J. Electrochem. Soc.*, **2012**, *159*, A1489-A1500.

(12) Fukushima, T.; Matsuda, Y.; Hashimoto, H.; Arakawa, R. Studies on Solvation of Lithium Ions in Organic Electrolyte Solutions by Electrospray Ionization-Mass Spectroscopy. *Electrochem. Solid-State Lett.*, **2001**, *4*, A127-A128.

(13) Matsuda, Y.; Fukushima, T.; Hashimoto, H.; Arakawa, R. Solvation of Lithium Ions in Mixed Organic Electrolyte Solutions by Eectrospray Ionization Mass Spectroscopy. *J. Electrochem. Soc.*, **2002**, *149*, A1045-A1048.

(14) Cresce, A. von; Xu, K. Preferential Solvation of Li^+ Directs Formation of Interphase on Graphitic Anode. *Electrochem. Solid-State Lett.*, **2011**, *14*, A154-A156.

(15) Gutmann, V. Empirical Parameters for Donor and Acceptor Properties of Solvents. *Electrochim. Acta*, **1976**, *21*, 661-670.

(16) Matsuda, Y. Stable Electrolytes for Lithium Batteries. *J. Power Sources*, **1987**, *20*, 19-26.

(17) Laurence, C.; Gal, J.F. Lewis Basicity and Affinity Scales: Data and Measurement, *John Wiley & Sons*, Chichester UK, **2010**.

(18) Bryantsev, V.C.; Giordani, V.; Walker, W.; Blanco, M.; Zecevic, S.; Sasaki, K., Uddin, J.; Addison, D.; Chase, G.V. Predicting Solvent Stability in Aprotic Electrolyte Li-Air Batteries : Nucleophilic Substitution by the Superoxide Anion Radical ($O^{\cdot-}$). *J. Phys. Chem. A*, **2011**, *115*, 12399-12409.

(19) Ye, L.H.; Lv, W.Q.; Cui, J.Y.; Liang, Y.C.; Wu, P.; Wang, X.N.; He, H.; Lin, S.J.; Wang, W.; Dickerson, J.H.; He, W.D. Lithium-Air Batteries: Performance Interplays with Instability Factors. *ChemElectroChem*, **2015**, *2*, 312-323.

(20) Takechi, K.; Higashi, S.; Mizuno, F.; Nishikoori, H.; Iba, H.; Shiga, T. Stability of Solvents against Superoxide Radical Species for the Electrolyte of Lithium-Air Battery. *ECS Electrochem. Lett.*, **2012**, *1*, A27-A29.

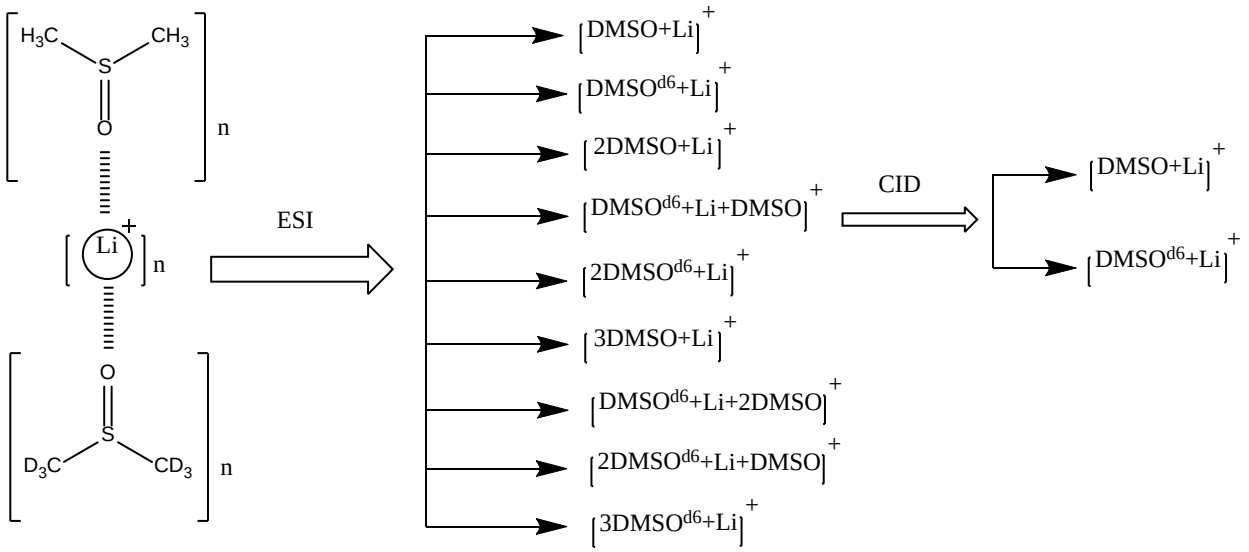
(21) Schwenke, K.U.; Meini, S.; Wu, X.H.; Gasteiger, H.A.; Piana, M. Stability of Superoxide Radicals in Glyme Solvents for Non-aqueous Li-O_2 Battery Electrolytes. *Phys. Chem. Chem. Phys.*, **2013**, *15*, 11830-11839.

(22) Mozhzhukhina, N.; De Leo, L.P.M.; Calvo, E.J. Infrared Spectroscopy Studies on Stability of Dimethyl Sulfoxide for Application in Li-Air Battery. *J. Phys. Chem. C*, **2013**, *117*, 18375-18380.

(23) Kwabi, D.G.; Batcho, T.P.; Amanchukwu, C.V.; Ortiz-Vitoriano, N.; Hammond, P.; Thompson, C.V.; Shao-Horn, Y. Chemical Instability of Dimethyl Sulfoxide in Lithium-Air Batteries. *J. Phys. Chem. Lett.*, **2014**, *5*, 2850-2856.

(24) Sharon, D.; Afri, M.; Noked, M.; Garsuch, A.; Frimer, A.; Aurbach, D. Ocidation of Dimethyl Sulfoxide Solutions by Electrochemical Reduction of Oxygen. *J. Phys. Chem. Lett.*, **2013**, 4, 3115-3119.

(24) Lu, J.; Li, L.; Park, J.B.; Sun, J.K.; Wu, F.; Amine, K. Aprotic and Aqueous Li-O_2 Batteries. *Chem. Rev.* **2014**, *114*, 5611-5640.

TABLE OF CONTENTS GRAPHIC AND SYNOPSIS

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. And the impact of the solvated Li^+ cation on the O_2 redox reaction was also investigated.