Supporting information for: Trade-offs in Capacity and Rechargeability in nonaqueous Li-O_2 Batteries: Solution-driven Growth vs Nucleophilic Stability

Abhishek Khetan[†,‡], Alan Luntz[§] and Venkatasubramanian Viswanathan[*,‡]
[†] Institute for Combustion Technology, RWTH, Aachen, Germany, 52056
[§] SUNCAT, SLAC National Accelerator Laboratory, Menlo Park, CA 94025-7015
[‡] Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, 15213
*** E-mail: venkvis@cmu.edu**

I. Half-wave potential of the Li^+/Li redox couple in various solvents.

Table S1 lists the Li^+/Li redox couple half-wave potential in various nonaqueous solvents, measured with respect to the Bis(biphenyl)chromium(I)/(0) redox couple [1]. The Gutmann Donor numbers (DN) have also been taken from the same sources [1,5].

SN	CAS	Solvent	Li^+/Li half-wave potential (V)	DN (kcal/mol)
1	123397	N-methylformamide (C_2H_5NO)	-1.66	27.0
2	68122	N,N-dimethylformamide (C_3H_7NO)	-1.62	26.6
3	617845	N,N-diethylformamide ($C_5H_{11}NO$)	-1.61	30.9
4	127195	N,N-dimethylacetamide (C_4H_9NO)	-1.69	27.8
5	685916	N,N-diethylacetamide ($C_6H_{13}NO$)	-1.76	32.2
6	872504	1-methyl-2-pyrrolidinone (C_5H_9NO)	-1.72	27.3
7	67685	Dimethylsulfoxide (C_2H_6SO)	-1.86	29.8
8	208252544	Tetramethylenesulfone ($C_4H_8O_2S$)	-1.26	14.8
9	67561	Methanol (CH_4O)	-1.49	19.0

10	67641	Acetone (C_3H_6O)	-1.40	17.0
11	108327	Propylene carbonate ($C_4H_6O_3$)	-1.25	15.1
12	512561	Trimethyl phosphate ($C_3H_9O_4P$)	-1.72	23.0
13	75058	Acetonitrile (C_2H_3N)	-1.20	14.1
14	632224	N,N,N,N-tetramethylurea ($C_5H_{12}N_2O$)	-1.76	31.0
15	100470	Benzonitrile (C_7H_5N)	-1.11	11.9

Table S1. Shift in the half-wave potentials for the Li^+/Li redox couple in different nonaqueous solvents with respect to the Bis(biphenyl)chromium(I)/(0) couple and solvents' Gutmann Donor numbers.

II. Half-wave potential of the O_2/O_2^- redox couple in various solvents.

Table S2 lists the O_2/O_2^- redox couple half-wave potential in various nonaqueous solvents, measured with respect to the Standard Calomel Electrode [2]. The half-wave potential values for solvents DMA (SN.6) and DEF (SN.7) were originally measured with respect to the Fc^+/Fc electrode in ref. [3]. We calibrated those values with respect the Standard Calomel Electrode using the data for the potential of the Fc^+/Fc redox couple with respect to the Standard Calomel Electrode from ref.[4]. $E^{Fc+/Fc}{}_{SCE}$= 0.467for DMA (SN.6) and $E^{Fc+/Fc}{}_{SCE}$=0.474 for DEF (SN.7). The Gutmann Acceptor numbers (AN) values were taken from ref.[5] and were calculated for the case of solvent DEF (SN.7) using the correlation $AN= -30.0+15.3\times\alpha+1.01\times E_T^{(30)}$ from the same work, where $\alpha = 0.0$ is the hydrogen bond donor ability and $E_T^{(30)} = 41.8$ is the Dimroth and Reichardt's polarity of DEF (SN.7).

SN	CAS	Solvent	Li^+/Li half-wave potential (V)	AN (kcal/mol)
1	7732185	Water (H_2O)	-0.410	54.8
2	67685	Dimethylsulfoxide (C_2H_6SO)	-0.780	19.3
3	68122	N,N-dimethylformamide (C_3H_7NO)	-0.860	16.0
4	110861	Pyridine (C_5H_5N)	-0.880	14.2
5	75058	Acetonitrile (C_2H_3N)	-0.870	18.9

6	127195	N,N-dimethylacetamide (C_4H_9NO)	-0.953	13.6
7	617845	N,N-diethylformamide ($C_5H_{11}NO$)	-0.976	12.2

Table S2. Shift in the half-wave potentials for the O_2/O_2^- redox couple in different nonaqueous solvents with respect to the Standard Calomel Electrode and solvents' Gutmann Acceptor numbers.

III. Data for pK_a values in DMSO, AN and DN for solvents in the Fig. 3 and Fig. 4

Table S3 lists the data for the experimentally determined or calculated pK_a values in DMSO as well as the solvents' Gutmann Acceptor (AN) and Donor (DN) numbers. Also mentioned in the table are the free energy of dissolution, $\Delta G^{sol}_{(HA)}$, and the rate of nucleophilic attack normalized with respect to the value for MeCN. For several solvents where the pK_a values were not available in DMSO, the linear correlation from our previous work [6] was used to predict the pK_a value in DMSO using the pK_a value in water by using the equation: pK_a(in DMSO) = (pK_a(in Water) + 6.3644)/1.0069. The reference for each pK_a value is mentioned in the last column. The Gutmann Acceptor and Donor numbers were taken from ref.[5,7,8]. Figure S1 shows all the points on the quadrant plot just like Fig. 4.

SN	CAS	Solvent	pKa in DMSO	AN (kcal-mol$^-$)	DN (kcal-mol$^-$)	$\Delta G^{sol}_{(HA)}$ (eV)	Rate	pka ref
1	872504	1-methyl-2-pyrrolidinone (C_5H_9NO)	35.2	13.3	27.3	-3.67E-01	1.61E+04	[9]
2	67663	Trichloromethane ($CHCl_3$)	20.2	23.1	4.0	7.26E-01	2.27E-07	[10]
3	141786	Ethyl acetate ($C_4H_8O_2$)	29.5	9.3	17.1	4.53E-02	1.38E+00	[11]
4	71363	1-butanol ($C_4H_{10}O$)	23.2	36.8	19.5	-5.56E-01	2.49E+13	[12]
5	75650	1,1-dimethyl-ethanol ($C_4H_{10}O$)	29.4	27.1	21.9	-5.12E-01	3.36E+09	[13]
6	110714	1,2-dimethoxy-ethane ($C_4H_{10}O_2$)	51.8	10.2	20.0	-1.06E-01	3.38E-09	[9]
7	75127	Formamide (CH_3NO)	23.5	39.8	24.0	-7.36E-01	1.76E+16	[11]

8	68122	Dimethylformamide (C_3H_7NO)	42.9	16.0	26.6	-4.17E-01	1.53E+01	[9]
9	127195	Dimethylacetamide (C_4H_9NO)	34.4	13.6	27.8	-3.80E-01	6.55E+04	[9]
10	75058	Acentonitrile (C_2H_3N)	31.3	18.9	14.1	0.00E+00	1.00E+00	[11]
11	67685	Dimethylsulfoxide (C_2H_6SO)	35.1	19.3	29.8	-5.13E-01	5.06E+06	[11]
12	67641	Acetone (C_3H_6O)	26.5	12.5	17.0	-2.52E-02	6.64E+02	[11]
13	7732185	Water (H_2O)	32.0	54.8	18.0	-6.19E-01	1.07E+10	[13]
14	64197	Acetic acid ($C_2H_4O_2$)	12.3	52.9	20.0	-6.99E-01	1.65E+21	[13]
15	67561	Methanol (CH_4O)	27.9	41.5	19.0	-5.83E-01	3.03E+11	[13]
16	67630	Isopropyl alcohol (C_3H_8O)	29.3	33.8	21.1	-5.81E-01	5.50E+10	[13]
17	512561	Trimethyl phosphate ($C_3H_9O_4P$)	9.3	16.3	23.0	-3.45E-01	6.06E+16	[14]
18	100470	Benzonitrile (C_7H_5N)	21.9	15.5	11.9	2.14E-01	1.31E+01	[11]
19	64186	Formic acid (CH_2O_2)	10.0	83.6	19.0	-5.53E-01	8.05E+19	[15]
20	71432	Benzene (C_6H_6)	49.0	8.2	0.1	1.46E+00	5.18E-34	[16]
21	100516	Benzyl alcohol (C_7H_8O)	21.2	36.8	23.0	-6.78E-01	2.48E+16	[17]
22	64175	Ethanol (C_2H_6O)	29.8	37.9	19.2	-5.56E-01	1.17E+10	[11]
23	98953	Nitrobenzene ($C_6H_5NO_2$)	10.3	14.8	4.4	8.52E-01	1.70E-04	[18]

24	75525	Nitromethane (CH_3NO_2)	16.3	20.5	2.7	9.06E-01	2.19E-08	[19]
25	67630	i-propanol (C_3H_8O)	30.3	33.5	36.0	-6.94E-01	1.36E+12	[11]
26	75650	t-butanol ($C_4H_{10}O$)	32.2	27.1	38.0	-5.55E-01	7.06E+08	[11]

Table S3. List of solvents with experimentally measured or calculated or estimated pK_a values in DMSO, Gutmann Acceptor and Donor Numbers, free energy of dissolution, $\Delta G^{sol}_{(HA)}$, and the rate of nucleophilic attack normalized with respect to the value for MeCN

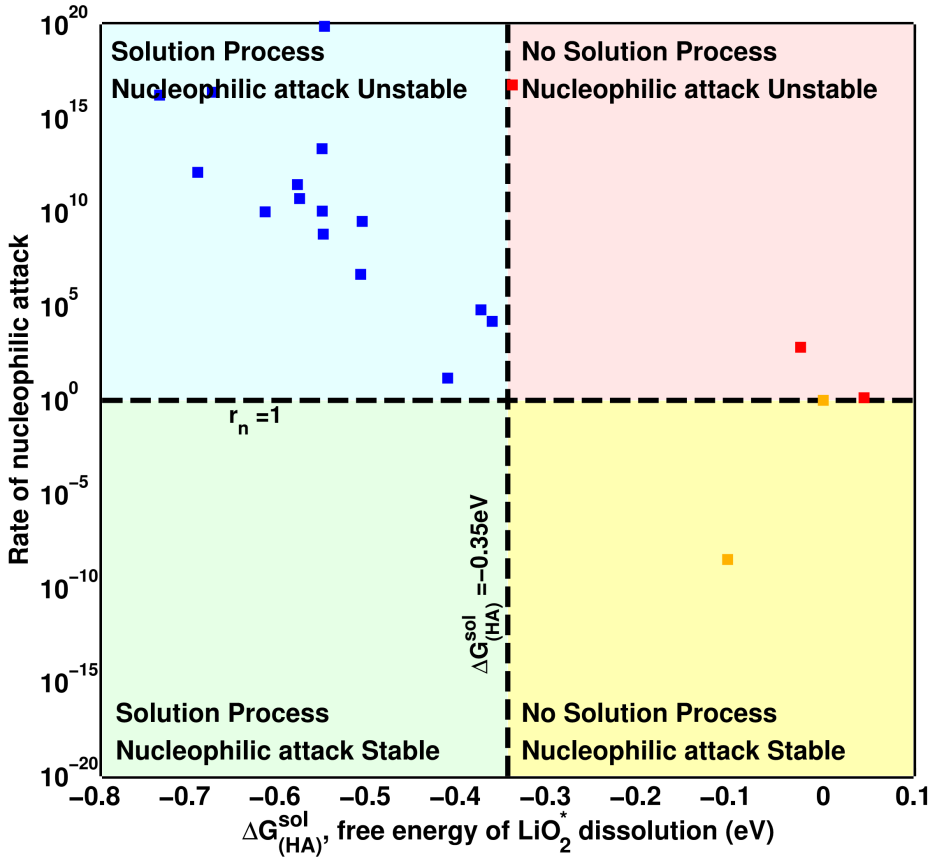

Figure S1. Solvent with free energy of dissolution, $\Delta G^{sol}_{(HA)}$, and the rate of nucleophilic attack normalized with respect to the value for MeCN like in Fig.4.

IV. H-abstraction pathway for degradation of solvents during nucleophilic attack by O_2^- anion.

Similar to the proton abstraction, another likely mechanism for solvent degradation can be described as given in Eq. (7) in the main text

$$O^-_{2(HA)} + HA \xrightarrow{k_f} HO^-_{2(HA)} + A^{\cdot}_{(HA)} \quad \ldots(1)$$

The rate of hydrogen abstraction for this reaction can be evaluated by considering the H-A bond dissociation reaction

$$HA \xrightarrow{\Delta G_{act}} H^{\cdot} + A^{\cdot} \ldots(2)$$

The net rate of nucleophilic attack can be expressed proportional to the rate determining step, which is the radical formation step, and is given by

$$r = A_o \frac{d[H^{\cdot}_{(HA)}]}{dt}[O^-_{2(HA)}] \ldots(3)$$

For several classes of organic solvents, a clear correlation between the activation energy for C-H bond activation, ΔG_{act}, and the solvents' pK_a in DMSO has been demonstrated in the work of Lu *et al.*[20], as can been seen in Fig. S2.

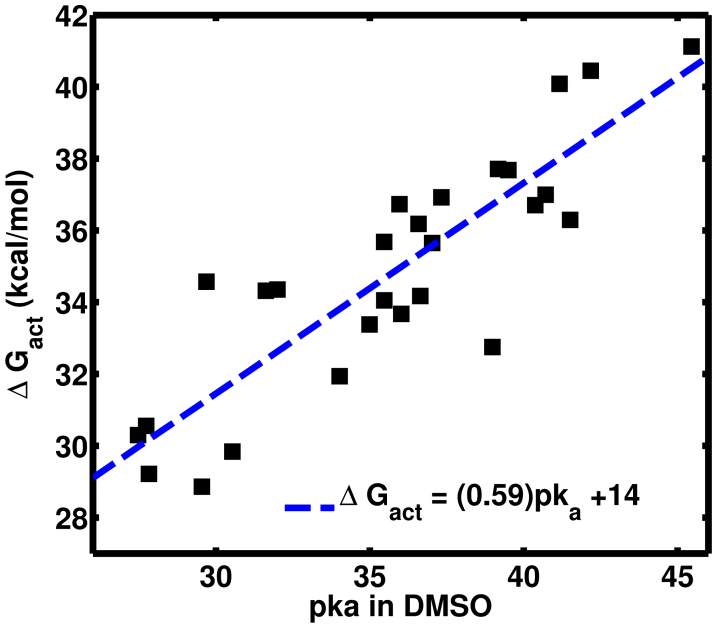

Figure S2. Linear correlation between the activation energy of the dissociation of the C-H bond in several organic solvents, ΔG_{act}, and their pK_a in DMSO

Using an Arrhenius type description the bond dissociation reaction given by Eq. (2), the rate of the rate determining step can be given as:

$$\frac{d[H^{\cdot}_{(HA)}]}{dt} = k_o e^{(-\Delta G_{act}/kT)} \propto \exp(-(0.59)pK_a) \ldots(4)$$

Which ultimately yields a rate law from Eq. (3) that is very similar to that for proton abstraction as described in the main text.

References

[1] Gritzner, G. Polarographic Half-Wave Potentials of Cations in Nonaqueous Solvents. Pure & App. Chem. 1990, 62, 9, 1839-1858.

[2] Sawyer, D. T.; Chiericato, G.; Angelis, C. T.; Nanni, E. J.; Tsuchiya, T. Effects of Media and Electrode Materials on the Electrochemical Reduction of Dioxygen. Anal. Chem. 1982, 54, 1720–1724.

[3] Bryantsev, V. S.; Uddin, J.; Giordani, V.; Walker, W.; Addison, D.; Chase, G. V. The Identification of Stable Solvents for Nonaqueous Rechargeable Li-Air Batteries. J. Electrochem. Soc. 2013, 160, A160–A171

[4] Jaworski, J. S.; Malik, M.; Kalinowski, M. K. Solvent Effect on the Hammett Reaction Constant for the Electroreduction of Substituted Benzophenones. J. of Phys. Org. Chem. 1992, 5, 590–594.

[5] Marcus, Y. The Properties of Organic Liquids that are Relevant to their Use as Solvating Solvents. Chem. Soc. Rev. 1993, 22, 409–416

[6] Khetan, A.; Pitsch, H.; Viswanathan, V. Solvent Degradation in Nonaqueous Li-O2 Batteries: Oxidative Stability versus H-Abstraction. J. Phys. Chem. Lett. 2014, 5, 2419–2424.

[7] Gutmann, V. Solvent Effects on the Reactivities of Organometallic Compounds. Coord. Chem. Rev. 1976, 18, 225.

[8] http://www.stenutz.eu/chem/solv21.php

[9] Bryantsev, V. S. Predicting the Stability of Aprotic Solvents in Li-Air Batteries: pKa Calculations of Aliphatic C–H Acids in Dimethyl Sulfoxide. Chem. Phys. Lett. 2013, 558, 42– 47.

[10] http://actachemscand.org/pdf/acta_vol_41a_p0480-0483.pdf

[11] http://www.chem.wisc.edu/areas/reich/pkatable/

[12] http://www.chemicalize.org/structure/#!mol=1-butanol&source=calculate

[13] http://evans.harvard.edu/pdf/evans_pKa_table.pdf

[14] http://research.chem.psu.edu/brpgroup/pKa_compilation.pdf

[15] https://www2.chemistry.msu.edu/faculty/reusch/virttxtjml/acidity2.htm

[16] http://chemweb.unp.ac.za/chemistry/Physical_Data/pKa_values.htm

[17] http://www.chemicalize.org/structure/#!mol=benzyl+alcohol&source=calculate

[18] http://www.chem.wisc.edu/courses/116/OtherDoc/pKas_of_Organic_Acids_and_Bases.pdf

[19] http://books.google.de/books?id=G_TqS6elYy0C&pg=PA365&lpg=PA365&dq=nitromethane+pka&source=bl&ots=ihU-MNeva5&sig=i...

[20] Lu, Q.; Yu, H.; Fu, Y. Linear Correlation between the C–H Activation Barrier and the C–Cu/C–H Bond Dissociation Energy Gap in Cu-promoted C–H Activation of Heteroarenes. Chem. Commun. 2013, 49, 10847–10849.