Supporting information for: Identifying Descriptors for Solvent Stability in Non-Aqueous Li-O₂ Batteries

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Indicators of solvent performance during charge and discharge, their HOMO levels and Gutmann Donor Numbers.

The formation of Li₂O₂ (reduction of O₂) during discharge and also its decomposition (release of O₂) during charge are both 2 e⁻ processes. Any deviation from this number indicates presence of undesirable parasitic side reactions. During charge, the solvent has been shown to be a major part in this deviation from ideal cell performance, eventually leading to its own decomposition and CO₂ release in the work of McCloskey et al. [1]. Table S1 shows these performance indicators values as e⁻/ORR for the electrons transferred per O₂ molecule during discharge and similarly e⁻/OER for the electrons transferred per O₂ molecule during charge, from the work of McCloskey et al. [1]. The HOMO level values of the solvents were computed at MP2=Full 6-31G* and taken from NIST's CCCBDB database [2]. The Gutmann Donor numbers were borrowed from various literature sources [3, 4, 5].

Solvent	e ⁻ /ORR	e ⁻ /OER	OER/ORR	HOMO level (eV) at MP2=Full 6-31G*	Gutmann Donor Number (kcal/mol)
Acetonitrile (MeCN, CH ₃ CN)	2.05	2.33	0.88	-12.273	14.1
Dimethoxyethane (DME, C ₄ H ₁₀ O ₂)	2.01	2.59	0.78	-11.444	20.0
Dimethylsulfoxide (DMSO, C ₂ H ₆ SO)	2.05	4.05	0.51	-9.838	29.8
N-Methyl-Pyrrolidone (NMP, C ₅ H ₉ NO)	1.96	3.35	0.58	-	27.3
Triglyme (TGE, C ₈ H ₁₈ O ₄)	2.04	2.71	0.75	-	-

Tetrahydrofuran (THF, C ₄ H ₈ O)	2.01	2.80	0.72	-10.969	20.0
Tri-(Ethylene Glycol)-substituted Trimethylsilane (1NM3, C ₁₂ H ₂₄ O ₄ Si)	2.14	4.44	0.48	-	-

Table S1. List of solvents with electrons involved during ORR and OER, computed HOMO level values and Gutmann Donor Numbers

HOMO level values and phase change data on solvents deemed acceptable during charging process.

Tables S2a and S2b list all solvents whose HOMO level values were ≤ -11.444 eV, which is the HOMO level of DME. The HOMO level values of the solvents were computed at MP2=Full 6-31G* and taken from NIST's CCCBDB database [2]. The melting and boiling point temperature data were taken from NIST's web book [6, 7]. The experimentally measured electric dipole moment values have been taken from the CCCBDB database [2]. The Dielectric constant values have been taken from Ref [8] and the O₂ solubility data at two different pressures have been taken from Ref [9].

SN	CAS	Solvent	HOMO (eV)	HOMO - LUMO gap (eV)	Melting point (°C)	Boiling point (°C)
1	75694	Trichlorofluoromethane (CFC13)	-12.677	15.573	-111.15	23.75
2	75434	Fluorodichloromethane (CHFC12)	-12.605	16.492	-135.00	8.85
3	56235	Carbon Tetrachloride (CCl4)	-12.627	15.149	-22.85	76.65
4	67663	Trichloromethane (CHCl3)	-12.346	15.609	-63.15	61.15
5	74873	Chloromethane (CH3Cl)	-11.827	17.154	-91.15	-26.15
6	75092	Dichloromethane (CH2Cl2)	-12.158	16.334	-75.09	39.85
7	107062	1,2 Dichloroethane (C2H4Cl2)	-12.004	16.863	-42.70	83.00

8	71556	1,1,1-Trichloroethane (C ₂ H ₃ Cl ₃)	-12.144	15.582	-30.40	74.08
9	79005	1,1,2-Trichloroethane (C ₂ H ₃ Cl ₃)	-12.149	16.195	-35.25	113.65
10	79209	Methyl acetate (C ₃ H ₆ O ₂)	-12.096	17.081	-98.00	56.85
11	109944	Ethyl formate (C ₃ H ₆ O ₂)	-12.397	17.291	-79.60	53.85
12	79094	Propanoic Acid (C ₃ H ₆ O ₂)	-12.203	17.110	-21.15	140.85
13	96480	γ -Butyrolactone (C ₄ H ₆ O ₂)	-11.756	16.550	-44.15	204.55
14	141786	Ethyl acetate (C ₄ H ₈ O ₂)	-12.000	17.032	-83.15	77.05
15	142621	Hexanoic acid (C ₆ H ₁₂ O ₂)	-12.084	17.018	-3.45	203.85
16	598981	Methyl pivalate (C ₆ H ₁₂ O ₂)	-11.696	16.723	-42.80	101.05
17	75218	Ethylene oxide (C ₂ H ₄ O)	-12.162	18.869	-112.60	11.85
18	75070	Acetaldehyde (C ₂ H ₄ O)	-11.528	14.852	-123.15	20.75
19	75569	Propylene oxide (C ₃ H ₆ O)	-11.735	18.421	-112.13	34.23
20	110883	1,3,5-Trioxane (C ₃ H ₆ O ₃)	-12.106	18.467	64.00	114.50
21	71363	1-Butanol (C ₄ H ₁₀ O)	-11.870	18.015	-85.15	117.45
22	75650	Ethanol, 1,1-dimethyl- (C ₄ H ₁₀ O)	-11.658	17.202	25.15	82.35

23	78831	1-Propanol, 2-methyl- (C ₄ H ₁₀ O)	-11.590	17.376	-108.00	107.65
24	123513	1-Butanol, 3-methyl- (C ₅ H ₁₂ O)	-11.808	17.699	-117.20	130.85
25	71410	1-Pentanol (C ₅ H ₁₂ O)	-11.859	18.002	-78.20	137.85
26	110714	Ethane, 1,2-dimethoxy- (C ₄ H ₁₀ O ₂)	-11.444	17.875	-69.21	84.85
27	107880	1,3-Butanediol (C ₄ H ₁₀ O ₂)	-11.692	17.450	-77.00	206.85
28	110634	1,4-Butanediol (C ₄ H ₁₀ O ₂)	-11.856	17.899	26.85	230.05
29	96413	Cyclopentanol (C ₅ H ₁₀ O)	-11.468	17.381	-19.00	139.85
30	107211	1,2-Ethenediol or Ethylene glycol (C ₂ H ₆ O ₂)	-11.926	17.650	-12.15	197.35
31	57556	Propylene glycol (C ₃ H ₈ O ₂)	-11.574	17.156	-60.00	186.85
32	75058	Acetonitrile (C ₂ H ₃ N)	-12.273	17.614	-45.15	81.65
33	109773	Malononitrile (C ₃ H ₂ N ₂)	-12.883	16.654	31.85	220.05
34	107120	Propionitrile or ethyl cyanide (C ₃ H ₅ N)	-12.134	17.185	-93.15	96.85
35	110598	Pentanenitrile (C ₅ H ₉ N)	-11.980	17.170	-96.23	140.85
36	10026047	Tetrachlorosilane (SiCl ₄)	-13.073		-68.75	56.85
37	992949	Methyl silane (CH ₆ Si)	-12.366		-157.00	-57.00

38	593782	Methyl hypochlorite (CH ₃ OCl)	-11.716		-120.4	9.18
39	75445	Carbon dichloride (CCl ₂ O)	-12.998		-118.00	8.30

Table S2a. List of solvents with acceptable HOMO level values for solvent stability with the same serial numbers as in Fig. 4 in the manuscript.

SN	CAS	Solvent	Electric dipole moment (Debye)	Dielectric Constant	O ₂ solubility (mmol L ⁻¹) at 1.013 bar	O ₂ solubility (mmol L ⁻¹) at 0.213 bar
1	75694	Trichlorofluoromethane (CFCI ₃)	0.450			
2	75434	Fluorodichloromethane (CHFCl ₂)	1.290			
3	56235	Carbon Tetrachloride (CCl ₄)	0.000	2.200	12.400	2.600
4	67663	Trichloromethane (CHCl ₃)	1.010			
5	74873	Chloromethane (CH ₃ Cl)	1.870	12.600		
6	75092	Dichloromethane (CH ₂ Cl ₂)	1.600	9.100	10.700	2.200
7	107062	1,2 Dichloroethane (C ₂ H ₄ Cl ₂)		10.700		
8	71556	1,1,1-Trichloroethane (C ₂ H ₃ Cl ₃)	1.780			
9	79005	1,1,2-Trichloroethane (C ₂ H ₃ Cl ₃)	1.500			
10	79209	Methyl acetate (C ₃ H ₆ O ₂)	1.720	7.300	11.100	2.300

11	109944	Ethyl formate (C3H6O2)	1.980	7.100		
12	79094	Propanoic Acid (C3H6O2)				
13	96480	γ -Butyrolactone (C4H6O2)				
14	141786	Ethyl acetate (C4H8O2)	1.780	6.000		
15	142621	Hexanoic acid (C6H12O2)				
16	598981	Methyl pivalate (C6H12O2)				
17	75218	Ethylene oxide (C2H4O)	1.890	14.000		
18	75070	Acetaldehyde (C2H4O)	2.690	21.800		
19	75569	Propylene oxide (C3H6O)	2.010			
20	110883	1,3,5-Trioxane (C3H6O3)	2.080			
21	71363	1-Butanol (C4H10O)	1.660	17.800	8.700	1.800
22	75650	Ethanol, 1,1-dimethyl- (C4H10O)	1.740			
23	78831	1-Propanol, 2-methyl- (C4H10O)	1.640	17.700	9.100	1.900
24	123513	1-Butanol, 3-methyl- (C5H12O)				
25	71410	1-Pentanol (C5H12O)		13.900	8.440	1.800

26	110714	Ethane, 1,2-dimethoxy- (C ₄ H ₁₀ O ₂)				
27	107880	1,3-Butanediol (C ₄ H ₁₀ O ₂)				
28	110634	1,4-Butanediol (C ₄ H ₁₀ O ₂)				
29	96413	Cyclopentanol (C ₅ H ₁₀ O)				
30	107211	1,2-Ethanediol or Ethylene glycol (C ₂ H ₆ O ₂)		37	0.580	0.120
31	57556	Propylene glycol (C ₃ H ₈ O ₂)				
32	75058	Acentonitrile (C ₂ H ₃ N)	3.920			
33	109773	Malononitrile (C ₃ H ₂ N ₂)	3.730			
34	107120	Propionitrile or ethyl cyanide (C ₃ H ₅ N)	4.020	27.700		
35	110598	Pentanenitrile (C ₅ H ₉ N)	4.120			
36	10026047	Tetrachlorosilane (SiCl ₄)	0.000			
37	992949	Methyl silane (CH ₆ Si)	0.740			
38	593782	Methyl hypochlorite (CH ₃ OCl)				
39	75445	Carbon dichloride (CCl ₂ O)	1.170			

Table S2b. List of solvents from Table S2a with other properties such as the electric dipole moment (Debye), dielectric constant, and O₂ solubility (mmol L⁻¹) at two different pressures.

HOMO level values and phase change data on other solvents.

Table S3 lists all other solvents for which some relevant properties were available. The HOMO level values of the solvents were computed at MP2=Full 6-31G* and taken from NIST's CCCBDB database [2]. The melting and boiling point temperature data were taken from NIST's Web book [6, 7].

CAS	Solvent	HOMO (eV)	HOMO - LUMO gap (eV)	Melting point (°C)	Boiling point (°C)
62759	N-Nitrosodimethylamine (C ₂ H ₆ N ₂ O)	-10.652	16.100		153.05
109739	1-Butanamine (C ₄ H ₁₁ N)	-10.354	16.374	-49.15	77.85
121448	Triethylamine (C ₆ H ₁₅ N)	-9.497	15.837	-114.70	89.15
872504	N-Methylpyrrolidone (C ₅ H ₉ NO)			-24.40	202.05
108189	Diisopropylamine (C ₆ H ₁₅ N)			-96.30	83.85
75456	Chlorodifluoromethane (CHClF ₂)	-13.141	18.029	-159.15	-40.15
75467	Trifluoromethane (CHF ₃)	-16.105	23.184	-162.95	-84.45
75694	Trichlorofluoromethane (CFCl ₃)	-12.677	15.573	-111.15	23.75
75718	Dichlorodifluoromethane (CCl ₂ F ₂)	-12.993	16.559	-157.95	-30.15
75729	Chlorotrifluoromethane (CClF ₃)	-13.760	18.425	-180.95	-81.45
75730	Tetrafluoromethane (CF ₄)	-18.383	29.409	-184.15	-128.05

75434	Fluorodichloromethane (CHFCl ₂)	-12.605	16.492	-135.00	8.85
56235	Carbon Tetrachloride (CCl ₄)	-12.627	15.149	-22.85	76.65
67663	Trichloromethane (CHCl ₃)	-12.346	15.609	-63.15	61.15
74873	Chloromethane (CH ₃ Cl)	-11.827	17.154	-91.15	-26.15
75092	Dichloromethane (CH ₂ Cl ₂)	-12.158	16.334	-75.09	39.85
107062	1,2 Dichloroethane (C ₂ H ₄ Cl ₂)	-12.004	16.863		
71556	1,1,1-Trichloroethane (C ₂ H ₃ Cl ₃)	-12.144	15.582	-30.40	74.08
79005	1,1,2-Trichloroethane (C ₂ H ₃ Cl ₃)	-12.149	16.195	-35.25	113.65
79016	1,1,2-Trichloroethylene (C ₂ HCl ₃)	-9.963	13.233	-84.65	86.05
127184	Tetrachloroethylene (C ₂ Cl ₄)	-9.949	12.821	-22.18	121.05
79209	Methyl acetate (C ₃ H ₆ O ₂)	-12.096	17.081	-98.00	56.85
109944	Ethyl formate (C ₃ H ₆ O ₂)	-12.397	17.291	-79.60	53.85
646060	1,3-Dioxolane (C ₃ H ₆ O ₂)	-11.377	17.908	-97.30	74.55
79094	Propanoic Acid (C ₃ H ₆ O ₂)	-12.203	17.110	-21.15	140.85
96480	γ-Butyrolactone (C ₄ H ₆ O ₂)	-11.756	16.550	-44.15	204.55

108327	Propylene carbonate (C ₄ H ₆ O ₃)			-54.53	241.70
141786	Ethyl acetate (C ₄ H ₈ O ₂)	-12.000	17.032	-83.15	77.05
922690	Ethene, 1,1-dimethoxy- (C ₄ H ₈ O ₂)	-8.889	15.217		
497267	1,3-Dioxolane, 2-methyl- (C ₄ H ₈ O ₂)	-11.320	17.791		81.55
105373	Ethyl propionate (C ₅ H ₁₀ O ₂)			-73.90	99.05
110496	Ethylene glycol methyl ether acetate (C ₅ H ₁₀ O ₃)			-65.10	144.55
100721	Tetrahydropyran-2-methanol (C ₆ H ₁₂ O ₂)			-70.00	187.05
142621	Hexanoic acid (C ₆ H ₁₂ O ₂)	-12.084	17.018	-3.45	203.85
598981	Methyl pivalate (C ₆ H ₁₂ O ₂)	-11.696	16.723	-42.80	101.05
75218	Ethylene oxide (C ₂ H ₄ O)	-12.162	18.869	-112.60	11.85
75070	Acetaldehyde (C ₂ H ₄ O)	-11.528	14.852	-123.15	20.75
557755	Ethenol (C ₂ H ₄ O)	-9.390	14.852		
75569	Propylene oxide (C ₃ H ₆ O)	-11.735	18.421	-112.13	34.23
110883	1,3,5-Trioxane (C ₃ H ₆ O ₃)	-12.106	18.467	64.00	114.50
60297	Ethoxy ethane (C ₄ H ₁₀ O)	-11.265	17.666	-119.15	34.55

557175	Methyl propyl ether (C ₄ H ₁₀ O)	-11.328	17.658		38.55
598538	Propane, 2-methoxy- (C ₄ H ₁₀ O)	-11.160	17.242		30.75
71363	1-Butanol (C ₄ H ₁₀ O)	-11.870	18.015	-85.15	117.45
15892236	2-Butanol (.+/-.)- (C ₄ H ₁₀ O)	-11.658	17.463		98.05
75650	Ethanol, 1,1-dimethyl- (C ₄ H ₁₀ O)	-11.658	17.202	25.15	82.35
78831	1-Propanol, 2-methyl- (C ₄ H ₁₀ O)	-11.590	17.376	-108.00	107.65
109999	Tetrahydrofuran (C ₄ H ₈ O)	-10.969	17.145	-108.05	65.85
2919235	Cyclobutanol (C ₄ H ₈ O)	-11.288	17.349		122.85
78842	Propanal, 2-methyl- (C ₄ H ₈ O)	-11.187	15.277	-72.15	62.85
123728	Butanal (C ₄ H ₈ O)	-11.357	15.553	-97.15	74.85
78933	2-Butanone (C ₄ H ₈ O)	-11.105	15.419	-86.65	79.85
123911	1,4-Dioxane (C ₄ H ₈ O ₂)	-10.715	17.393	11.85	101.15
505226	1,3-Dioxane (C ₄ H ₈ O ₂)	-11.534	17.882		105.55
1634044	Methyl tert-butyl ether (C ₅ H ₁₂ O)			-109.00	55.20
598754	2-Butanol, 3-methyl- (C ₅ H ₁₂ O)	-11.686	17.566		111.85

137326	1-Butanol, 2-methyl- (C ₅ H ₁₂ O)	-11.770	17.875		128.85
123513	1-Butanol, 3-methyl- (C ₅ H ₁₂ O)	-11.808	17.699		130.85
6032297	2-Pentanol (C ₅ H ₁₂ O)	-11.732	17.672		118.85
71410	1-Pentanol (C ₅ H ₁₂ O)	-11.859	18.002	-78.20	137.85
584021	3-Pentanol (C ₅ H ₁₂ O)	-11.557	17.328		114.85
108203	Di-n-propyl ether (C ₆ H ₁₄ O)	-11.242	17.507	-85.50	68.51
100663	Anisole (C ₇ H ₈ O)	-8.318	12.232	-23.15	153.85
109864	2-Methoxyethanol (C ₃ H ₈ O ₂)			-85.10	124.45
3031752	Hydroperoxide, 1-methylethyl (C ₃ H ₈ O ₂)	-11.880	17.729		
109875	Methane, dimethoxy- (C ₃ H ₈ O ₂)	-11.274	17.395	-105.15	42.15
107982	1-Methoxy-2-propanol (C ₄ H ₁₀ O ₂)			-142.00	118.55
110805	2-Ethoxyethanol (C ₄ H ₁₀ O ₂)			-100.00	135.15
110714	Ethane, 1,2-dimethoxy- (C ₄ H ₁₀ O ₂)	-11.444	17.875	-69.21	84.85
534156	1,1-Dimethoxyethane (C ₄ H ₁₀ O ₂)	-11.168	17.186		64.55
107880	1,3-Butanediol (C ₄ H ₁₀ O ₂)	-11.692	17.450	-77.00	206.85

110634	1,4-Butanediol (C ₄ H ₁₀ O ₂)	-11.856	17.899	26.85	230.05
563804	2-Butanone, 3-methyl- (C ₅ H ₁₀ O)	-10.868	15.196	-94.40	93.85
96413	Cyclopentanol (C ₅ H ₁₀ O)	-11.468	17.381	-19.00	139.85
690028	Dimethylperoxide (C ₂ H ₆ O ₂)	-11.376	17.858		
107211	1,2-Ethanediol or Ethylene glycol (C ₂ H ₆ O ₂)	-11.926	17.650	-12.15	197.35
504632	1,3-Propanediol or Trimethylene glycol(C ₃ H ₈ O ₂)	-11.388	16.926	58.85	213.85
57556	Propylene glycol (C ₃ H ₈ O ₂)	-11.574	17.156	-60.00	186.85
111466	3-oxa-1,5-pentanediol or Diethylene glycol (C ₄ H ₁₀ O ₃)			-10.00	245.00
112276	Triethylene glycol (C ₆ H ₁₄ O ₄)			-7.20	287.40
112607	Tetraethylene glycol (C ₈ H ₁₈ O ₅)			-4.10	314.05
75138	Isocyanic Acid (HNCO)	-12.172	16.588		
75127	Formamide (CH ₃ NO)	-11.255	16.614	2.55	
60355	Acetamide (C ₂ H ₅ NO)	-11.093	16.338	78.85	221.25
68122	Dimethylformamide or DMF (C ₃ H ₇ NO)	-10.099	15.515	-60.45	152.85
79050	Propanamide (C ₃ H ₇ NO)	-11.078	16.356	79.65	213.05

616455	2-Pyrrolidone (C ₄ H ₇ NO)	-10.458	15.833	25.57	245.05
541355	Butanamide (C ₄ H ₉ NO)	-11.062	16.394	115.65	216.05
127195	Dimethylacetamide or DMA (C ₄ H ₉ NO)				165.05
872504	N-Methyl-2-pyrrolidone (C ₅ H ₉ NO)				202.05
420053	Cyanic Acid (HOCN)	-12.191	16.366		
75058	Acetonitrile (C ₂ H ₃ N)	-12.273	17.614	-45.15	81.65
109773	Malononitrile (C ₃ H ₂ N ₂)	-12.883	16.654	31.85	220.05
107120	Propionitrile or ethyl cyanide (C ₃ H ₅ N)	-12.134	17.185	-93.15	96.85
62957602	Ethoxyacetonitrile (C ₄ H ₇ NO)	-12.073	16.699		
4426113	Cyclobutanecarbonitrile (C ₅ H ₇ N)	-11.728	16.788		149.55
110598	Pentanenitrile (C ₅ H ₉ N)	-11.980	17.170	-96.23	140.85
67685	Dimethyl sulfoxide (C ₂ H ₆ SO)	-9.838	15.166	18.50	190.85
67710	Dimethyl sulfone (C ₂ H ₆ O ₂ S)	-11.952	17.360	108.85	237.85
616422	Sulfurous acid, dimethyl ester (C ₂ H ₆ O ₃ S)	-11.288	15.479	~~	125.85
77781	Sulfuric acid, dimethyl ester (C ₂ H ₆ O ₄ S)			-32.00	196.85

10026047	Tetrachlorosilane (SiCl ₄)	-13.073		-68.75	56.85
992949	Methyl silane (CH ₆ Si)	-12.366		-157.00	-57.00
4109960	Dichlorosilane (SiH ₂ Cl ₂)	-12.467			8.15
593782	Methyl hypochlorite (CH ₃ OCl)	-11.716		-120.4	9.18
353504	Carbonic difluoride (CF ₂ O)	-14.988			-83.15
353491	Carbonic chloride fluoride (CFCIO)	-13.649			
75445	Carbon dichloride (CCl ₂ O)	-12.998		-118.00	8.30

Table S3. List of solvents with acceptable HOMO level values for solvent stability with the same serial numbers as in Fig. 4 in the manuscript.

Insensitivity to the choice of level of theory used for computing the HOMO level.

The HOMO level values of 33 solvents computed at MP2=Full 6-31G* were set against those computed at three other higher levels theory – Configuration Interaction (CID) in Fig. SI1, Quadratic Configuration Interaction (QCISD) in Fig. SI2 and Coupled Cluster (CCD) in Fig. SI3. As can be see, there exists a clear linear correlation of the type $y = mx + c$, where $m \approx 1$. Therefore, the solvent stability trends presented in the paper will remain unaffected, even if higher level theories for computed values of HOMO levels were used. All values were taken from NIST's CCCBDB database [2].

Figure S1. Correlation between HOMO Level values computed at MP2=Full 6-31G* and CID Full 6-31G*

Figure S2. Correlation between HOMO Level values computed at MP2=Full 6-31G* and QCISD Full 6-31G*

Figure S3. Correlation between HOMO Level values computed at MP2=Full 6-31G* and CCD Full 6-31G*

Effectiveness of the Gutmann Donor Number, acid dissociation constant, pKa, and the Gibbs activation energy for the nucleophilic substitution reaction, ΔG_{act} , as descriptors for solvent stability.

With the aim of finding similar effective descriptors for solvent stability, we also considered the Gutmann Donor Number (DN) [4, 5] of solvents, which provides a semi-empirical description of solvent interaction. The Gutmann DN is defined as the negative enthalpy value for the 1:1 adduct formation between a Lewis base, which is the solvent in this case, and the standard Lewis acid antimony pentachloride (SbCl_5) in a dilute solution in the non-coordinating solvent 1,2-dichloroethane ($\text{C}_2\text{H}_4\text{Cl}_2$), which has a zero DN. The higher is the DN, the higher is the solvation energy. From the point of view of electrocatalysis, these numbers are quite relevant because they essentially determine the solvents' ability to solvate cations and adsorbates, thus having a profound influence on the reaction thermodynamics [10]. For the case of Li- O_2 batteries, the utility of these numbers has been previously demonstrated by Laoire et al. [11] in the context of the reversibility of the $\text{O}_2 \rightleftharpoons \text{O}_2^- \rightleftharpoons \text{O}_2^{2-}$ redox couples. Invoking Pearson's HSAB theory, they pointed out that the DN can help in predicting the stability of reaction intermediates. In principle, hole states and defect states on the Li- O_2 surface can be considered to be cationic in the sense that they are electron deficient and go down in Fermi level upon occupation by electrons. A solvent with a higher DN can be expected to interact stronger with these electron accepting states by means of electron transfer. Therefore, solvents with high DN can be predicted to be unstable against oxidation during the charging process.

In Fig. S4, we plot the Gutmann DN for a set of solvents against their e^-/OER values from the work of McCloskey et al. [1], within an error limit wherever available. The Gutmann Donor numbers were borrowed from various literature sources [3, 4, 5] and have been tabulated in Table S1.

As can be seen, there exists an expected and similar anti-correlation between the DN and solvent stability. Despite being a well-defined measure of solvation, application of DN is beset by variations in the value for a given solvent, as we have observed in existing literature. The amount of solvation is an inexact quantity and its measurement and calibration is a function of the experimental technique [11]. Additionally, the presence of indeterminable artefacts of chemical interaction between the solvent, the adduct and the electrolyte and a complex layered solvation structure hinder the true determination of the solvents' electron donating tendency. Moreover, DN cannot be determined as simply as HOMO levels for a large number of solvents, because the experimental process is time consuming and tedious. Therefore, we argue that the HOMO level is a more suitable choice for a descriptor-based screening study.

Other descriptors such as the acid dissociation constant, pK_a , and the Gibbs activation energy for the nucleophilic substitution reaction, ΔG_{act} , have been proposed as key factors which may help determine the stability in the work of Bryantsev et al. [12-16]. Correlations between pK_a and e^-/OER , and ΔG_{act} and e^-/OER have been shown in Figs. S5 and S6 respectively. As can be clearly seen in Fig. S5, there is no clear correlation between the pK_a values and the chosen metric of solvent stability e^-/OER . The pK_a values (in DMSO) for the solvents MeCN, DME, NMP have been taken from Bryantsev et al. [12-16] and the pK_a for DMSO (in DMSO) has been chosen from Ref [17]. The correlation between ΔG_{act} and e^-/OER for solvents is quite the opposite, as seen in Fig S6. If the activation energy for nucleophilic substitution is higher, then one can naturally expect higher stability. However, as can be seen with increasing activation energy, the solvent is seen to be more prone to degradation. Thus we do not believe this is an effective descriptor. The ΔG_{act} values were taken from Bryantsev et al. [15, 16].

Figure S4. Correlation between Gutmann Donor Number (kcal/mol) and e^-/OER .

Figure S5. Correlation between acid dissociation constant pK_a (in DMSO) and e^-/OER .

Figure S6. Correlation between activation energy ΔG_{act} for nucleophilic substitution by O_2^- and e^-/OER

Comment on the choice of the metric for cell rechargeability or solvent stability.

The chosen metric of solvent stability in this study is electrons per O_2 molecule released during OER. It can be argued that in order to consider, the total cell rechargeability, the electrons per O_2 consumed during ORR must also be taken into account. A parameter for measuring the total recyclability can be defined as $(e^-/ORR)/(e^-/OER)$; the ideal value of this new metric of cell

recyclability being 1. Presented in Fig. S7 is a correlation between the $(e^-/ORR)/(e^-/OER)$ value and our chosen metric of solvent stability during charging process, e^-/OER , the ideal value for which is 2. As can be seen clearly, these quantities are strongly anti-correlated, indicating that when the stability during charging is low (i.e., e^-/OER is further from 2), the cell recyclability is also low (i.e., $(e^-/ORR)/(e^-/OER)$ is much lower than 1). This further strengthens the argument that oxidative stability of solvents is more crucial than stability during charging in case of Li-Air batteries. The e^-/OER and e^-/ORR values have taken from the work of McCloskey et al. [1] and have been tabulated in Table S1.

Figure S7. Correlation between the rechargeability metric ORR/OER and e^-/OER

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