Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Introducing competitive adsorption species in sulfonimide salt-based electrolytes for inhibiting aluminium corrosion

Weiran Xue [a,b,#], Qiuchen Wang [a,b,#], Guochen Sun [b], Quan Li [a], Xiqian Yu [a,b,*] and Hong Li [a,b,*]

[a] Beijing Advanced Innovation Center for Materials Genome Engineering, Institute of Physics, Chinese Academy of Sciences, Beijing, 100190, China

[b] Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, China

E-mail: xyu@iphy.ac.cn, hli@iphy.ac.cn

[#] These authors contributed equally to this work.

Experimental Section

1. Materials and Electrode Preparation

Ethylene carbonate (EC), diethyl carbonate (DEC) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Dodo Chem Co., Ltd. 1-ethyl-3-methylimidazolium nitrate ([EMIM]NO_3) was purchased from Adamas Reagent Co., Ltd. The no-additive electrolyte (1 M LiTFSI in EC:DEC 1:1 in vol.) served as the baseline electrolyte to which various concentrations of [EMIM]NO_3 additive were added. The $LiCoO_2$ was purchased from Ningbo Shanshan Co., Ltd. In this study, a cathode slurry com-prising of $LiCoO_2$ powders, PVdF binder and conductive carbon black with a weight ratio of 90:5:5 was cast on an aluminum foil with a blade and dried in a vacuum oven at 120 °C for 8 hours. Afterwards, the obtained cathodes were punched into small disks (Φ12 mm, with a mass loading of ~ 4.6 mg cm^{-2}). The lithium foils with a thickness of 200 μm were purchased from China Energy Lithium Co., Ltd.

2. Electrochemical Tests

The $LiCoO_2$ || Li coin cells containing 100 μL of different electrolytes were assembled in an argon-filled glovebox (H_2O < 0.1 ppm, O_2 < 0.1 ppm). These assembled coin cells were then kept at 25 °C for 8 hours to ensure adequate electrolyte infiltration before further tests. The electrochemical performance of these cells was evaluated on Landt Battery Test System (Wuhan LAND Electronic Co., Ltd). Cycling tests were conducted in the voltage range of 3 - 4.2 V and the cells were charged and discharged at 0.1C in the first cycle and then cycled at 0.5C. A high-low temperature chamber (Guangzhou GWS Co., Ltd) was used to provide constant testing temperatures. Electrochemical impedance spectroscopy (EIS) tests were conducted in the charged state (4.2 V) by using an electrochemical workstation (Autolab, Metrohm) in a frequency range of 200 kHz to 20 mHz. Homemade three-electrode coin cells were prepared for the cyclic voltammetry (CV) measurements with details shown in Figure S4. The CV tests were carried out at a scanning rate of 10 mV s^{-1} in a potential range from 2.0 to 4.5 V vs. Li^+/Li (calibrated).

3. Characterizations

After the cycling tests, $LiCoO_2$ || Li cells were disassembled in a glove box to obtain $LiCoO_2$ cath-odes in the charged state (4.2 V). The $LiCoO_2$ cathodes were then washed three times utilizing dimethyl carbonate (DMC) to remove residual electrolytes and dried in a vacuum chamber. The surface morphol-ogy of cycled cathodes were characterized using scanning electron microscopy (SEM, S-8100, Hitachi).

The aluminum electrodes in the three-electrode coin cells were obtained with the same method after the CV tests and their surface morphologies were also characterized by SEM. The Raman spectra of pristine aluminium foil and aluminium foils after immersion in the no-additive electrolyte and the 0.1 M additive electrolyte were obtained using a HORIBA LabRAM HR Evolution system equipped with a frequency-doubled Nd:YAG laser (532 nm green).

4. Theoretical Calculations

The adsorption configurations of various adsorbates on the (110) facet of Al_2O_3 were optimized by density functional theory (DFT) method carried out in the Vienna Ab initio Simulation Package (VASP) code. The generalized gradient approximation (GGA) of PBE exchange-correlation functional was used. The plane-wave cutoff energy was set as 400 eV. The threshold values of energy convergence and force were set as 10^{-5} eV and 0.03 eV $Å^{-1}$, respectively. To eliminate the interaction between adjacent images, a vacuum space larger than 15 Å was constructed along the vertical direction. In the general models, the k-point mesh was sampled with a separation of 0.03 $Å^{-1}$. The 2×1 size (110) plane of α-Al_2O_3 retained a thickness of 5 molecular layers and the bottom two layers were fixed to simulate the adsorption surface. In addition, the adsorption energy of different adsorbates is obtained by the following formula,

$$E_{ads} = E_T - E_s - E_a$$

where E_T, E_s and E_a are the energy of the total adsorption system, the Al_2O_3 substrate and the adsorbates respectively. Besides, the DFT calculation results are presented in Table S2 and a list of atomic coordinates of the optimized geometries (adsorbates and three layers of the Al_2O_3 substrate) are presented at the end of the supplementary information.

Supplementary Figures

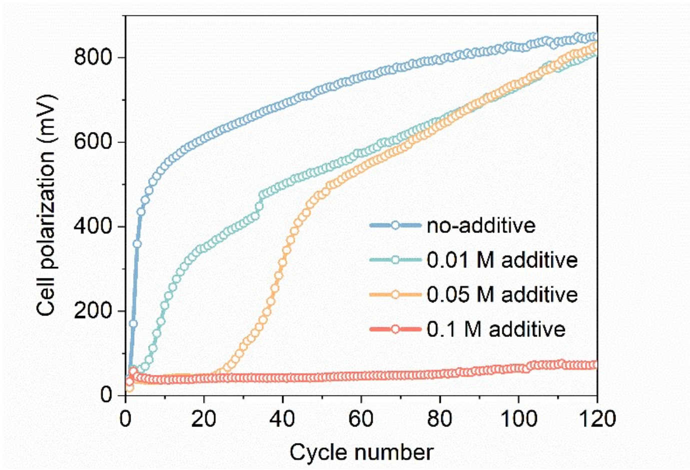

Figure S1. The polarizations of $LiCoO_2$ || Li cells using different electrolytes. The cell polarization was determined by subtracting the mid-voltage of discharge process from the mid-voltage of charge process at each charge-discharge cycle.

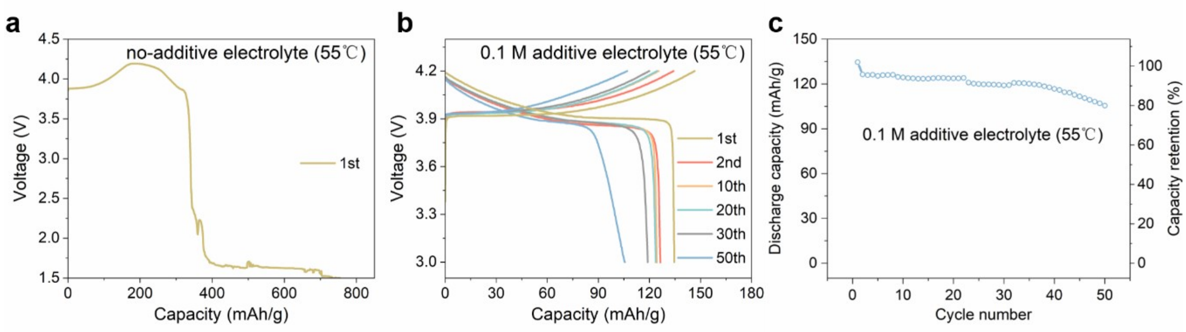

Figure S2. The charge-discharge curves of $LiCoO_2$ || Li cells using (a) no-additive electrolyte and (b) 0.1 M additive electrolyte at the elevated temperature of 55 °C. (c) The discharge capacity and capacity retention of $LiCoO_2$ || Li cell with the 0.1 M additive electrolyte at 55 °C.

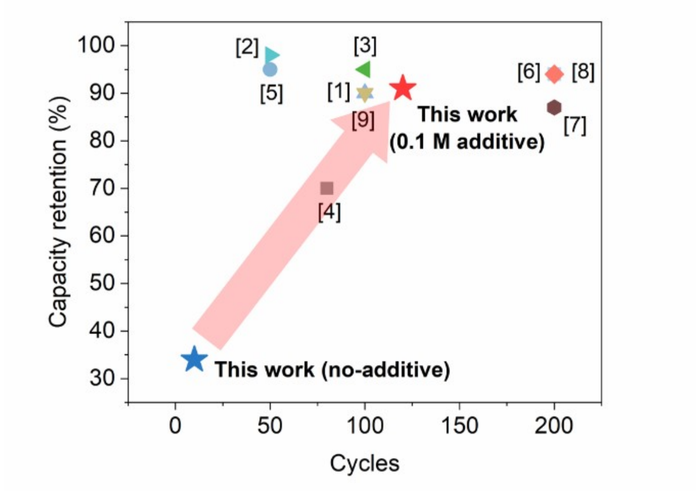

Figure S3. Summary of the cycling stability of 4 V-class cathodes (with aluminium current collector) in LiTFSI-based electrolytes achieved by various approaches.

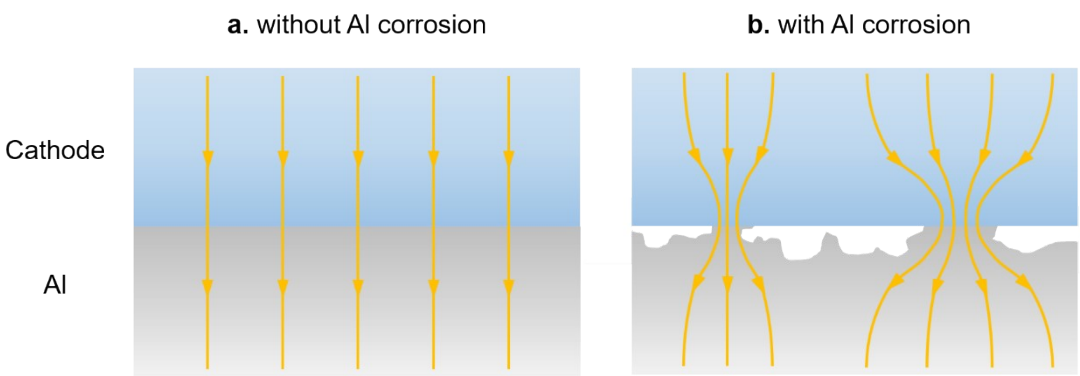

Figure S4. Schematic illustrations of electron transfer process at the cathode/aluminum current collector interface (a) without and (b) with aluminum corrosion.

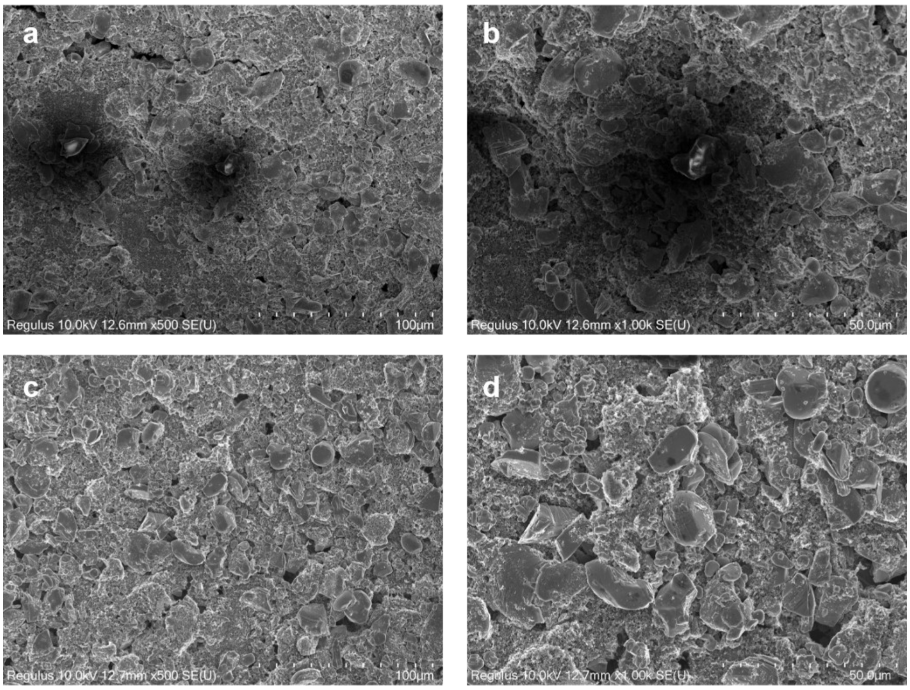

Figure S5. SEM images of disassembled $LiCoO_2$ cathodes in the (a, b) no-additive electrolyte and (c, d) 0.1 M additive electrolyte after 20 charge-discharge cycles.

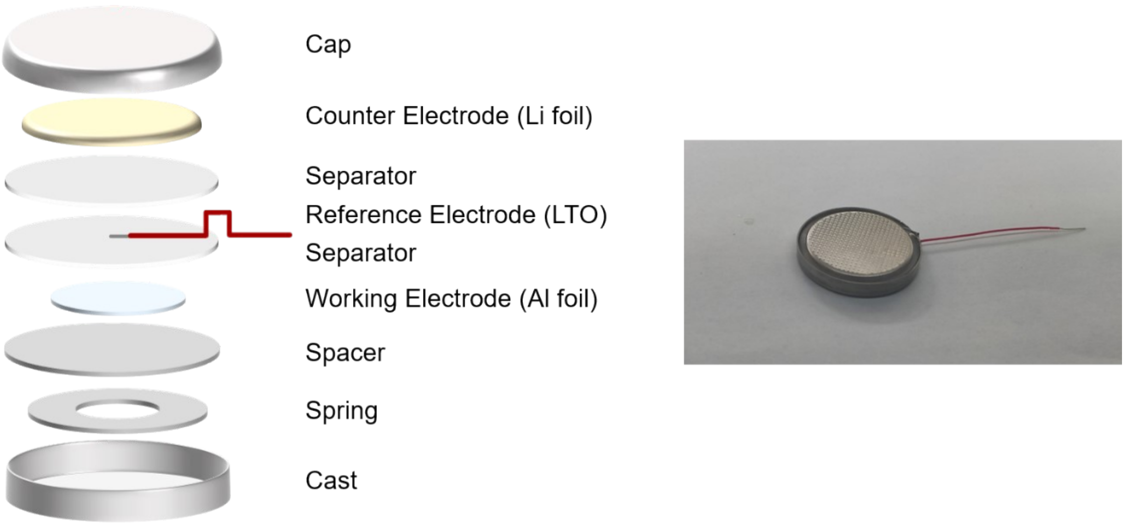

Figure S6. The inner structure and image of the homemade three-electrode coin cell. The $Li_4Ti_5O_{12}$ was casted on an enameled copper wire and served as the reference electrode (LTO). The aluminum foil was used as the working electrode and the lithium foil was used as the counter electrode.

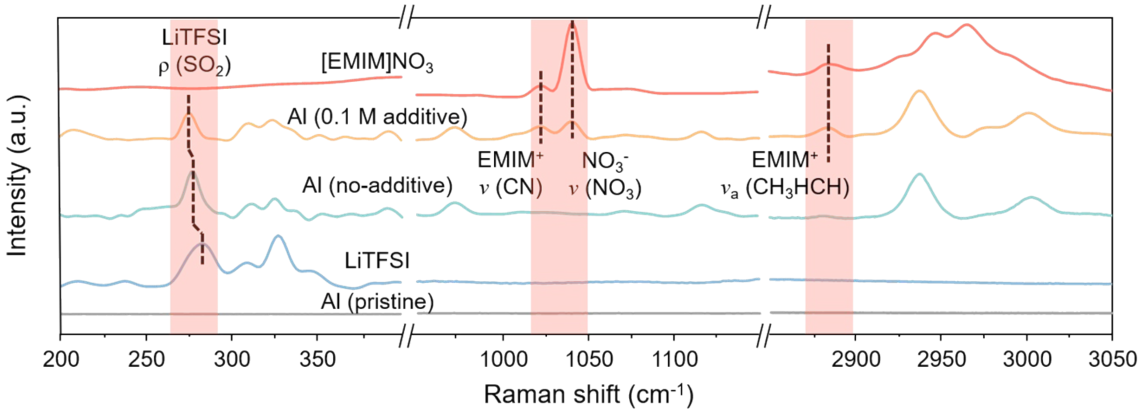

Figure S7. Raman spectra of pure $[EMIM]NO_3$, pure LiTFSI, pristine aluminium foil and aluminium foils after immersion in the no-additive electrolyte and 0.1 M additive electrolyte (vibrational modes: v = stretching; ρ = rocking; v_a = asymmetric stretching).

Table S1. Summary of the cycling stability of 4 V-class cathodes (with aluminium current collector) achieved in LiTFSI-based electrolytes by different methods

Ref.	Method	Electrolyte	Cell configuration	Voltage range	C-rate	Capacity retention (cycles)
[1]	Chromate conversion coating	1M LiTFSI EC/EMC 3:7 vol.	NMC333 || Li	2.7 ~ 4.2 V	1C	90% (100)
[2]	Concentrated electrolytes	2.3M LiTFSI EC:DME 1:2 vol.	NMC622 || Graphite	2.8 ~ 4.2 V	0.5C	98.7% (50)
[3]	Concentrated electrolytes	3.5M LiTFSI DMC/C_2[FSI] 1:1 vol.	NMC523 || Li	2.8 ~ 4.5 V	C/6	95% (100)
[4]	Concentrated electrolytes	5M LiTFSI in EC:DEC 3:7 vol.	NMC811 || Li	3.0 ~ 4.6 V	1C	70% (80)
[5]	Low solubility solvents	1M LiTFSI in F-C4	NMC111 || Li	3.0 ~ 4.3 V	0.2C	95% (50)
[6]	Low solubility solvents	1M LiTFSI in MCP	NMC111 || Graphite	2.8 ~ 4.2 V	1C	94.4% (200)
[7]	Partially hydrogenated anion	1M LiDFTFSI in EC:EMC 3:7 vol.	NMC111 || Li	2.7 ~ 4.2 V	0.2C	87% (200)
[8]	Adding LiBOB	0.75M LiTFSI + 0.25M LiBOB in FEC/1,2-BC 1:1 mol.	NMC111 || Graphite	3.0 ~ 4.2 V	0.2C	94.5% (200)
[9]	Adding LiDFOB and $LiPF_6$	0.8M LiTFSI + 0.2M LiDFOB + 0.01M $LiPF_6$ in EC:PC 1:1 vol.	LCO || Li	3.0 ~ 4.2 V	0.5C	90% (100)
This work	Adding competitive adsorption species $[EMIM]NO_3$	1M LiTFSI in EC:DEC 1:1 vol.	LCO || Li	3.0 ~ 4.2 V	0.5C	90.2% (120)

Table S2. The calculated energies of the total adsorption system, the Al_2O_3 substrate and the adsorbates used for deducing the values of the adsorption energy of different adsorbates

Adsorbates	Energy (eV)			
	Adsorbates	Substrate	Total	Ads
NO_3^-	-28.071	-933.375	-966.007	-4.561
$EMIM^+$	-106.786	-933.375	-1045.27	-5.109
$TFSI^-$	-86.992	-933.375	-1022.551	-2.184

Reference:

[1] Piao N, Wang L, Anwar T, Feng X, Tian G, Wang J, Tang Y, He X, *Corros. Sci.*, 2019, **158**, 108100.

[2] Liang H, Zuo X, Zhang L, Huang W, Chen Q, Zhu T, Liu J, Nan J, *J. Electrochem. Soc.*, 2020, **167**, 090520.

[3] Wang Z, Sun Y, Mao Y, Zhang F, Zheng L, Fu D, Shen Y, Hu J, Dong H, Xu J, Wu X, *Energy Storage Mater.*, 2020, **30**, 228-237.

[4] Qian K, Liu Y, Zhou X, Gosztola DJ, Nguyen H, Li T, *Energy Storage Mater.*, 2021, **41**, 222-229.

[5] Bolloli M, Kalhoff J, Alloin F, Bresser D, Phung Le ML, Langlois B, Passerini S, Sanchez JY, *J. Phys. Chem. C.*, 2015, **119**, 22404-22414.

[6] Brox S, Röser S, Streipert B, Hildebrand S, Rodehorst U, Qi X, Wagner R, Winter M, Cekic-Laskovic, *ChemElectroChem.*, 2017, **4**, 304-309.

[7] Qiao L, Oteo U, Martinez-Ibañez M, Santiago A, Cid R, Sanchez-Diez E, Lobato E, Meabe L, Armand M, Zhang H, *Nat. Mater.*, 2022, **21**, 455-462.

[8] Wang Z, Hofmann A, Hanemann T, *Electrochim. Acta,* 2019, **298**, 960-972.

[9] Geng Z, Lu J, Li Q, Qiu J, Wang Y, Peng J, Huang J, Li W, Yu X, Li H, *Energy Storage Mater.*, 2019, **23**, 646-652.

Cartesian coordinates of the optimized adsorption geometries

Al_2O_3-NO_3^-

N	O	Al
1	39	48

Cartesian

9.863546584	6.924930020	7.339530140
3.232665593	5.419654616	3.229200169
9.840045775	6.981263906	4.180249989
3.264913933	2.873692575	3.269220024
9.735989778	1.277288833	4.251780137
3.315962958	16.567142818	3.444249868
9.821506759	4.123311587	4.164839968
7.609167018	2.647197122	3.244609848
1.126471701	4.225872491	4.252929986
7.635148722	0.081187121	3.246219978
1.009881556	6.764875320	4.280990049
7.606816859	5.462733237	3.435739964
1.105843222	1.350522885	3.981760159
11.956292821	8.149364079	3.240010113
5.557808475	1.465179020	4.238670155
11.979009984	5.591970089	3.238859922
5.364710257	4.072942422	4.280990049
11.910597022	2.720431174	3.388130084
5.396828055	6.888313118	4.078130111
3.242457467	13.699912208	3.240240082
9.861065688	15.271794773	4.240969852
3.260083073	11.135724673	3.262319908
9.796569397	9.518444161	4.274319902
3.306040153	8.283902741	3.387670144
9.759882020	12.424280160	4.122980013
7.631492747	10.904424162	3.280489907
1.138483190	12.514580291	4.231770039
7.627184641	8.359456859	3.285779893
1.063541728	15.076944758	4.275240123
7.615303889	13.786567190	3.458280072
0.994475468	9.670379987	4.048459917
11.963996206	16.433929485	3.253120095
5.465502492	9.738975141	4.238900125
11.973396062	13.892607330	3.257489860
5.341992706	12.327352397	4.216819957
11.938667410	11.045922282	3.462189898
5.462238728	15.163765653	4.154949903
9.784296433	8.069171310	6.469440252
7.615956019	6.599850143	5.648570031
10.007163067	5.810015337	6.638259888
4.597017706	4.121323347	2.551390074
4.515939567	0.128242508	4.895320132

1	8.459504221	4.121323347	2.551390074
2	8.293040616	0.248697691	5.058620155
3	1.931504538	4.121323347	2.551390074
4	1.797941792	0.028166960	5.148089990
5	11.125017584	4.121323347	2.551390074
6	11.205050602	16.456628952	5.014690131
7	8.948451615	1.359967088	2.551390074
8	9.078620054	5.571259109	5.047349930
9	12.812113988	1.359967088	2.551390074
10	12.758584066	5.323555430	4.930279970
11	6.284113721	1.359967088	2.551390074
12	6.368977794	5.535138958	4.862659991
13	2.420451737	1.359967088	2.551390074
14	2.496568278	5.676470671	4.950520039
15	0.244408304	6.882845396	2.551390074
16	0.753461738	2.634273437	5.343129933
17	4.108070312	6.882845396	2.551390074
18	3.776186666	3.011876385	5.145330012
19	10.636070190	6.882845396	2.551390074
20	10.856455150	2.645374548	4.885200098
21	6.772407817	6.882845396	2.551390074
22	6.756349697	2.769972008	4.955350086
23	4.597017706	12.405723580	2.551390074
24	4.343861651	8.335928814	4.878989890
25	8.459504221	12.405723580	2.551390074
26	8.334819745	8.240658206	5.120029926
27	1.931504538	12.405723580	2.551390074
28	0.750850542	8.314389750	5.357390106
29	11.125017584	12.405723580	2.551390074
30	11.070443320	8.186478227	5.014920101
31	8.948451615	9.644367197	2.551390074
32	8.910589158	13.908016501	4.939250156
33	12.812113988	9.644367197	2.551390074
34	12.665886650	13.996493563	5.064370081
35	6.284113721	9.644367197	2.551390074
36	6.313098103	13.650537287	4.911420062
37	2.420451737	9.644367197	2.551390074
38	2.464842109	13.711510318	4.986170128
39	0.244408304	15.167244888	2.551390074
40	0.211768311	11.130754196	4.965470120
41	4.108070312	15.167244888	2.551390074
42	4.095405914	11.122304484	4.998359889
43	10.636070190	15.167244888	2.551390074

10.655785064	11.000026596	4.950979978
6.772407817	15.167244888	2.551390074
6.981826408	10.591274220	5.103929996

Al_2O_3-EMIM$^+$

H	C	N	O	Al
11	6	2	36	48

Cartesian

4.618820875	6.996507164	7.309800088
8.641113120	6.977784177	6.957900077
7.958284641	9.369324906	7.831200063
4.525470550	8.791239540	8.983500302
4.582133497	9.989329971	7.672500014
5.279062928	10.961917958	9.888600111
6.591451827	11.086183839	8.703000247
6.644590315	9.835074326	9.989400208
7.583708263	4.994001827	7.599000335
5.806394949	4.995658982	7.782600224
6.789119624	6.227217919	8.653799593
5.419675955	7.511299679	6.760199815
7.770800346	7.505831957	6.505499929
7.323371384	8.617929576	7.366199791
5.207124338	9.432783669	8.402100205
5.991137263	10.377370873	9.290400445
6.700469617	5.633226137	7.732799649
6.041402643	8.525973278	7.608900368
6.571345519	6.539871109	6.537600160
3.236712807	5.402422871	3.247200027
9.873600127	6.873401193	4.298399985
3.263477768	2.843371726	3.253800049
9.748523438	1.258731759	4.219200164
3.272616928	16.550077479	3.460500017
9.897100935	4.069959938	4.009500146
7.618176219	2.630296956	3.264599964
1.128691219	4.241447081	4.258499891
7.622353587	0.075553725	3.245999962
0.998261694	6.822534535	4.253400117
7.563079784	5.507966259	3.484200016
1.124252182	1.340747349	4.133999795
11.938536673	8.177696688	3.248400092
5.506237278	1.481250732	4.258199930
11.997549779	5.611355247	3.228300065
5.326195282	4.052728440	4.235399812

1	12.015305928	2.726396141	3.468900025
2	5.423070455	6.860145928	4.042800218
3	3.265044281	13.679366647	3.256499916
4	9.807536545	15.277758753	4.284300059
5	3.277317245	11.130091532	3.262799978
6	9.684157107	9.494419365	4.353599846
7	3.277969764	8.267831400	3.468900025
8	9.741081529	12.410859970	4.003200084
9	7.605381083	10.898459194	3.247499987
10	1.113415674	12.498840281	4.241699874
11	7.651076883	8.325325195	3.252899945
12	1.045524494	15.048115397	4.232700169
13	7.586580592	13.786401277	3.471900076
14	1.076206029	9.651325668	4.102499932
15	11.968957219	16.436083391	3.261299953
16	5.583006533	9.669717323	4.287300110
17	11.959034414	13.901720695	3.257400021
18	5.413800947	12.284274270	4.244100004
19	12.005644597	11.032667018	3.389699981
20	5.421112119	15.180996904	4.131900072
21	4.597017706	4.121323347	2.551200092
22	4.567380415	0.079364554	4.947000146
23	8.459504221	4.121323347	2.551200092
24	8.427647898	0.105377568	4.993199855
25	1.931504538	4.121323347	2.551200092
26	1.978897977	16.432604156	4.943700135
27	11.125017584	4.121323347	2.551200092
28	11.310673891	16.319936384	5.082000196
29	8.948451615	1.359967088	2.551200092
30	10.133414056	5.290749096	5.424000174
31	12.812113988	1.359967088	2.551200092
32	12.823994740	5.578218074	4.968599975
33	6.284113721	1.359967088	2.551200092
34	6.346260242	5.402754203	4.817099869
35	2.420451737	1.359967088	2.551200092
36	2.637703671	5.329023153	5.072700083
37	0.244408304	6.882845396	2.551200092
38	0.234224632	2.777427971	4.960500151
39	4.108070312	6.882845396	2.551200092
40	4.042790375	2.869881761	5.028300136
41	10.636070190	6.882845396	2.551200092
42	10.678371489	2.622012663	4.968300015
43	6.772407817	6.882845396	2.551200092

6.975298103	2.589371994	5.090999901
4.597017706	12.405723580	2.551200092
4.613990209	8.281748835	4.994700104
8.459504221	12.405723580	2.551200092
8.613826377	8.055750626	4.741200060
1.931504538	12.405723580	2.551200092
1.972369867	8.224586865	4.941000044
11.125017584	12.405723580	2.551200092
11.443453186	8.443460196	5.063100010
8.948451615	9.644367197	2.551200092
8.988924927	13.787063942	5.050799847
12.812113988	9.644367197	2.551200092
12.710276633	13.870405602	5.025900006
6.284113721	9.644367197	2.551200092
6.328895916	13.746470559	4.950300157
2.420451737	9.644367197	2.551200092
2.509232676	13.602984446	5.037900209
0.244408304	15.167244888	2.551200092
0.009530880	11.104906332	4.884899855
4.108070312	15.167244888	2.551200092
3.883246120	11.200674679	5.091299862
10.636070190	15.167244888	2.551200092
9.989798351	11.167205679	5.423399806
6.772407817	15.167244888	2.551200092
6.778152476	10.991079144	4.988700002

Al_2O_3-TFSI-

C	N	O	F	Al	S
2	1	40	6	48	2

Cartesian

5.888778126	10.148390181	9.138300419
6.875680947	6.544013009	8.793599904
5.271882104	8.214810836	7.064699829
3.245982704	5.401428874	3.242399991
9.801530411	6.978116003	4.242900163
3.292723236	2.834921767	3.250799999
9.762623612	1.242328592	4.250999987
3.266872269	16.538147544	3.459299952
9.753093018	4.142034327	4.009800106
7.617001139	2.612568460	3.267600015
1.143313856	4.208475327	4.228499830
7.631101313	0.067103642	3.237899914
1.024504290	6.790888110	4.274999946

1	7.583577525	5.499350633	3.444600105
2	1.119943687	1.351682671	4.126499891
3	11.964518377	8.155329047	3.246900067
4	5.503756771	1.460042630	4.258499891
5	11.964779073	5.621296695	3.264899924
6	5.353873847	4.071451180	4.240500033
7	12.030581181	2.757876654	3.410099968
8	5.440696256	6.869258799	4.137900174
9	3.237887887	13.680195225	3.262799978
10	9.854015990	15.279912660	4.286099821
11	3.272747276	11.115345025	3.246299922
12	9.823333969	9.496573271	4.214999825
13	3.235276642	8.224752284	3.423300013
14	9.854015990	12.405557667	3.990899920
15	7.670399545	10.901773504	3.314400092
16	1.129213390	12.493041227	4.247999936
17	7.606556163	8.368072485	3.255300075
18	0.959877067	15.092189003	4.258499891
19	7.569999523	13.774140504	3.384599984
20	1.081689603	9.634260330	4.114800096
21	11.947937307	16.461765342	3.224399909
22	5.353873847	9.694404783	4.265699834
23	11.977835683	13.902880111	3.245100081
24	5.347345931	12.353200262	4.215299785
25	12.002641530	11.028359205	3.443400040
26	5.448791074	15.158298424	4.153799862
27	4.827716905	10.632199429	6.803399920
28	3.400826642	9.398486093	8.466299772
29	4.202203893	6.488839032	8.717699647
30	5.464197064	5.787316363	6.683400124
31	5.737981208	11.479858870	9.251699746
32	7.155732700	9.861417954	8.801399767
33	5.580917849	9.568647660	10.314299762
34	7.919508580	7.135188219	8.204399943
35	7.099199712	5.224473761	8.918099999
36	6.687674481	7.078025756	10.020300150
37	4.597017706	4.121323347	2.551200092
38	4.572733252	0.036451360	4.920900017
39	8.459504221	4.121323347	2.551200092
40	8.427647898	16.477506339	4.951499999
41	1.931504538	4.121323347	2.551200092
42	1.952133016	16.431278827	4.908899814
43	11.125017584	4.121323347	2.551200092

1	11.226723423	0.108359951	4.953300208
2	8.948451615	1.359967088	2.551200092
3	8.927300965	5.511611407	4.979399890
4	12.812113988	1.359967088	2.551200092
5	12.680117561	5.636871285	5.053199977
6	6.284113721	1.359967088	2.551200092
7	6.337251819	5.400931629	4.956900179
8	2.420451737	1.359967088	2.551200092
9	2.498526614	5.306158266	5.023499876
10	0.244408304	6.882845396	2.551200092
11	0.068805120	2.831607950	4.889700115
12	4.108070312	6.882845396	2.551200092
13	4.110681556	2.867562188	5.008800030
14	10.636070190	6.882845396	2.551200092
15	10.081712122	2.821335170	5.379599780
16	6.772407817	6.882845396	2.551200092
17	7.048412161	2.502054594	5.133900046
18	4.597017706	12.405723580	2.551200092
19	4.546099028	8.250268322	4.941000044
20	8.459504221	12.405723580	2.551200092
21	8.393571376	8.352995140	4.988100082
22	1.931504538	12.405723580	2.551200092
23	1.992084351	8.202550062	4.906800091
24	11.125017584	12.405723580	2.551200092
25	11.207531498	8.139588544	4.999199957
26	8.948451615	9.644367197	2.551200092
27	9.574747883	13.702728779	5.350800008
28	12.812113988	9.644367197	2.551200092
29	12.729730032	13.907850588	5.012100041
30	6.284113721	9.644367197	2.551200092
31	6.508285393	13.599174372	4.849800020
32	2.420451737	9.644367197	2.551200092
33	2.662771187	13.346002971	5.087399930
34	0.244408304	15.167244888	2.551200092
35	0.135782398	11.083864019	4.904999882
36	4.108070312	15.167244888	2.551200092
37	4.265656231	11.071603246	4.898999780
38	10.636070190	15.167244888	2.551200092
39	10.523266466	11.007481818	5.127300024
40	6.772407817	15.167244888	2.551200092
41	7.694031091	11.096622532	5.351399928
42	4.656552983	9.557546302	7.800900042
43	5.256998284	6.740353279	7.785900235