Density Functional Theory and Conductivity Studies of Boron-Based Anion Receptors

SAND2015-9044C

Kevin Leung, Mangesh I. Chaudhari, Susan Rempe, Kyle R. Fenton, Harry D. Pratt III, Chad L. Staiger, and Ganesan Nagasubramanian

Sandia National Laboratories

Journal of The Electrochemical Society, **162** (9) A1927-A1934 (2015)

Acknowledgement

Zonghai Chan, Chris Orendorff

Sandia National Laboratories is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Deparment of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

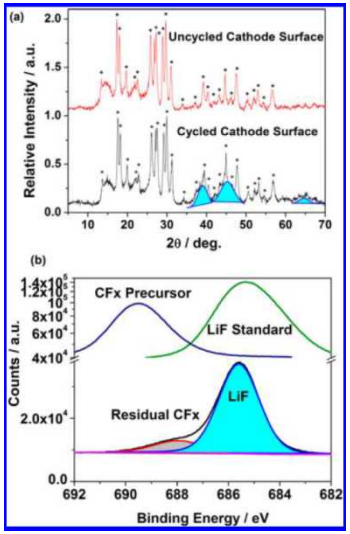
Sandia National Laboratories

Problem

- Lithium primary power sources are a commonly used power source
- Safety concerns exist with these power sources.
- *Power source with similar/increased electrochemical performance (as compared to commercial) and increased safety important*
- *Control over fabrication and build parameters*
- Proposed solution offers potential for double the run time for equivalent weight and volumes.

Introduction

- Boron-based anion receptor ("ABA") improves electrolyte conductivity in primary/thermal batteries, Li-air batteries by coordinating to F^- and O_2^-
- (Also helps rechargeable LIB via effect on interfaces, SEI …)
- CF_x batteries – no PF_6^-, conductivity all due to dissolved LiF, anion receptor key



Pushing the Theoretical Limit of Li-CF_x Batteries: A Tale of Bifunctional Electrolyte

Ezhiylmurugan Rangasamy,[†] Juchuan Li,[‡] Gayatri Sahu,[†] Nancy Dudney,[‡] and Chengdu Liang*[,†]

J. Am. Chem. Soc. 2014, 136, 6874–6877

- focus on CFx, but modeling insight (specific solvent effects) applicable to other batteries

Method

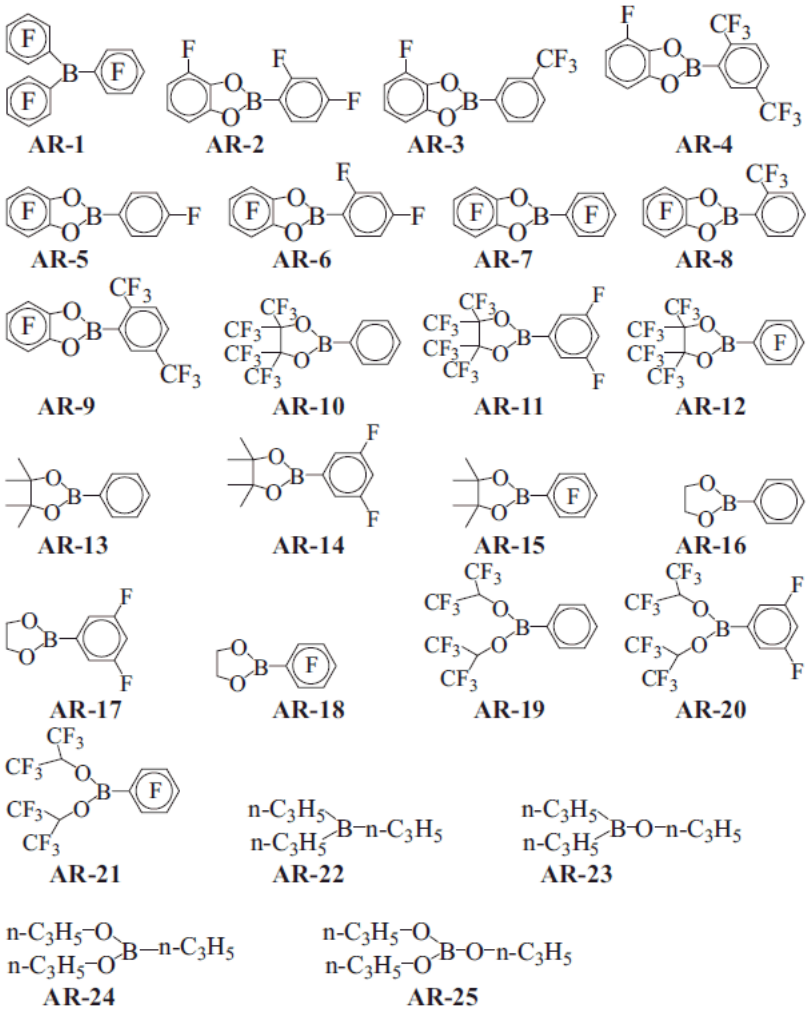
- G09 (cluster), VASP (LiF solid)
- DFT/PBE0
- dielectric continuum solvent for G09
- different types of solvation models (see below)
- 2032 coin cell, 3:7 EC/EMC, 1.0 M ABA,
- 1.0 M LiF added, filtered using 2 μm pore

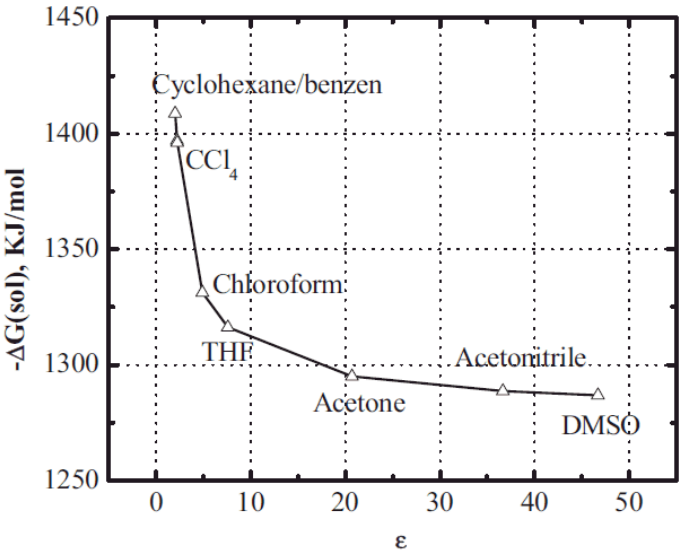
Previous modeling work

Journal of The Electrochemical Society, **156** (8) A672-A676 (2009)
0013-4651/2009/156(8)/A672/5/$25.00 © The Electrochemical Society

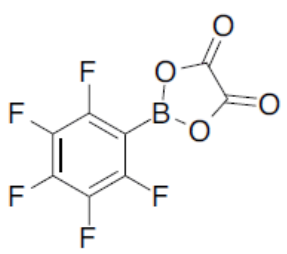
Computational Estimates of Fluoride Affinity of Boron-Based Anion Receptors

Zonghai Chen[*,z] **and K. Amine**[*]

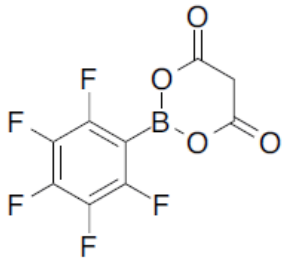




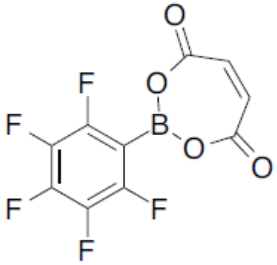
ABA we consider here



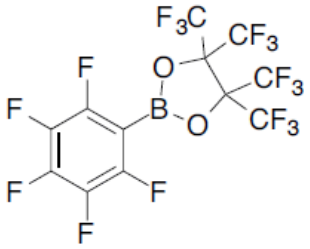
(a) ABAO



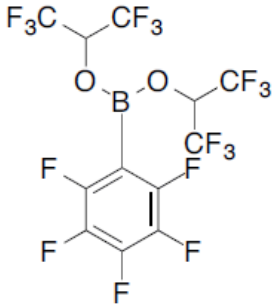
(b) ABAM



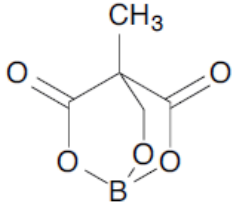
(c) ABAE



(d) ABA12



(e) ABA21



(f) ABAT

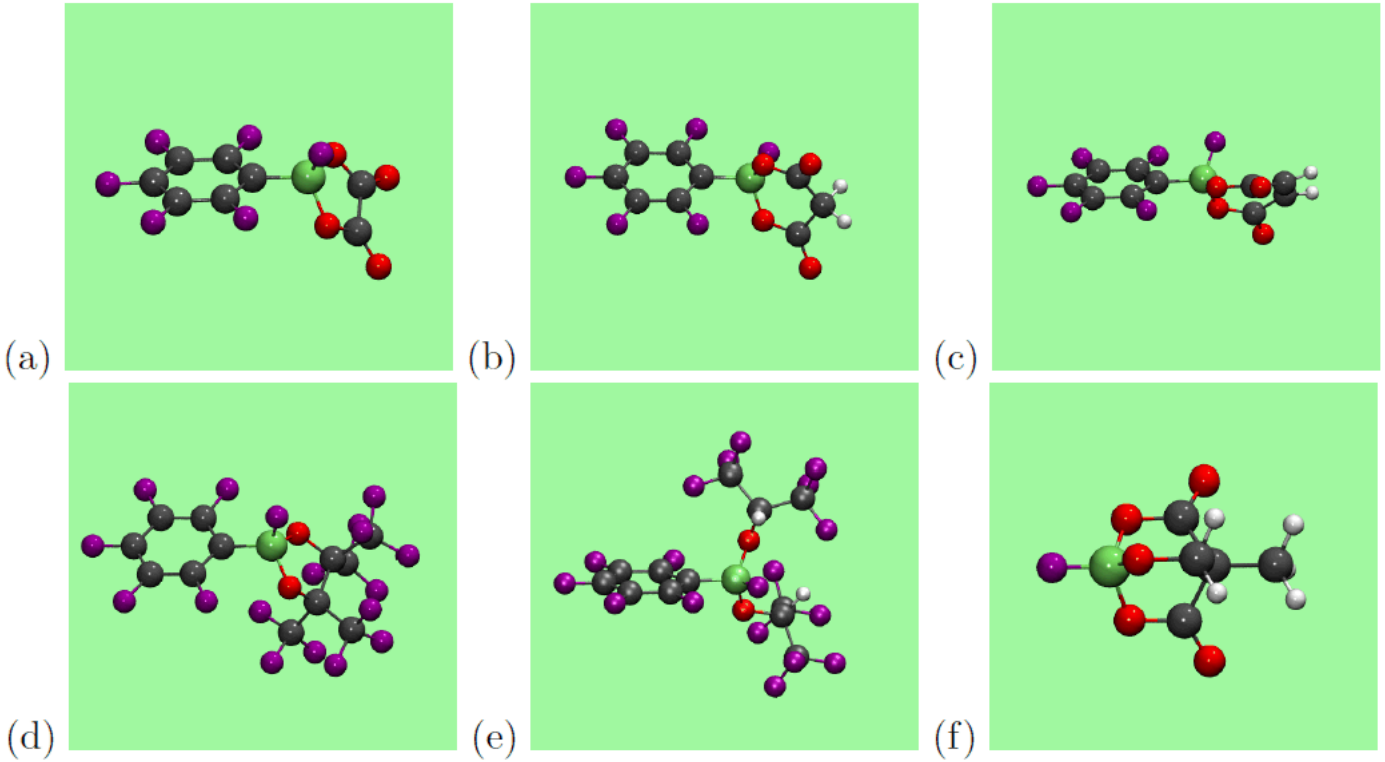
- Many have multiple C_6F_5 e^- -withrdrawing groups -- bad for electrolyte viscosity
- (ABA15, not shown, is ABA12 with H -> F)

Boron Esters as Tunable Anion Carriers for Non-Aqueous Batteries Electrochemistry

Devaraj Shanmukaraj,† Sylvie Grugeon,† Grégory Gachot,† Stéphane Laruelle,† David Mathiron,‡ Jean-Marie Tarascon,† and Michel Armand*,†

J. AM. CHEM. SOC. 2010, *132*, 3055–3062

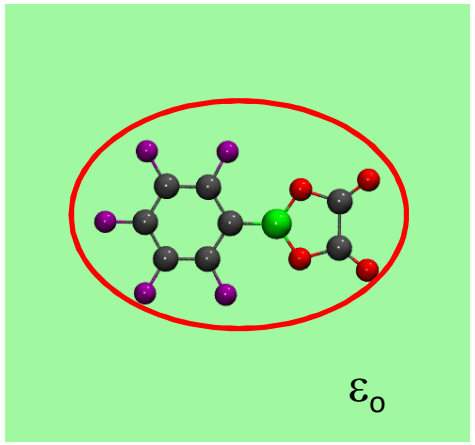
Gas Phase & “dielectric solvation” results ABA + F^- -> ABA-F^-



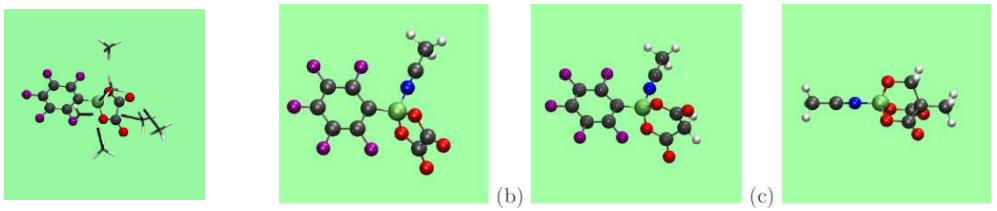
	ABAO	ABAM	ABAE	ABA12	ABA15	ABA21	ABAT
ABA-F^- (ϵ_o=1)	-4.396	-4.171	-4.128	-3.741	-2.679	-4.234	-5.411
ABA-F^- (ϵ_o=40)	-5.962	-5.650	-5.660	-5.450	-4.566	-5.581	-7.238

But boron binds to solvent: specific solvent effect

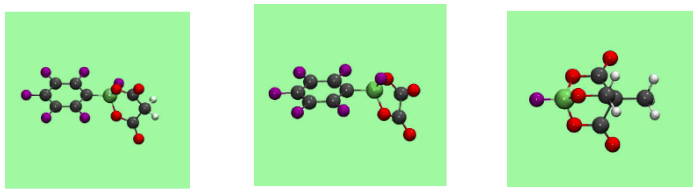
1. Purely implicit (so far)



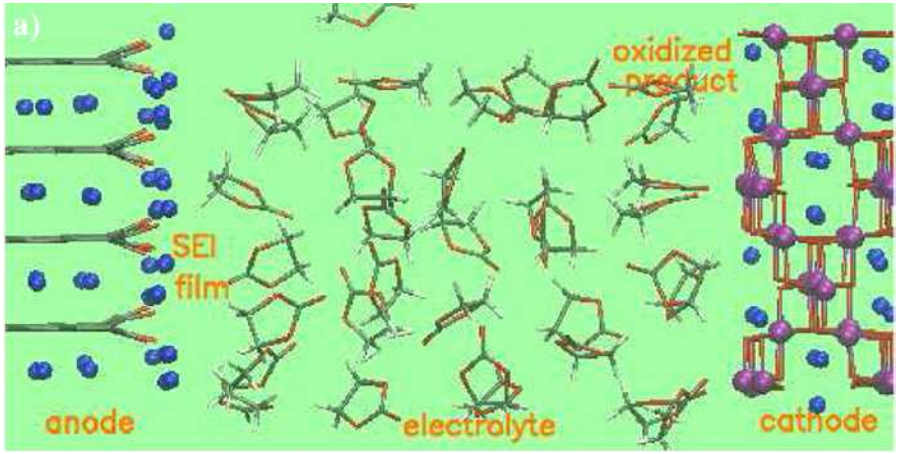
2. Mixed implicit + explicit (henceforth)
solvent compete with F^- for B-site



recall:

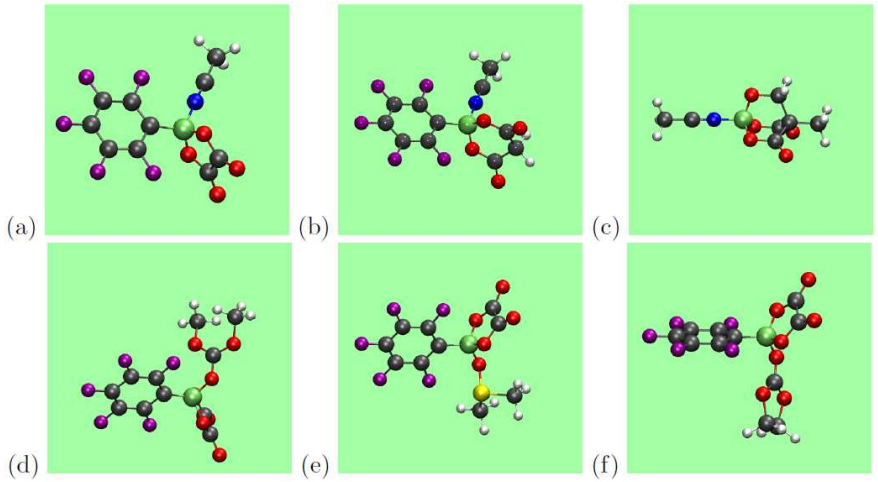


3. Purely explicit (best, costliest)



Not used here, in future

Survey of other solvent molecules gives similar trend



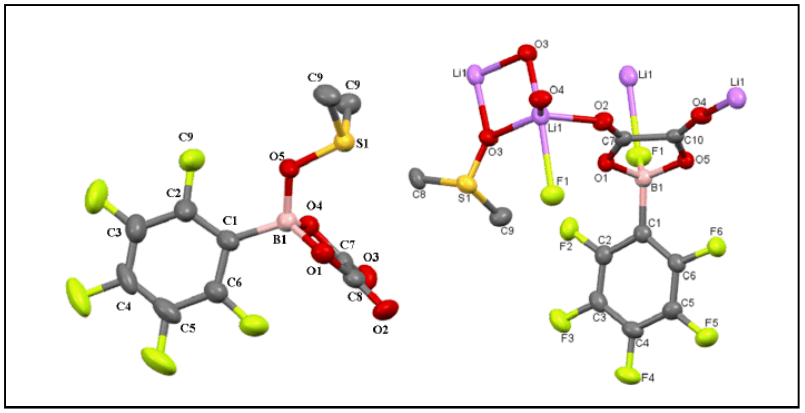
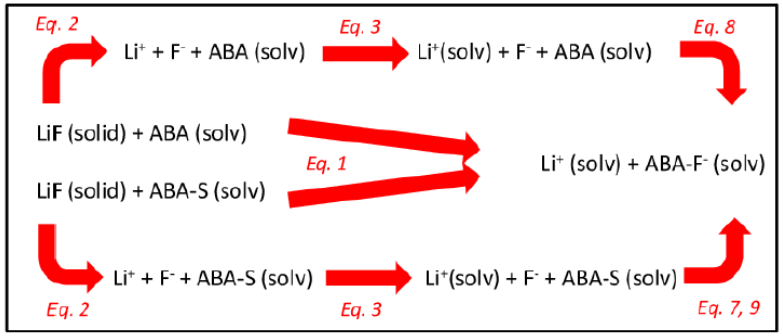


FIG. 5: X-ray crystal structures of ABAO-DMSO prior to solvent exchange (left panel) and ABAO-F^- after solvent exchange (right panel). The color scheme used is slightly different from Figs. 3-4. F, B, and Li are in green, light pink, and dark pink instead of purple, dark green, and dark blue. Protons are subsumed into carbon atoms.

	CH_3CN	DMSO	DMC	EC
ϵ_o	35.7	46.7	3.1	40.0
ABAO-F	-5.958	-5.968	-5.496	-5.962
ABAM-F	-5.637	-5.653	-5.215	-5.650
ABAT-F	-7.232	-7.245	-6.672	-7.238
ABAO-S	-0.248	-0.686	-0.087	-0.114
ABAM-S	-0.001	-0.414	-0.139	+0.083
ABAT-S	-1.532	-2.059	-1.346	-1.450
ABAO-F*	-5.710	-5.282	-5.409	-5.848
ABAM-F*	-5.636	-5.239	-5.076	-5.650
ABAT-F*	-5.700	-5.186	-5.326	-5.788

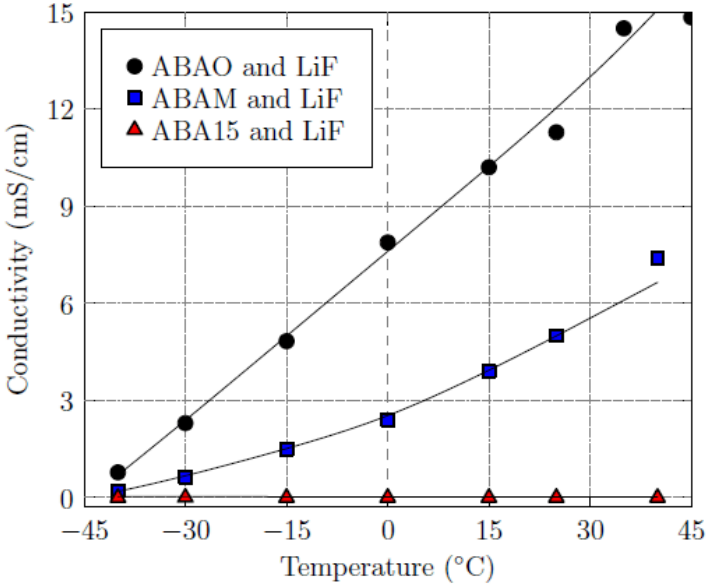
- DMSO binds exceptionally strongly to boron site
- Confirmed by X-ray scattering of ABAO-DMSO complexes when DMSO used in synthesis not removed in addition purification step

From ABA-F binding constants to LiF solubility



LiF free energy: -10.1 eV

	CH_3CN	DMSO	DMC	EC
Li^+S_4	-4.746	-5.008	-2.195	-4.445
ABAO-F/Li^+	-10.456	-10.290	-7.604	-10.293
ABAM-F/Li^+	-10.382	-10.247	-7.271	-10.095
ABAT-F/Li^+	-10.446	-10.194	-7.521	-10.223

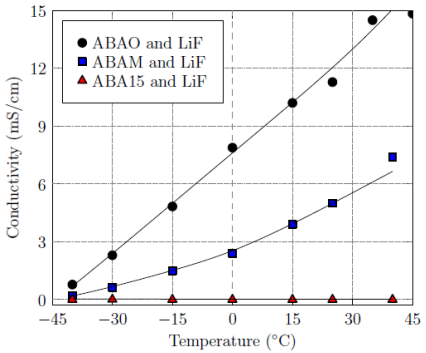


ABAO/EC : 43.3 M
ABAM/EC : 0.94 M

solubility systematically by 10x estimated, trends more accurante

- Measured conductivity ABAO > ABAM > ABA15, in agreement with DFT rankings

Digression: LiF solubility in EC absence of AAB



- LiF predicted to be almost insoluble in ABA15
- any solubility likely due to intrinsic LiF (no ABA)
- What is intrinsic LiF solubility in EC (ignore cosovlent)?

- $Li^+ + F^-$ (well-separated ions) solubility predicted to miniscule

- when ABA is absent, LiF "dissolves" as ionic aggregates, not Li^+ and F^-

Predicted solubility

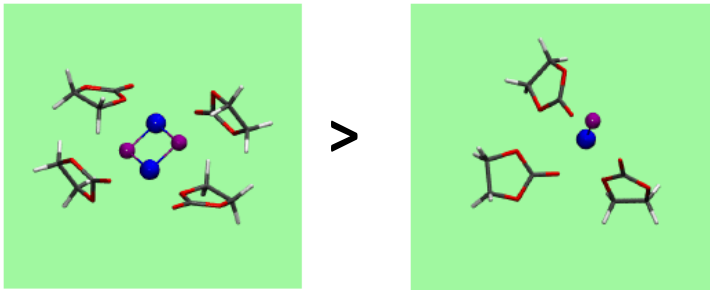


Table 6
Comparison of solubility values of lithium salts in DMC at 25 °C, with and without filtration.

Salt	Solubility with filtration $\pm 10^{-4}$ (mol L^{-1})	Solubility without filtration $\pm 10^{-4}$ (mol L^{-1})
LiF	2×10^{-4} [25]	2.19×10^{-2} [10]
Li_2CO_3	1×10^{-4} [25]	3.5×10^{-3} [this work][a]
LiOH	7×10^{-4} [25]	1.9×10^{-3} [this work][a]

[a] At 20 °C.

Journal of Molecular Liquids 153 (2010) 146–152

Lithium fluoride dissolution equilibria in cyclic alkylcarbonates and water

Jennifer Jones [a], Mériem Anouti [a,*], Magaly Caillon-Caravanier [a], Patrick Willmann [b], Daniel Lemordant [a]

- Measured LiF solubility depends on filtration pore size – consistent with ionic aggregate formation

see also:

Computational Study on the Solubility of Lithium Salts Formed on Lithium Ion Battery Negative Electrode in Organic Solvents

Ken Tasaki*,† and Stephen J. Harris‡ *J. Phys. Chem. C* **2010**, *114*, 8076–8083

Conclusions

- Anion receptors (ABA) needed to improve LiF solubility for CFx batteries
- Specific solvent effect important
- ABAO (simple oxalate-based receptor) as good as more bulky ABAs
- In absence of ABA's, LiF dissolves as ionic aggregates; expt. depend on pore size

Supporting slides

$$\mathrm{LiF(solid) + ABA(solv) \leftrightharpoons Li^+(solv) + ABA - F^-(solv).} \quad (1)$$

The dissolution process can be broken up into steps of a thermodynamic cycle:

$$\mathrm{LiF(solid) \leftrightharpoons Li^+ + F^-;} \quad (2)$$

$$\mathrm{Li^+ \leftrightharpoons Li^+(solv);} \quad (3)$$

$$\mathrm{ABA(solv) + F^- \leftrightharpoons ABA - F^-(solv).} \quad (4)$$

$$K_{\mathrm{diss}} = \exp(-\Delta G_{\mathrm{diss}}/k_{\mathrm{B}}T)\,, \quad (5)$$

$$= [\mathrm{Li^+}][\mathrm{F^-}]\,, \quad (6)$$

$$\mathrm{ABA(solv) + S\ (solv) \leftrightharpoons ABA - S\ (solv)} \quad (7)$$

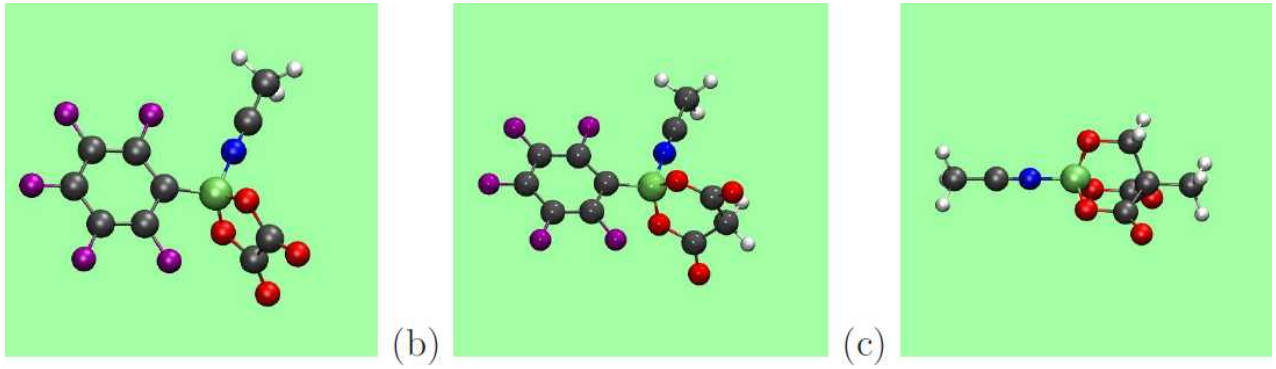
$$\mathrm{ABA(solv) + F^- \leftrightharpoons ABA - F^-(solv)} \quad (8)$$

$$\mathrm{ABA - S\ (solv) + F^- \leftrightharpoons ABA - F^-(solv) + S\ (solv).} \quad (9)$$

$$\mathrm{LiF(solid) + ABA(solv) + 4S(solv) \leftrightharpoons Li^+S_4(solv) + ABA - F^-(solv);} \quad (10)$$

$$\mathrm{LiF(solid) + ABA - S(solv) + 3S(solv) \leftrightharpoons Li^+S_4(solv) + ABA - F^-(solv),} \quad (11)$$

Specific solvent effect reduces selectivity, especially for ABAT



	ABAO	ABAM	ABAE	ABA12	ABA15	ABA21	ABAT
ABA-F$^-$ (ϵ_o=1)	-4.396	-4.171	-4.128	-3.741	-2.679	-4.234	-5.411
ABA-F$^-$ (ϵ_o=40)	-5.962	-5.650	-5.660	-5.450	-4.566	-5.581	-7.238
ABA-S (ϵ_o=40)	-0.249	-0.002	-0.069	NA	NA	-0.034	-1.533
ABA-F$^-$*(ϵ_o=40)	-5.714	-5.648	-5.591	-5.405	-4.521	-5.547	-5.705

If we don't use explicit solvent – binding constant off by 10^{25}