On the hunt for molecular organic battery materials

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Why batteries?

- the 'Energiewende':
  can you run an industrialized country with renewable energies only?
- transportation accounts for about one third of the energy bill;
  electrification of mobile power systems is difficult
- both fuel cells and (lithium ion) secondary batteries will be important
- current batteries cost about 500 to 750 $ per kWh and can supply 150Wh/kg
  $\rightarrow$ **250$/kWh and 300Wh/kg in 2020** would be a major step forward

Lithium-ion batteries

'Intercalation chemistry'

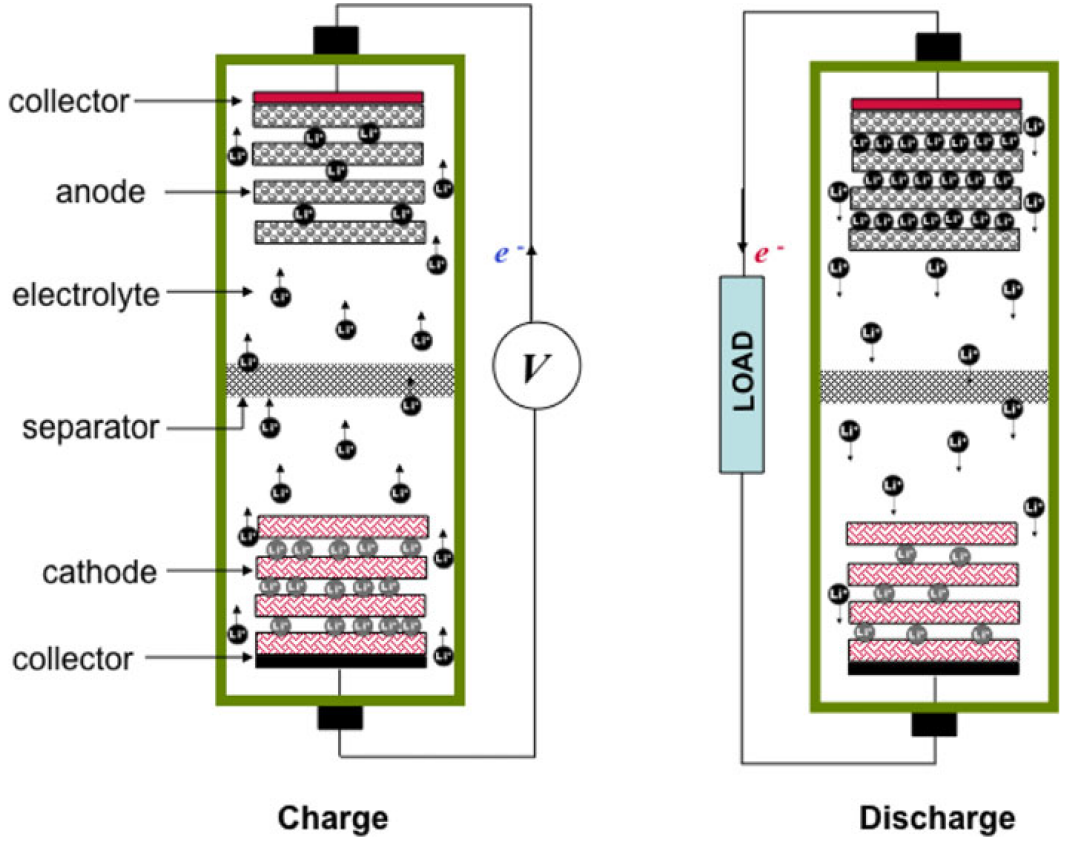
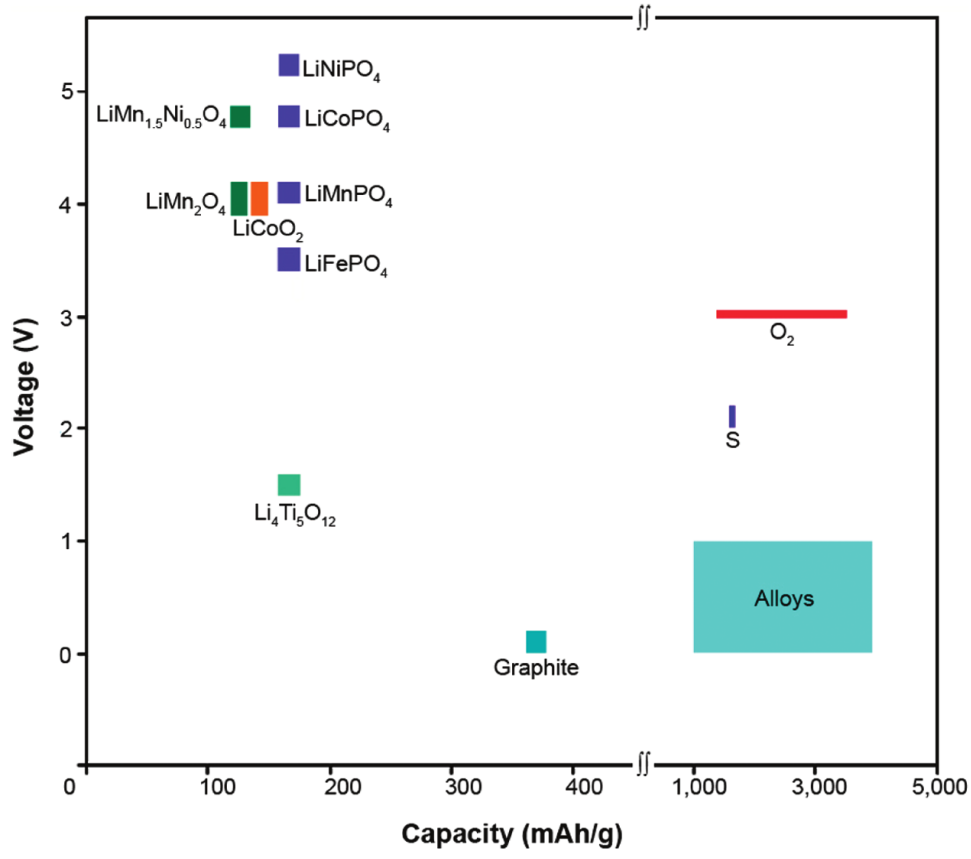


Figure: Schaefer *et al.*, Appl. Nanosci. 2011, DOI:10.1007/s13204-011-0044-x.

How to build better batteries?

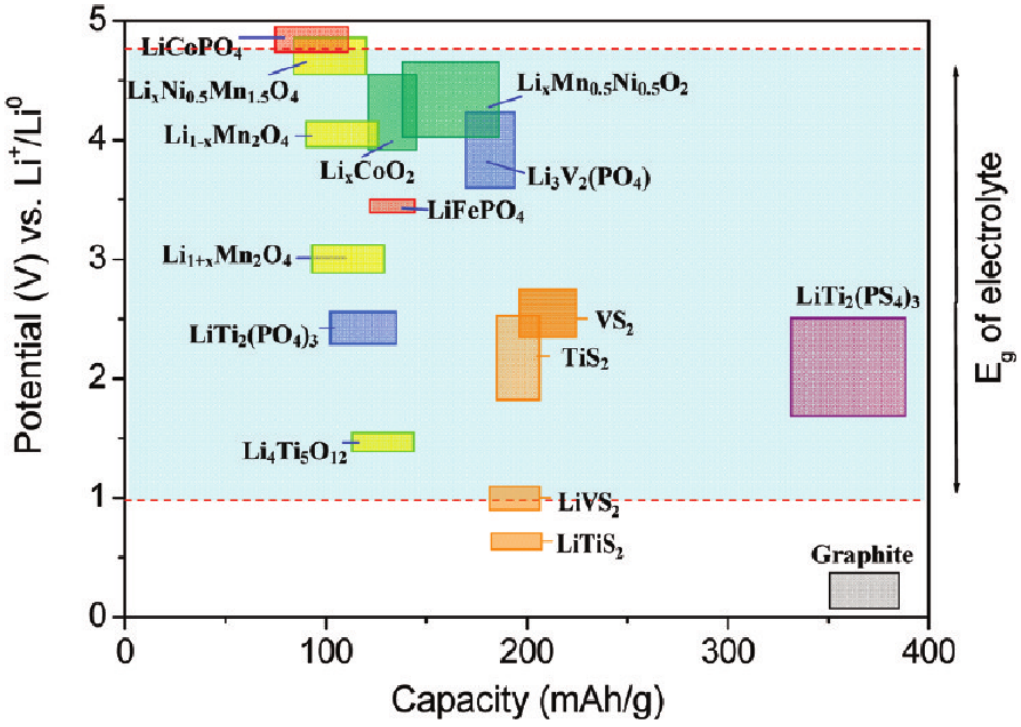
Voltage ($\rightarrow$ chemical potentials), capacity ($\rightarrow$ charge per mass or volume), ...
$\rightarrow$ materials from the upper left and right ends of the periodic table of elements



Figures: Manthiram, J. Phys. Chem. Lett. 2011, 2, 176184.

Why electrolyte materials?

- outside of focus for many years, opposed to cathode materials
- found to be more and more often roadblocks for further progress



- main issues: electrochemical stability & flash point vs ion conductivity/viscosity

Figure: Goodenough/Kim, Chem. Mater. 2010, 22, 587603.

Electrochemical stability: the (approximate) frontier orbital picture

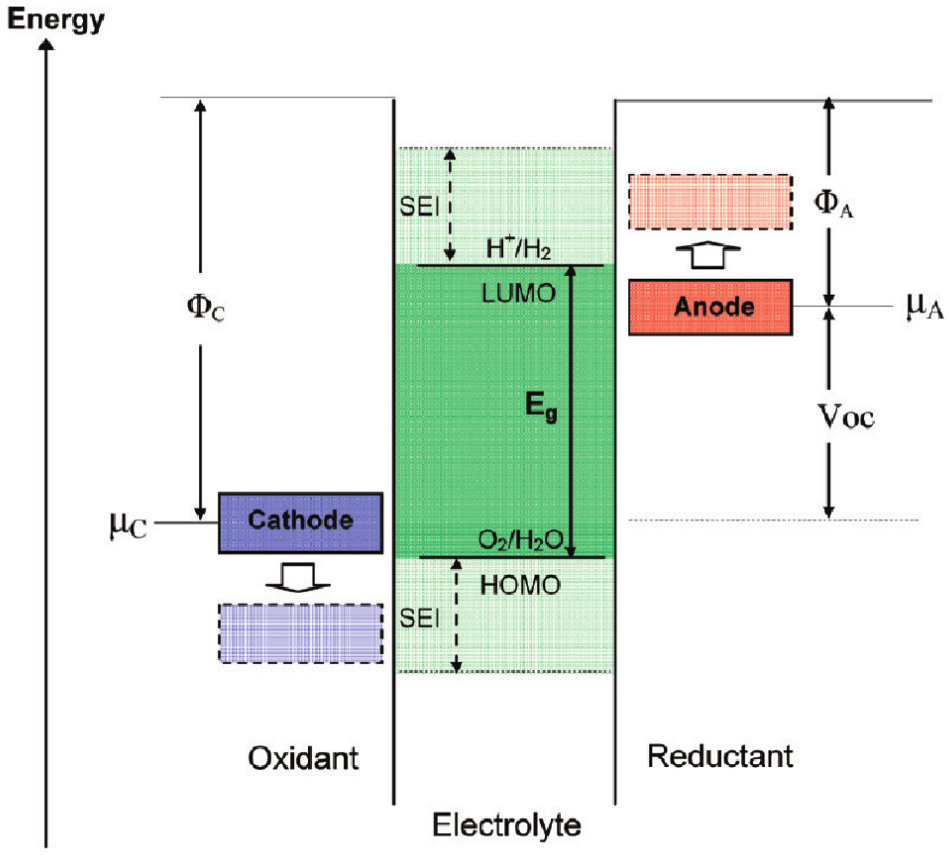


Figure: Goodenough/Kim, Chem. Mater. 2010, 22, 587603.

Solid electrolyte interface (SEI) formation

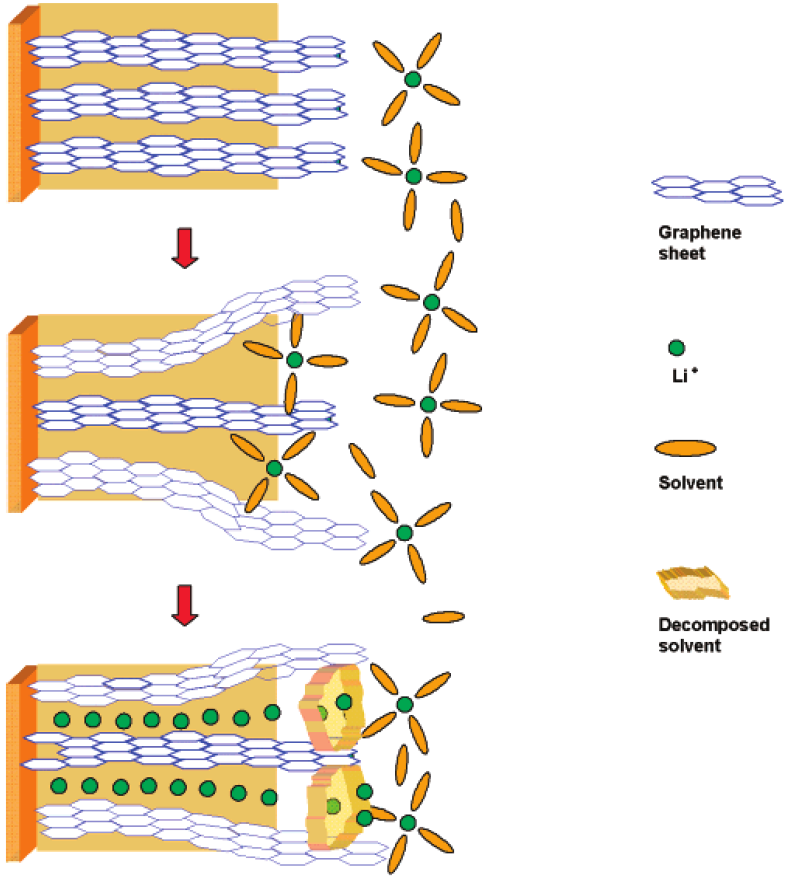
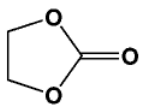


Figure: Xu, Chem. Rev. 2004, 104, 4303-4417.

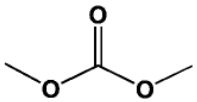
Current electrolytes

- solvents: mixtures of cyclic (highly polar, highly viscous) and linear (less polar, less viscous) organic carbonates, typically 50:50 EC/EMC
- salts: typically LiPF6
- additives: e.g. flame-retardants

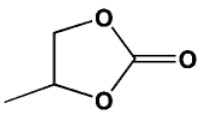
solvents are the least stable component of the electrolyte



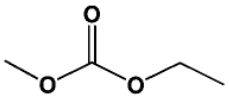
EC



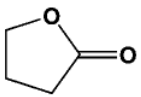
DMC



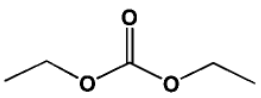
PC



EMC



γBL

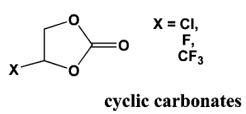


DEC

Alternative electrolytes

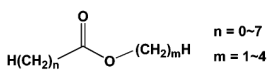
- gel polymers – safer, lower ion conductivity
- ionic liquids – more stable, safer, higher viscosity, too expensive?
- polymers and solids – very safe, low ion conductivity

more stable electrolyte solvents: esters, carbamates, F-ethers, sulfamides, sulfones

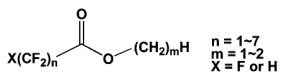


cyclic carbonates

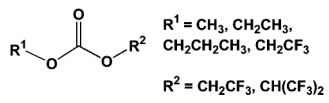
γBL



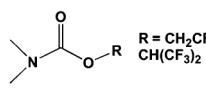
linear esters



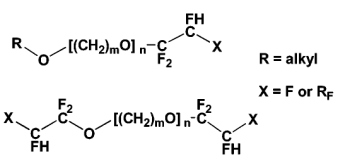
fluorinated esters



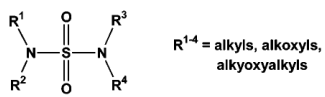
fluorinated carbonates



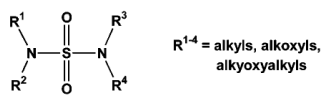
fluorinated carbamates



fluorinated ethers

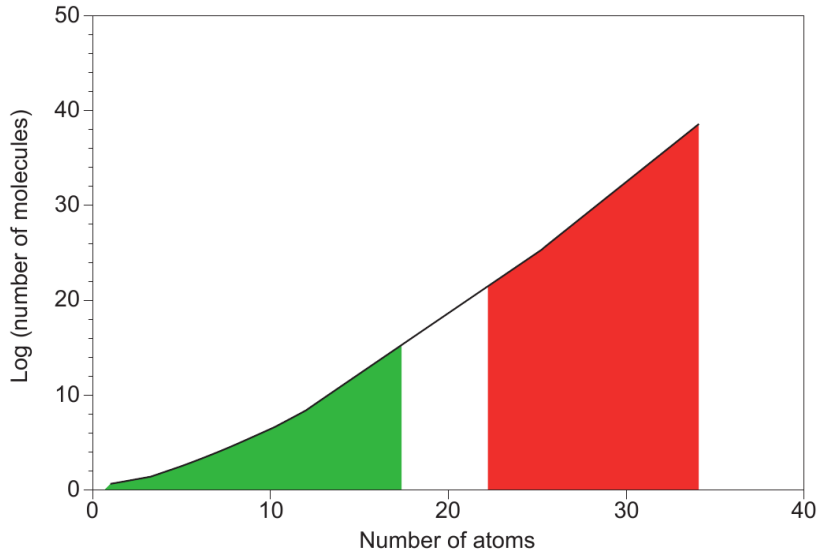


sulfamides



sulfamides

Why molecular organic materials?



Shoichet, Nature Chemistry 2013, 5, 9.

- **chemical space** is the ensemble of all organic molecules to be considered when searching for new drugs: 10^{60} molecules
- GDB-13 database: chemically stable and synthetically feasible molecules up to 13 atoms of C, N, O, Cl, S: 977 million structures
- **chemical space is vast** – chemical intuition vs diversity orientation;
  chemical space is rather uniform – retrosynthesis etc. works

Reymond *et al.*, WIREs Comput Mol Sci 2012, 2, 717.

State of the art: Static computational studies

- **focus on SEI formation in standard systems**
- **Balbuena and co-workers** made use of density functional theory (DFT) methods to publish a first series of thorough investigations into the reductive decomposition of solvent molecules starting around 2000
- subsequently, similar studies on reductive and oxidative decomposition of several solvents and additives by **Tasaki, Han, Curtiss, Johansson, Xing, Borodin, ...**
- Li+ de/solvation and intercalation investigated by for instance **Bhat, Henderson/Borodin, Tasaki/Winter (see later), ...**
- standard applications now include the computation of orbital values (HOMO/LUMO) as estimators for redox stability and/or spectra (e.g. Cekic-Laskovic *et al.*, *Electrochimica Acta* **2012**, *78*, 251.)

For details and references see: MK, Computational studies of SEI formation, *Specialist Periodical Reports: Chemical Modeling: Applications and Theory*, London **2014**. *in press*

Insight from static studies

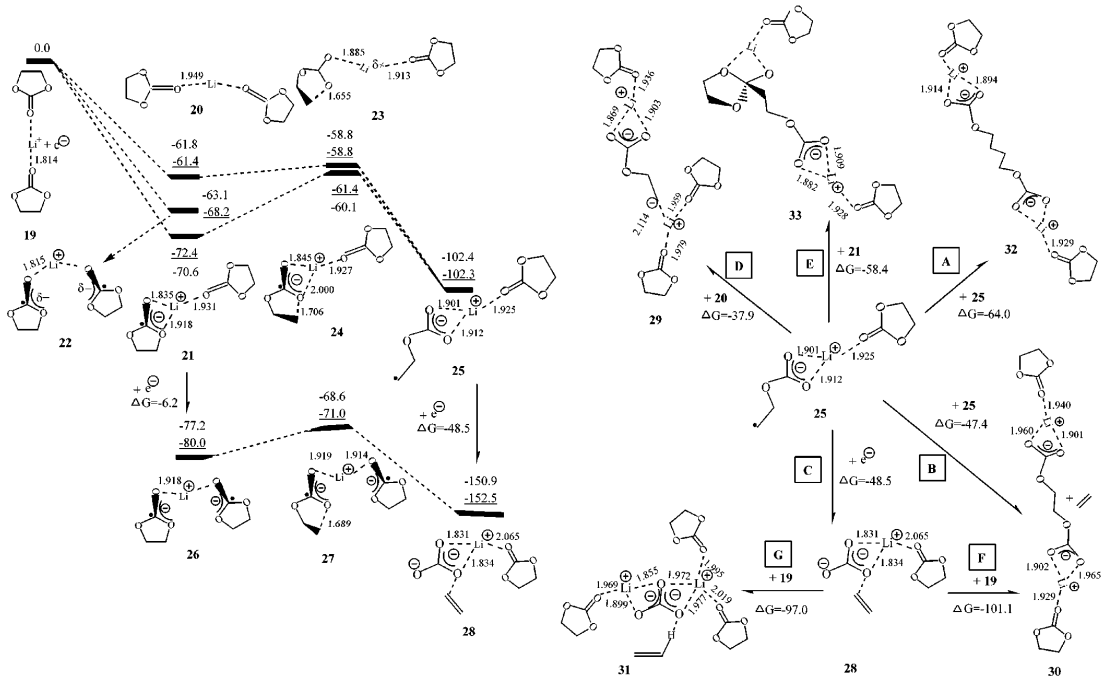


Figure 3. (a) Potential energy (underlined data) and Gibbs free energy profile at 298.15 K for the reductive dissociation process of $Li^+(EC)_2$ calculated with B3PW91/6-311++G(d,p)// B3PW91/ 6-31G(d) method. (b) Termination paths for the radical anion from the reductive dissociation process $Li^+(EC)_2$ calculated with B3PW91/6-311++G(d,p)//B3PW91/6-31G(d) method.

- complex picture of competing one- and two-electron decomposition pathways (e.g., Balbuena: EC decomposes in stepwise two-electron process to LBDC, LEDC, Lithiumcarbonate plus ester and carbide compounds)
- especially Borodin's work emphasizes the importance of at least one explicit solvent molecule (H-abstraction) and counter ions

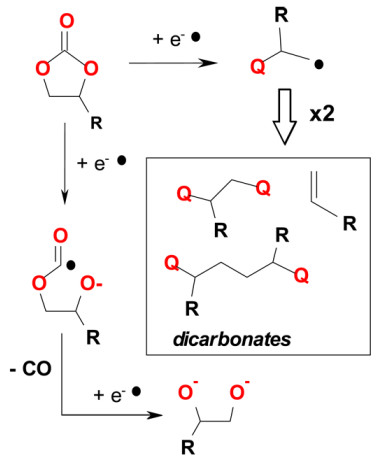
State of the art: Dynamic computational studies

- **focus on ionic liquids and again SEI formation**
- classical molecular dynamics (MMMD) studies on electrolyte bulk properties by **Tasaki, Borodin & Co. (Smith, Xing, Bedrov, ...) and others**, as well as on electrolyte structuring on polarized electrodes by **Borodin & Co.**
- extensive work on ionic liquids by **Borodin & Co.**, see also (polymer/ionic liquid) Diddens/Heuer, *ACS Macro Lett.* **2013**, *2*, 322; *J. Phys. Chem. B* **2014**, *118*, 1113.
- reactive force field (ReaxFF) MD studies on SEI formation (**van Duin, Bedrov, ...**) – but reaction barriers remain problematic
- first series of *ab initio* MD studies on SEI formation by **Leung and co-workers** from 2010 on; subsequently several AIMD studies also by others on Li+ de/solvation, intercalation, etc.

For details and references see: MK, Computational studies of SEI formation,
Specialist Periodical Reports: Chemical Modeling: Applications and Theory, London **2014**. *in press*

Insight from dynamic studies

Scheme 2. Current Scenarios for Reduction of Cyclical Carbonates and the Formation of SEI Components[a]



[a]In this Scheme, Q stands for the $-OCO_3^-$ Li^+ group.

Shkrob *et al.* J. Phys. Chem. C **2013** *117*, 19255.

- Leung's AIMD studies suggest a fast two-electron, CO-realizing route to LEDC; he even double-checked his results with static computations
- neither Leung's (barriers with GGA DFT) nor Balbuena's (biased pathway selection) work is likely the final answer
- first experimental observation of SEI-relevant radical intermediates by **Abraham and co-workers** illustrates the complexity of SEI formation, emphasizing rapid H-abstraction and migration, as well as radical and anionic polymerization

  Shkrob *et al.* J. Phys. Chem. C **2013** *117*, 19255; *J. Phys. Chem. C* **2013** *117*, 19270.

State of the art: Screening studies

- large body of work by **Ceder and co-workers** on electrode materials

- several studies by **Han and co-workers** on electrolyte solvents and SEI additives
  e.g. *Journal of Power Sources*, **2009**, *187*, 581. (108 molecules with DFT)
  Journal of Power Sources, **2011**, *196*, 5109. (now also Li+ binding affinity)
- **Hall/Tasaki**: electronic properties for over 7000 EC derivatives with PM3
  Journal of Power Sources, **2010**, *195*, 1472.
- **Tasaki**: six graphite intercalation compounds ($\rightarrow$ **Tasaki/Winter**)
  J. Phys. Chem. C **2014**, *118*, 1443.
- other work includes **Dahn** (e.g. redox shuttles), **Ceder** (ionic liquids), ... as well as several studies on Li-air electrolyte solvents by **Bryantsev and co-workers**

- **Amine/Curtiss and co-workers**: electronic properties and SEI formation, library with 400 compounds as of May 2013, unpublished ongoing work

For details and references see: MK, Computational studies of SEI formation,
Specialist Periodical Reports: Chemical Modeling: Applications and Theory, London **2014**. *in press*

General strategy

- **dynamic studies:**
  development of a QM/MM approach for electrochemical systems
  (FOR1376 DFG research group)

- **static studies:**
  standard quantum chemistry tool box (DFT-D, MP2, CEPA, CC)
  $\rightarrow$ 'redox fingerprinting' to estimate SEI composition

- **screening studies:**
  beyond orbital energies ...
  - state of the art **computational chemistry** for basic properties
  - methods from **chemical engineering** for estimating collective properties
  - tools from **chemoinformatics** for structure generation, data handling, ...

Last QMCIAA talk -1-

- benchmark study on computing electrochemical stability windows

$$V_{ox} = -\Delta G_{ox}/nF \quad and \quad V_{red} = -\Delta G_{red}/nF$$

- oxidation and reduction potentials

$$\Delta G_{ox} = \Delta G(X) - \Delta G(X^{+}) \quad and \quad \Delta G_{red} = \Delta G(X^{-}) - \Delta G(X)$$

- electronic energies plus enthalpic/entropic/solvation (RRHO/COSMO) effects

$$\Delta G = \Delta H - T\Delta S + \Delta G_{solvation}$$

Last QMCIAA talk -2-

- ... or just HOMO and LUMO values? From semiempirical QM (SQM) instead of hybrid DFT methods?

$$E_{HOMO} \approx IP = \Delta E_{ox} \approx \Delta G_{ox} \quad \textit{and} \quad E_{LUMO} \approx EA = \Delta E_{red} \approx \Delta G_{red}$$

- evaluation of electronic structure theory methods and approximations for **ranking(!)** compounds with respect to redox stability
- suggested screening protocol: SQM orbital energies for pre-screening, CEPA/QZVP free energy-based for final results

MK *Phys. Chem. Chem. Phys.* **2014**, *16*, 7919.

But ...

- ... looking at the electrochemical stability only does not allow to make helpful suggestions for experimentalists
- at least viscosities and flash points have to be taken into account

- accurate *ab initio* predictions practically impossible
- classical MD methods need extensive parametrization for acceptable results

- chemical engineering models like COSMOTHERM can do the job
- 'melting point prediction is black magic' (A. Klamt) $\rightarrow$ only purely empirical 'quantitative structure property relationship' (QSPR) methods available

... sad but true ...

COSMO-RS/COSMOTHERM

- alternative to group contribution method on one side and simulation on the other for calculating thermodynamic properties of liquid mixtures
- available for arbitrary species as system-specific parameters are derived from DFT
- enthusiastically taken up by chemical engineers over the last few years

- get 'sigma profiles' from DFT/COSMO calculations to estimate intermolecular interactions
- use simplified statistical thermodynamics models to estimate macroscopic properties
- global parameters fitted to large sets of experimental data

A. Klamt, F. Eckert, W. Artl, *Annu. Rev. Chem. Biomol. Eng.* **2010**, *1*, 101.

The extended tool box: cosmotherm

Viscosity [cP] MAD=0.22, Pearson=0.95, Kendall=0.78				**Flash Point [°C]** MAD=22.86, Pearson=0.95, Kendall=0.73			
Electrolyte	**Calculated**	**Measured**	**Deviation**	**Electrolyt**	**Calculated**	**Measured**	**Deviation**
1,3-DL	0,74	0,59	0,15	1,3-DL	-24,0	1	-25,0
2-Me-1,3-DL	0,87	0,54	0,33	2-Me-1,3-DL	-6,5		
2-Me-THF	0,62	0,47	0,15	2-Me-THF	-16,6	-11	-5,6
4-Me-1,3-DL	0,86	0,60	0,26	4-Me-1,3-DL	-8,1	-2	-6,1
BL	1,10	1,73	-0,63	BL	63,1	97	-33,9
DEC	0,76	0,75	0,01	DEC	-1,5	31	-32,5
DEE	0,90			DEE	12,1	20	-7,9
DMC	0,61	0,59	0,02	DMC	-30,7	18	-48,7
DME	0,55	0,46	0,09	DME	-31,5	0	-31,5
DMM	0,40	0,33	0,07	DMM	-61,8	-17	-44,8
EA	0,50	0,45	0,05	EA	-30,0	-3	-27,0
EB	0,75	0,71	0,04	EB	4,3	19	-14,7
EC	1,81	1,90	-0,09	EC	97,5	160	-62,5
EMC	0,69	0,65	0,04	EMC	-15,3		-15,3
MB	0,65	0,60	0,05	MB	-12,2	11	-23,2
NMO	1,60	2,50	-0,90	NMO	111,7	110	1,7
PC	1,79	2,53	-0,74	PC	102,8	132	-29,2
THF	0,50	0,46	0,04	THF	-37,4	-17	-20,4
VL	1,41	2,00	-0,59	VL	85,4	81	4,4

Table 1: Viscosity and flash point

The extended tool box: QSPR/cosmotherm

Melting Point [°C] MAD=17.69, Pearson=0.87, Kendall=0.75				**Boiling Point [°C]** MAD=22.64, Pearson=0.98, Kendall=0.76			
Electrolyte	**Calculated**	**Measured**	**Deviation**	**Electrolyte**	**Calculated**	**Measured**	**Deviation**
1,3-DL	-75,7	-95,0	19,3	1,3-DL	96,8	78	18,8
2-Me-1,3-DL	-40,9			2-Me-1,3-DL	123,9		
2-Me-THF	-97,2	-137,0	39,8	2-Me-THF	112,1	80	32,1
4-Me-1,3-DL	-40,9	-125,0	84,1	4-Me-1,3-DL	121,2	85	36,2
BL	-36,7	-43,5	6,8	BL	237,9	204	33,9
DEC	-37,0	-74,3	37,3	DEC	124,8	126	-1,2
DEE	-69,7	-74,0	4,3	DEE	144,5	121	23,5
DMC	-15,0	4,6	-19,6	DMC	78,9	91	-12,1
DME	-59,6	-58,0	-1,6	DME	80,7	84	-3,3
DMM	-98,4	-105,0	6,6	DMM	36,6	41	-4,4
EA	-83,8	-84,0	0,2	EA	84,2	77	7,2
EB	-86,9	-93,0	6,1	EB	134,0	120	14,0
EC	22,6	36,4	-13,8	EC	284,3	248	36,3
EMC	-38,0	-53,0	15	EMC	103,2	110	-6,8
MB	-83,6	-84,0	0,4	MB	109,1	102	7,1
NMO	40,1	15,0	25,1	NMO	320,0	270	50,0
PC	-15,2	-48,8	33,6	PC	299,0	242	57,0
THF	-100,1	-109,0	8,9	THF	81,9	66	15,9
VL	-17,3	-31,0	13,7	VL	278,4	208	70,4

Table 2: Melting and boiling point

Screening at work: nitrile solvents

- generate all stable (poly-)nitriles (e.g. no double or triple bonds etc.) up to 12 heavy atoms: $(NC)_{n=1\rightarrow5}C_{12-2n}H_{1\rightarrow23}$ $\rightarrow$ about 5000 compounds
- compute viscosities, boiling/flash/melting points, electrochemical stabilities and free energies of solvation of Li+, Mg2+, Al3+ and PF6- ions
- (compute free energies of solvation for a database of about 60 ionic liquid anions and 110 cations)

- ... this gives lots of numbers – but how to pick 'best' structures?
- keep only structures which are above average for all properties
- drop structures which are not pareto-optimal

T. Husch, N. D. Yilmazer, A. Balducci, MK, submitted.

Nitrile solvents: results

slide available on request

Screening at work: sulfonyl solvents

slide available on request

Screening at work: cyano-ester solvents

slide available on request

So we can make experimentalists happy, what's next?

1. More/accurate properties

- properties described very accurately:
  (ideal) electrochemical stability (via empirical, SQM, DFT, higher-level)
- properties described comparably well:
  melting/flash/boiling points, pure viscosities (via cosmotherm/QSPR)
- properties we like to be better at:
  free energies of solvation, solubilities, mixed viscosities (via cosmotherm)
- properties we have only a rough idea about:
  dielectric constants, conductivities (via dipole moments, viscosities, orbitals)
- properties not yet included in our scheme:
  toxicity, synthetic feasibility and cost (possible via QSPR)

What's next -2-

2. Multifunctionalization: chemical vs 'functional group' space

- virtual drug design screens chemical space because small structural differences can easily lead to less favorable interactions with target proteins
- for liquid phase properties, many features are averaged out
  $\rightarrow$ closer to the chemical intuition of functional groups
- is it more efficient to screen 'functional group space' for multifunctional electrolytes?

3. Model system based estimators for complex properties

- 'screenable' estimators for relationships suggested by experimentalists
- for instance Li+ binding affinity, graphite intercalation compound stability (next slides)
- systematically generated experimental references missing

Li+ binding affinity as estimator for graphite exfoliation

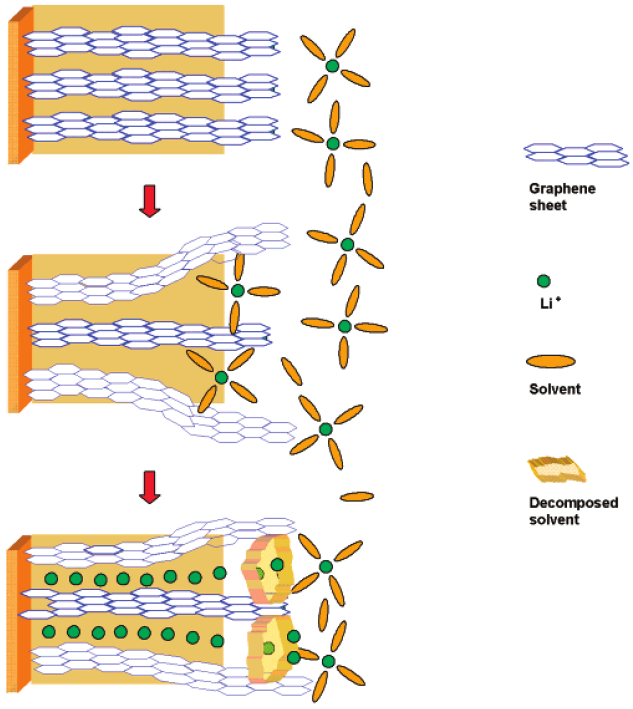
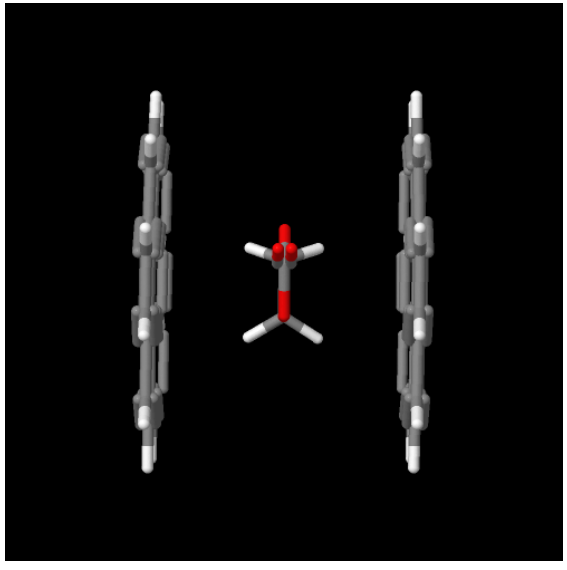


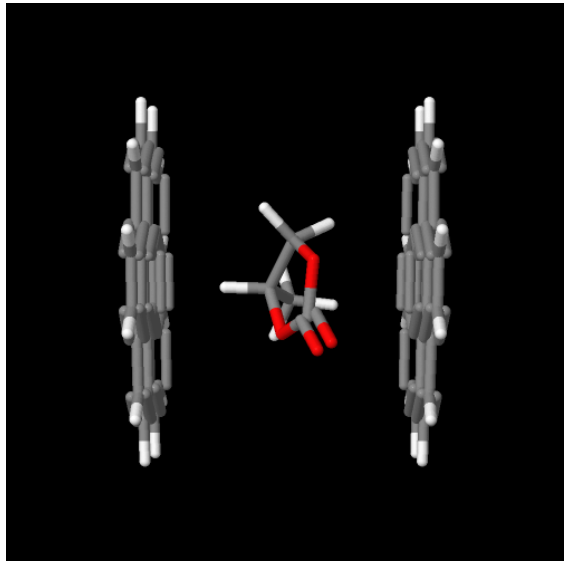
Figure: Xu, Chem. Rev. 2004, 104, 4303-4417.

- PC vs EC: **'a single methyl group delayed the emergence of Li ion technology by four decades!'** (Xu/v.Cresce, J. Mater. Chem. 2011, 21, 9849.)
- automatic Li+ bonded model system generation to compute Li+ binding affinity
- no systematically obtained experimental data available yet

Automatic graphite intercalation compound (GIC) model system generation

- Tasaki/Goldberg/Winter: EC-GICs more stable than PC-GICs; increased interlayer distance for PC-GICs Tasaki *et al. Electrochimica Acta* **2011**, *56* 10424.
- coronen sandwich setup reproduces both features at PM6-DH+ level: Heat of Formation -14.2 vs -12.1 kcal/mol; interlayer distance 7.0 vs 7.6 $\AA$





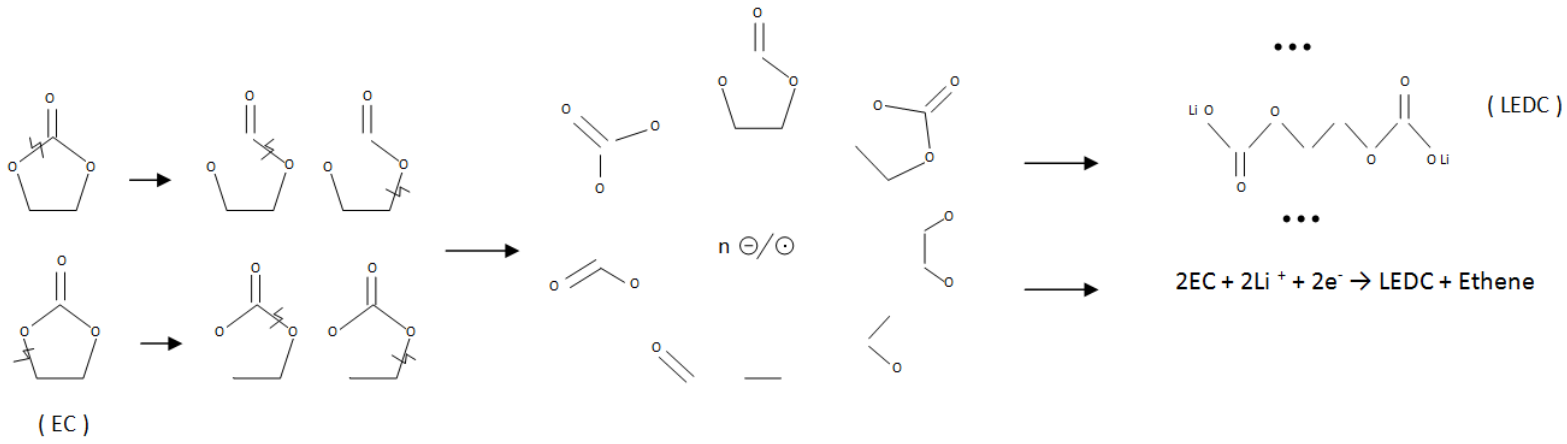
PM6-DH+: MK, J. Chem. Theory Comput., 2010, 6, 3808.

The computational battery researcher's holy grail: predicting SEI composition and properties

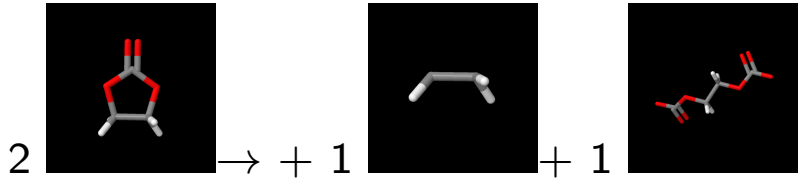
- effective electrochemical stability is much higher for compounds which form stable SEI films
- no computational model available for the atomic-scale description of SEI formation
- static (quantum chemistry) studies are biased, dynamic (AIMD) studies inaccurate, QM/MM might help a bit
- none of these approaches is 'screenable'

'You can't compute cake.' (D. Bressanini)

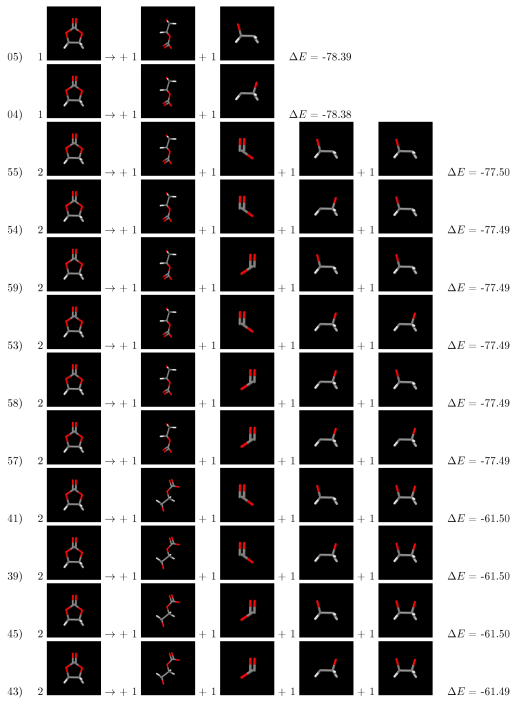
Can we screen for critical SEI components? – 'Redox fingerprints'

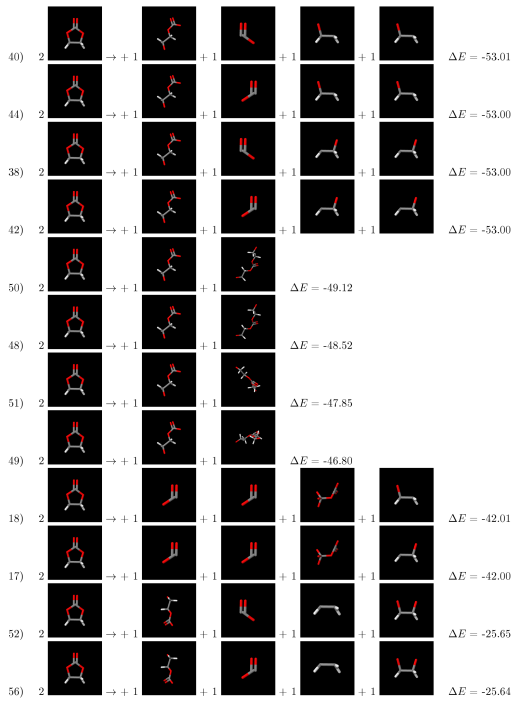


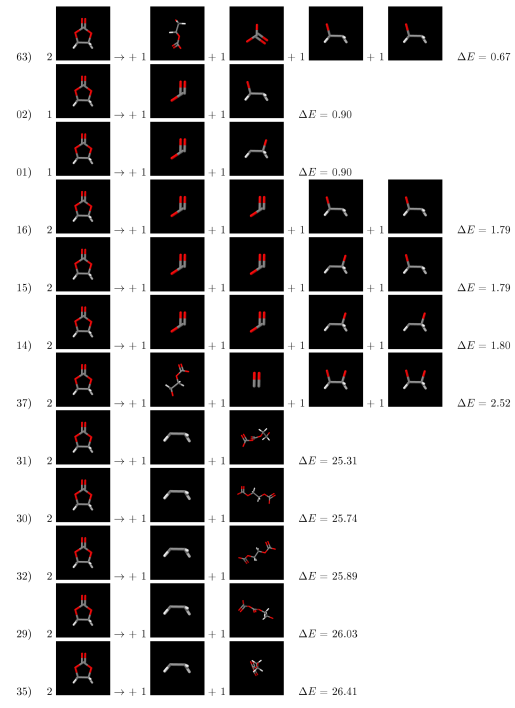
- automatic setup of all possible redox pathways (for a given set of basic rules for allowed redox steps)
- currently implemented for simple reduction steps, which by fragmentation and recombination lead to ...



... as well as ...







... and many more possible decomposition pathways ...

Redox fingerprints: results & outlook

- all suggested products (and many more) are generated
- results in agreement with previous static studies

- currently available: solubility-check
- upcoming: oxidation, explicit solvent effects, counter-ions
- more complicated: polymerization-check
- biggest challenge: (fast, automatic) barriers!
- implicit electrode effects?

- benchmark studies on the redox fingerprints of typical solvents
- comparison to experimental high-throughput work (Meet/Münster)

MK, submitted.

How QMC could be useful for battery research

- FCIQMC references for EC decomposition pathways
- QMC(/MM) MD studies of initial SEI formation

- QMC studies of Li+ desolvation and intercalation
- QMC studies on electrode materials ...

Summary & Outlook

- large scale computational screening of basic and collective properties
- 'blind' predictions in agreement with experiment
- additional model system based estimators (BEs, GICs and redox fingerprints)
- experimental high-throughput studies in preparation at Meet/Münster

http://qmcathome.org

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