Computational high-throughput screening of advanced battery electrolyte solvents and additives

Martin Korth

Institute for Theoretical Chemistry, Ulm University

The Towler Institute, Vallica Sotto - 31/07/2012

quantum chemistry based computational material science at the Institute for Theoretical Chemistry in Ulm

- biomaterials
 - focus: fast modeling of hydrogen-bond effects
 - improved scoring functions for protein ligand interactions
 - upcoming: organic-inorganic interfaces
- energy materials
 - focus: computational high-throughput screening
 - advanced battery electrolyte solvents and additives
 - upcoming: 'green' electrode materials

Why batteries?

- ► increasing global energy demand, rising carbon dioxide emissions, finite fossil fuel supplies and soaring fuel prices → renewable energy concepts needed
- \blacktriangleright personal transportation is an area with major impact on the energy bill \rightarrow electrification of the automobile necessary
- candidates to power future mobility are fuel cells and secondary batteries → technological and organizational problems have to be solved
- the above outlined problems are of especially high importance for Germany, because of the exceptional role of the German car industry





Figures: bmu.de and teslamotors.com

Electrification of the automobile

- economical reasoning is a major driving force for battery research: batteries will contribute substantially to future value chains
- safety is of utmost importance: millions of lithium-ion cells would travel by car every day – imagine some of them going up in flames occasionally ...
- \blacktriangleright current systems 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
- the most important factors for the success of electric vehicles are regulations and costumer sentiments (e.g. presumed loss of mobility)

vehicle type	mass (kg) ^b	$C_d \times A (m^2)$	city (Wh _{net} /mile)	highway (Wh _{net} /mile)
sub-compact	1200(2)	0.60	138	156
compact car	1400(4)	0.64	154	171
mid-size car	1550(4)	0.67	166	183
full-size car	1700(5)	0.71	178	194
minivan	2200(7)	0.93	224	250
van	2500(8)	1.56	283	361



Table and figure: Wagner et al., J. Phys. Chem. Lett. 2010, 1, 22042219.

How does a Lithium-ion battery work?



'Intercalation chemistry'

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

How to improve Lithium-ion 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.

Advanced battery trends

- high voltage transition metal cathodes
- graphite, silicon nanocomposite anodes
- polymer gel electrolytes, 5V electrolytes
- optimized production processes

electrode material	cell voltage (V)	capacity (mA h/g)	specific energy (mW h/g)	advantages	disadvantages
layered LiCoO ₂ cathode (2-d structure)	~4	140	560	high electronic and Li ⁺ ion conductivity; revolutionized the portable electronics market	expensive and toxic Co; safety concerns; only 50% of the theoretical capacity can be utilized
spinel LiMn ₂ O ₄ cathode (3-d structure)	~4	120	480	inexpensive and environmentally benign Mn; high electronic and Li ⁺ ion conductivity; excellent rate capability; good safety	severe capacity fade at elevated temperatures (55 °C)
olivine LiFePO4 cathode (1-d structure)	~3.5	160	560	inexpensive and environmentally benign Fe; covalently bonded PO ₄ groups lead to excellent safety	low electronic and Li ⁺ ion conductivity; needs small particle size and carbon coating to realize high rate capability; high processing cost
graphite anode	~ 0.1	370	_	inexpensive and environmentally benign C; low operating potential maximizes cell voltage	SEI layer formation and lithium plating lead to safety concerns; high processing cost

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

'Superbatteries' – beyond transition metal cathodes

- lithium-sulfur: solubility of Li-sulfur species problematic
- lithium-air: contaminant filtering and catalyst for reversible operation needed
- lithium metal anodes: growth of lithium-metal dendrites problematic
- superbatteries might be a good starting point for 'latecomers'



Figures: Scrosati et al., Energy Environ. Sci., 2011, 4, 3287. Jeong et al., Energy Environ. Sci., 2011, 4, 1986.

Why electrolytes?

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



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

The role of frontier orbitals



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



Future electrolytes

- gel polymers 5V electrolytes
- ionic liquids very stable, but too expensive?
- polymers and solids very safe, but ion conductivity too low?

more stable electrolyte solvents: esters, carbamates, ethers, sulfamides + sulfones



Why theory?

- understand basic processes
- design new materials

Why screening?

- systematically transfer insight into innovation
- use existing know-how from virtual drug design

Some recent theoretical work on batteries

- Sastry and co-workers: mesoscale modelling, e.g. of conduction phenomena Journal of Power Sources 2010, 195, 7904.
- Ceder and co-workers: thermodynamics and kinetics of Li/graphite intercalation Phys. Rev. B, 2010, 82, 125416.
- Kaxiras and co-workers: deformation of silicon electrodes Nano Lett. 2011, 11, 2962.
- Ceder and co-workers: high-throughput screening for cathode materials Science 2006, 311,977. Chem. Mater. 2011, 23, 3854. J. Mater. Chem., 2011, 21, 17147. Chem. Mater. 2011, 23, 3495.
- \rightarrow emphasis on cathode materials

Some recent theoretical work on electrolytes

- DFT modelling of solvent decomposition processes
 e.g. J. Phys. Chem. B 2009, 113, 5181. J. Phys. Chem. B 2009, 113, 16596.
- Kent and co-workers: electrolyte properties from *ab initio* molecular dynamics J. Phys. Chem. B 2011, 115.
- Leung and co-workers: initial stages of SEI formation with *ab initio* MD Phys. Chem. Chem. Phys., 2010, 12, 6583.
- Smith and co-workers: solvent decomposition from reactive FF simulations J. Phys. Chem. A, 2012, DOI: 10.1021/jp210345b
- \rightarrow focus on understanding solvent decomposition in current systems

Some recent theoretical work on screening electrolytes

- Han et al., electronic properties for 108 molecules with DFT Journal of Power Sources, 2009, 187, 581.
- Hall/Tasaki: electronic properties for over 7000 EC derivatives with PM3 Journal of Power Sources, 2010, 195, 1472.
- Park et al., electronic properties & Li binding affinity of 32 molecules with DFT Journal of Power Sources, 2011, 196, 5109.
- Amine/Curtiss and co-workers: electronic properties and SEI formation ongoing work, library with 275 entries as of May 2011
- \rightarrow small-scale exploratory screening studies with promising results

Computational high-throughput screening

Basic question: What are the rules for the 'better electrolytes' game?



- computation bottleneck: accuracy vs applicability!
- innovation bottleneck: how to crawl through 'chemical space'?

Computational high-throughput screening

electronic structure theory calculations

- model elementary processes with high-level methods to derive guidelines for structure generation (complementary to experimental studies)
- predict electrochemical windows and dipole moments with DFT and/or PM6
- use empirical models for melting/boiling points, dielectric constant, viscosity, ...
- evaluate chemical reactivity predictions with DFT and/or PM6
- analyze screening outcome with more sophisticated calculations

Computational high-throughput screening

chemoinformatics tasks

- structure generation (fully automatic, randomized, constrained)
 e.g. Kerber *et al.*, Commun. Math. Comput. Chem. 1998, 37, 205; ...
- reactivity prediction (lithiation, ...)
 e.g. Goodman and co-workers, Org. Lett., 2005, 7, 3541; ...
- structure evaluation (in terms of functional groups, etc.)
 e.g. Cosgrove/Willett, J. Mol. Graph. Mod. 1998, 16, 19; ...
- algorithms from virtual drug design etc. will need adjustments and further development for material science

Screening at work: data base studies

example setup 1

- 100000 molecules from NIST database
- 25000 molecules with 1st/2nd row elements and less/equal than 12 heavy atoms
- 23000 successful PBE/TZVP calculations
- ▶ 1200 molecules with HOMO/LUMO gap larger than EC
- 200 molecules with dipole moment larger 1 D
- 83 molecules with at least 1 C atom and more elements than just OH or HCF
- overall: 83 candidates out of 100000 database entries

Screening at work: data base studies

example results 1

- 6-33 atoms, 3-12 heavy atoms, 1-6 'functional atoms', 1-3 'functional elements'
- PBE/TZVP: gaps 6.7 to 8.0 eV, dipole moments 1.3 to 6.4 D (EC: 6.2eV, 5.4D)
- (di-/tri-)nitriles, fluoroethers, sulfonamides, sulfones, ...
- systematic trends for fluorination and substitution patterns
- very few, but very good multifunctional molecules → is multifunctionalization a rule in the 'better electrolytes' game?

Screening at work: structure library studies

example setup & results 2:

Is multifunctionalization a rule in the 'better electrolytes' game?

- start from multifunctional sulfone
- a) generate 5000 structures with 'defunctionalized' sulfone formula
- b) generate 5000 structures with 'cyano functionalized' sulfone formula
- screen for HOMO/LUMO gap with PM6 (reference gap 10.7 eV)
- a) HOMO/LUMO gaps 4.9 to 9.5, on average 8.1 eV
- b) HOMO/LUMO gaps 5.1 to 9.9, on average 8.7 eV

 \rightarrow very recent ORNL publication on the importance of multi-functionalization: Shao *et al.*, JPCB, 2012, 116, 3235. (12 functionalized sulfones with DFT)

But honestly, how trustworthy are these results?

Calculating electrochemical properties

electrochemical window (plus additional shift for reference electrode)

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

oxidation and reduction potentials

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

In from electronic energies plus thermal, entropy and solvation effects

$$\Delta G = \Delta H - T \Delta S pprox \Delta E + \Delta G_{temperature/entropy} + \Delta G_{solvation}$$

... or just HOMO and LUMO values? From SQM instead of DFT?

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

Electronic effects 1: DFT

Density functional theory (DFT): orbital approximation - barely acceptable



Electronic effects 2: SQM

Semiempirical QM methods (SQM): orbital approximation - very good



SQM vs DFT – SQM itself barely acceptable (though with orbitals SQM \approx DFT)



Geometry and temperature/entropy effects

SQM: geometry effects - barely acceptable for IPs



SQM: temperature/entropy effects - barely acceptable for IPs



Solvent effects (with COSMO)

SQM: solvent effects - qualitatively less important



SQM vs DFT - random numbers?



Overall effects

SQM vs SQM including geometry, temperature/entropy and solvent effects



SQM overall vs SQM with corrections calculated seperately



Summary of findings so far

 orbital approximation barely acceptable for DFT, SQM itself barely acceptable in comparison to DFT

- either use SQM HOMO/LUMO values (fast) or DFT ΔE values (accurate?) SQM ΔE or DFT HOMO/LUMO values are not worth the (intermediate) effort
- geometry and temperature/entropy effects are significant – how well are they described by SQM methods?
- solvent effects are important
 and they seem to be badly described at SQM level!
- SQM orbital based predictions have very limited accuracy
- DFT calculations need geometry, temperature/entropy and solvent corrections
- further evaluation e.g. at CEPA[1]/TZVPP level necessary

Next generation computational high-throughput screening

Screening for physical properties

- we want DFT-level redox potentials, i.e. based on free energies and including solvent effects with COSMO-RS, etc.
- we want to take all important properties into account for screening (low-level models are acceptable were high-level approaches are impracticable):
 - Iow melting point, high boiling point, high flash-point
 - high dielectric constant, low viscosity
 - Iow toxicity and cost
- (semi-)empirical models for melting points, dielectric constants, viscosities, etc.
 e.g. Preiss *et al.*, ChemPhysChem 2011, 12, 2959.
- chemoinformatics models also for toxicity, synthetic pathways (\rightarrow cost)?
- ... but that's still not enough ...

The central problem: SEI formation

The EC/PC disparity – screening for chemical reactivity

- current Lithium ion battery technology became possible with the move from propylene (PC) to ethylene carbonate (EC), which forms a protective solid electrolyte interface (SEI) on graphite electrodes
- 'a single methyl group delayed the emergence of Li ion technology by four decades!' (Xu/v.Cresce, J. Mater. Chem. 2011, 21, 9849.)
- ▶ graphit electrodes are likely to stay with us for some time → we better take SEI formation properties into account
- ► screening criteria: low LUMO value, small chemical hardness, high dipole moment (Halls/Tasaki), low Li⁺ binding affinity (≈ low dipole) (Park *et al.*)
- ... is there any chance to do this more properly?

Our solution: SEI related reactivity prediction

Chemical reactivity databases

- we want to be able to screen for reactivity patterns in the most general way: Li⁺ binding affinity for SEI formers, ethyl radical binding for redox shuttles, ...
- fast and fully automated screening possible through integration of reactivity predictions from chemoinformatics with quantum chemistry calculations
- reactivity patterns to be extracted from higher-level ab initio studies (as well as integration of results from upcoming publications in the field)
- successful build-up of chemical reactivity databases will depend on integration of cell chemistry specific theoretical and experimental work
- ... network building capability as indicator for SEI formation?

Summary

- ongoing development of a fast and flexible screening procedure for advanced battery electrolyte solvents and additives
- all important physical properties will be taken into account, resorting to lower-level models where necessary
- integrating chemoinformatics reactivity prediction with quantum chemistry will allow to efficiently screen for reactivity patterns
- application to 5V and 'superbattery' electrolytes, as well as 'green' electrodes possible; integration with experimental high-throughput screening technologies needed

No QMC at all?

- together with Tobias Schwabe, University of Hamburg: polarized embedding (PE) QMC/MM for water, solvent effects and redoxpotentials
- continued interest in QMC for biomolecular applications and thermochemistry (despite several disappointing experiences in the past ...)

Acknowledgments

- Axel Groß, Institute for Theoretical Chemistry, Ulm University
- Stefan Grimme, Mulliken Center for Theoretical Chemistry, Bonn University
- Dr. Barabara Mez-Starck Foundation
- German Academy of Sciences Leopoldina