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

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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**
- personal transportation is an area with major impact on the energy bill → **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 ...
- 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)

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

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

Advanced battery trends

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

<table>
<thead>
<tr>
<th>electrode material</th>
<th>cell voltage (V)</th>
<th>capacity (mA h/g)</th>
<th>specific energy (mW h/g)</th>
<th>advantages</th>
<th>disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>layered LiCoO₂ cathode (2-d structure)</td>
<td>~4</td>
<td>140</td>
<td>560</td>
<td>high electronic and Li⁺ ion conductivity; revolutionized the portable electronics market</td>
<td>expensive and toxic Co; safety concerns; only 50% of the theoretical capacity can be utilized</td>
</tr>
<tr>
<td>spinel LiMn₂O₄ cathode (3-d structure)</td>
<td>~4</td>
<td>120</td>
<td>480</td>
<td>inexpensive and environmentally benign Mn; high electronic and Li⁺ ion conductivity; excellent rate capability; good safety</td>
<td>severe capacity fade at elevated temperatures (55 °C)</td>
</tr>
<tr>
<td>olivine LiFePO₄ cathode (1-d structure)</td>
<td>~3.5</td>
<td>160</td>
<td>560</td>
<td>inexpensive and environmentally benign Fe; covalently bonded PO₄ groups lead to excellent safety</td>
<td>low electronic and Li⁺ ion conductivity; needs small particle size and carbon coating to realize high rate capability; high processing cost</td>
</tr>
<tr>
<td>graphite anode</td>
<td>~0.1</td>
<td>370</td>
<td>—</td>
<td>inexpensive and environmentally benign C; low operating potential maximizes cell voltage</td>
<td>SEI layer formation and lithium plating lead to safety concerns; high processing cost</td>
</tr>
</tbody>
</table>

'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'

Why electrolytes?

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

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

- EC
- DMC
- PC
- EMC
- γBL
- DEC
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

- Ceder and co-workers: thermodynamics and kinetics of Li/graphite intercalation

- Kaxiras and co-workers: deformation of silicon electrodes
  Nano Lett. 2011, 11, 2962.

- **Ceder and co-workers: high-throughput screening for cathode materials**

→ emphasis on cathode materials
Some recent theoretical work on electrolytes

- DFT modelling of solvent decomposition processes
- Kent and co-workers: electrolyte properties from *ab initio* molecular dynamics
- Leung and co-workers: initial stages of SEI formation with *ab initio* MD
- **Smith and co-workers: solvent decomposition from reactive FF simulations**

→ 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
- Hall/Tasaki: electronic properties for over 7000 EC derivatives with PM3
- 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

→ 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?
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

→ 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)

\[ V_{\text{ox}} = -\frac{\Delta G_{\text{ox}}}{nF} \quad \text{and} \quad V_{\text{red}} = -\frac{\Delta G_{\text{red}}}{nF} \]

- oxidation and reduction potentials

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

- ... from electronic energies plus thermal, entropy and solvation effects

\[ \Delta G = \Delta H - T \Delta S \approx \Delta E + \Delta G_{\text{temperature/entropy}} + \Delta G_{\text{solvation}} \]

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

\[ E_{\text{HOMO}} \approx IP = \Delta E_{\text{ox}} \approx \Delta G_{\text{ox}} \quad \text{and} \quad E_{\text{LUMO}} \approx EA = \Delta E_{\text{red}} \approx \Delta G_{\text{red}} \]
Electronic effects 1: DFT

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

DFT: basis set effects – augmentation for EAs needed
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?

**Graphs showing comparisons between SQM and DFT methods.**

- **IP/eV with PM6/COSMO**
  - Data range: 7 to 13 IP/eV.

- **EA/eV with PM6/COSMO**
  - Data range: -2 to 2 EA/eV.

- **∆G**
  - Data range: -3.5 to 3.5 ∆G/eV.

- **ΔG**^cosmo^/eV with DFT/TZVPP
  - Data range: -3.5 to 3.5 ∆G^cosmo^/eV.
Overall effects

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

SQM overall vs SQM with corrections calculated separately
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 $\Delta E$ values (accurate?) – SQM $\Delta E$ 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):
  - low melting point, high boiling point, high flash-point
  - high dielectric constant, low viscosity
  - low 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 (→ 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 \textit{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 ...)


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