Mass transport at electrified ionic liquid–electrode interfaces

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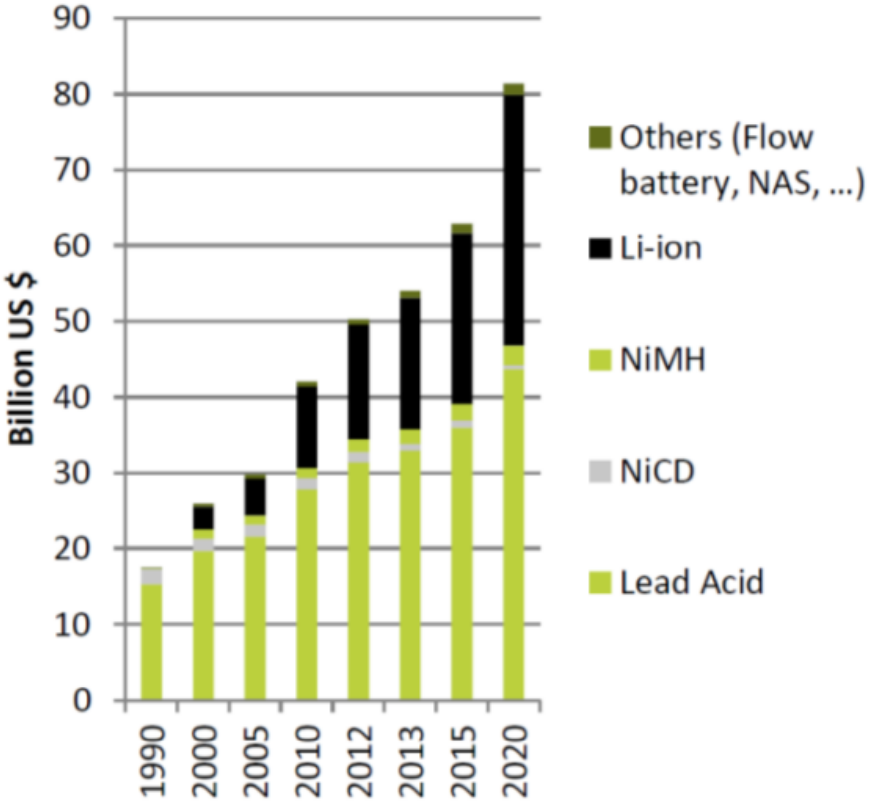
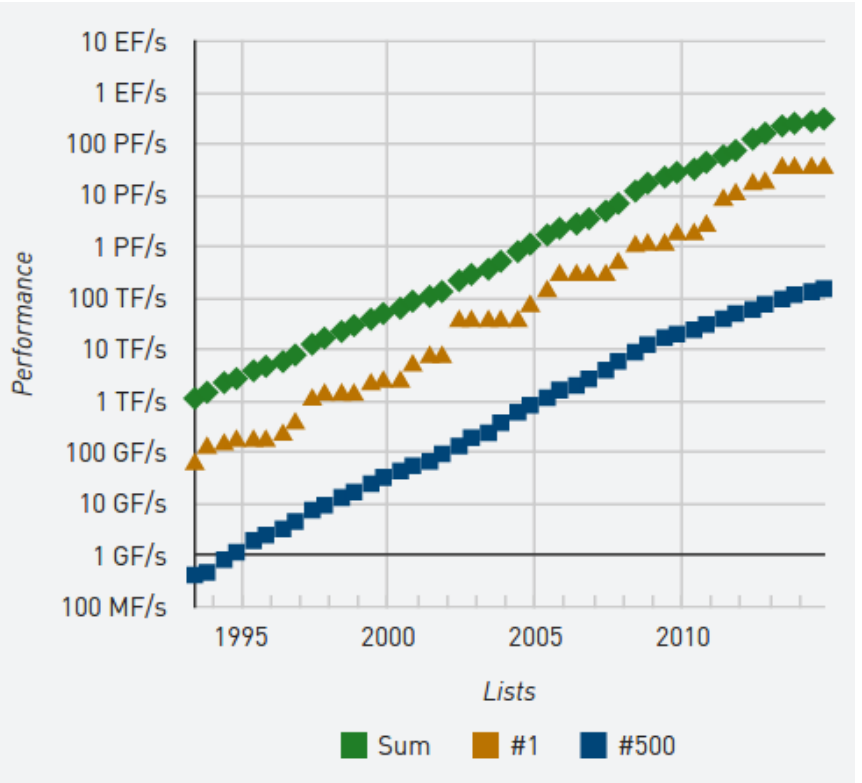
Current developments

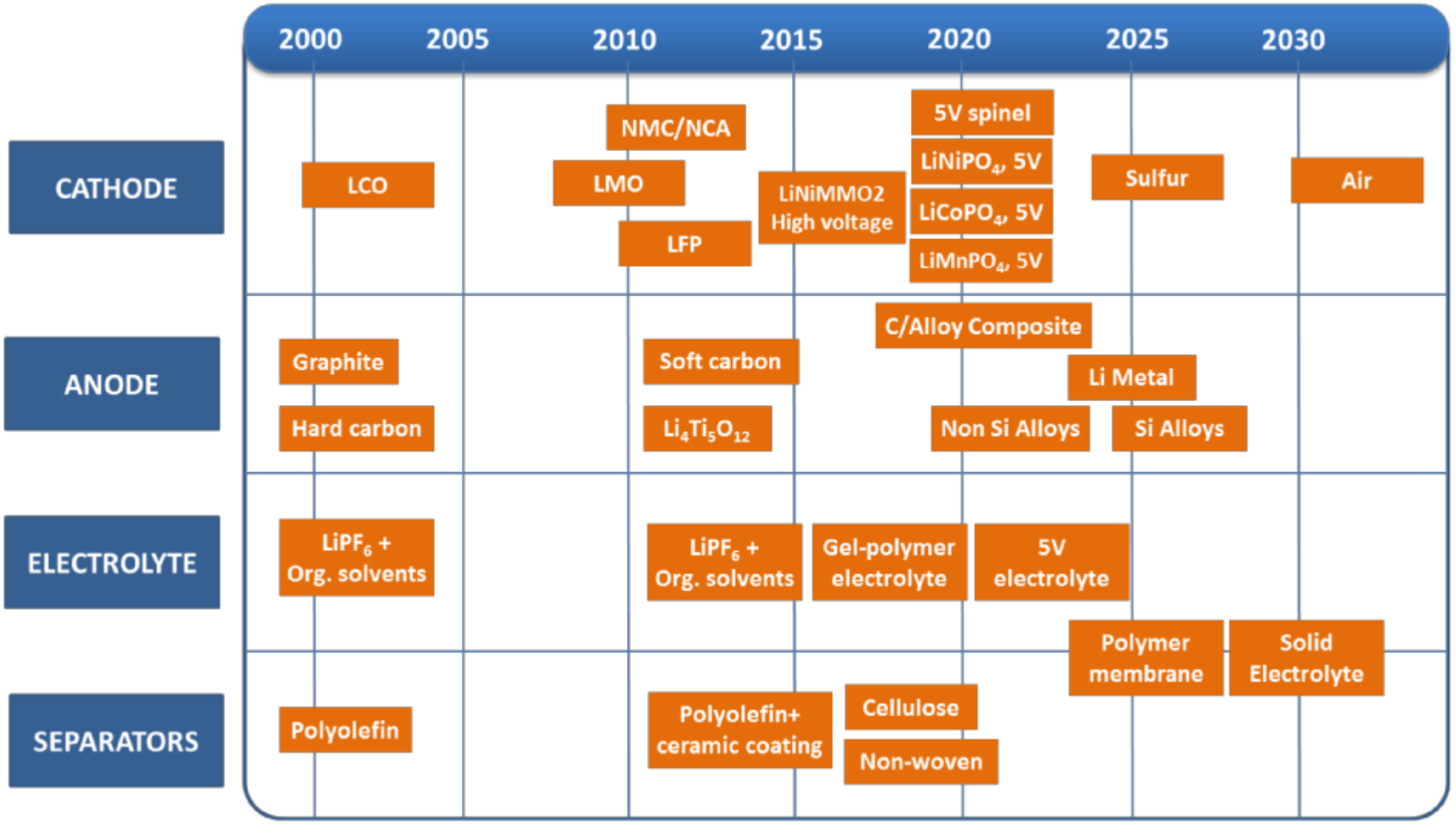
Energy sources, AVICCENNE



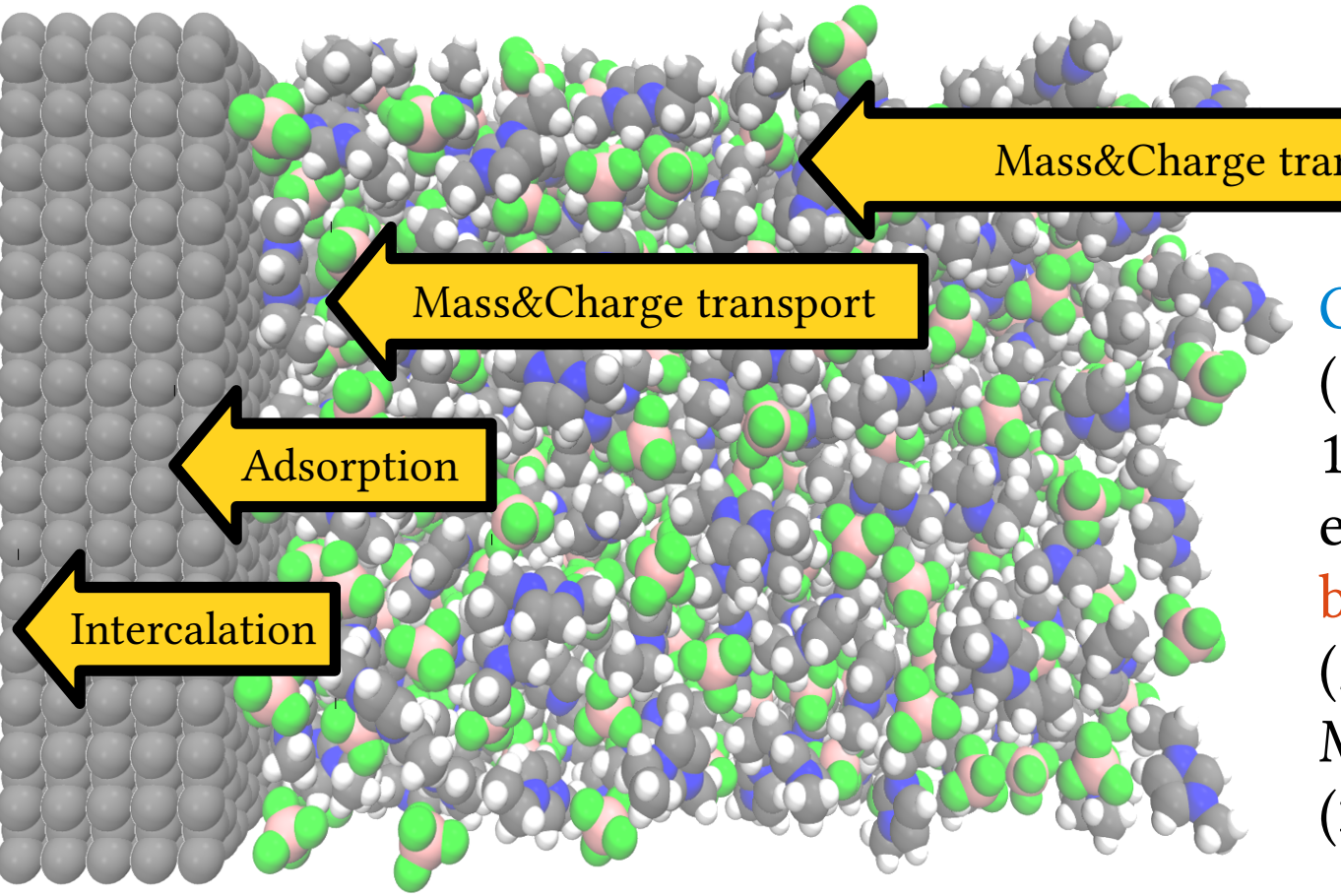
Computer power, top500.org



The battery market and materials trends



Ionic liquid–electrode interface



Computational screening:
(1) 2185 Li intercalation and 18226 Li conversion electrodes
build-a-battery.meteor.com
(2) 11000 electrolytes
M. Korth, PCCP 16 (2014).
(3) Few studies of interfaces

Electrode

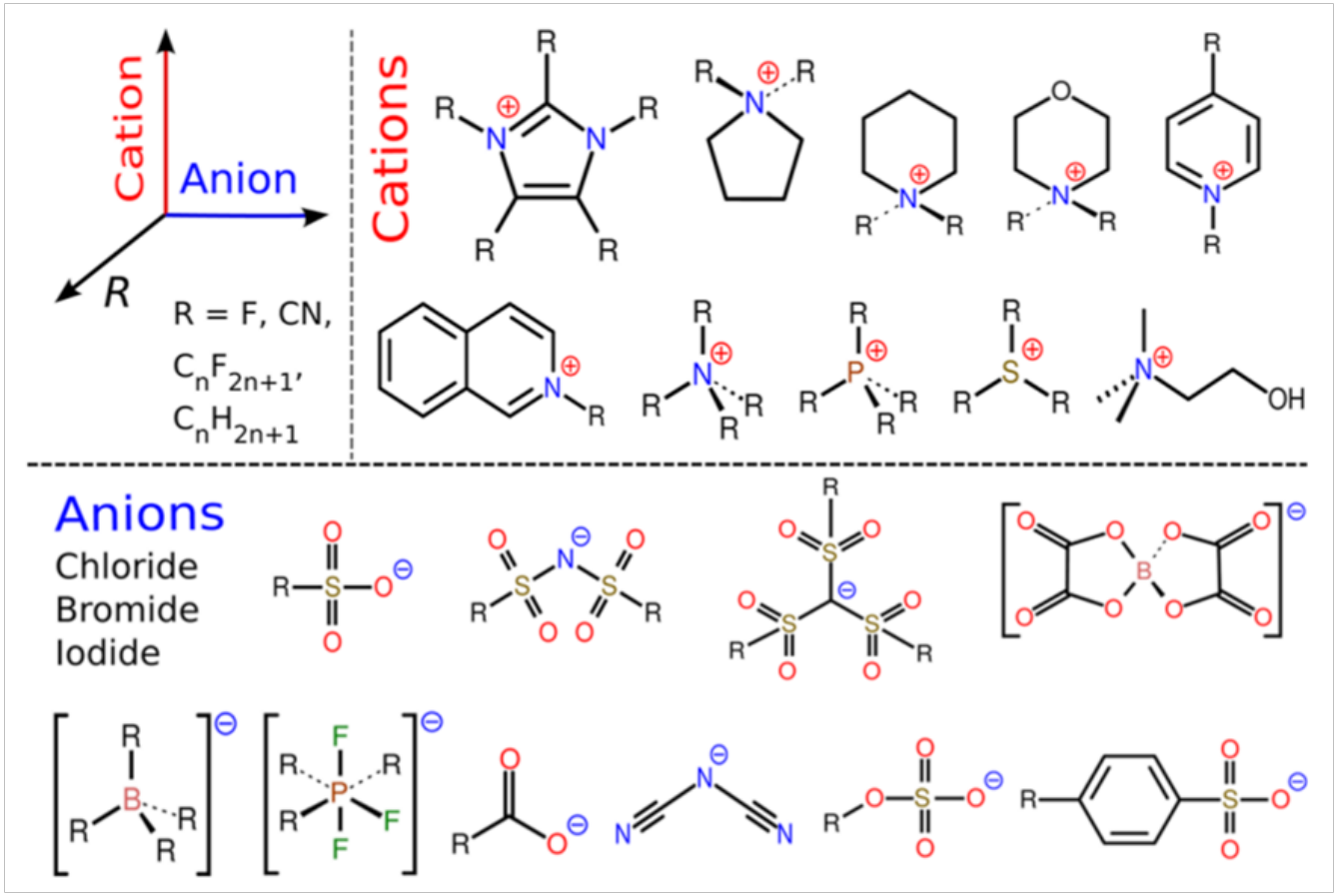
Surface

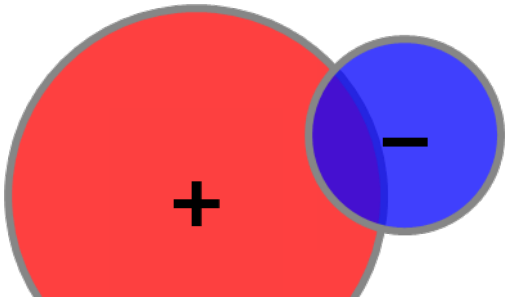
Electrical Double Layer (3 nm)

Electrolyte

Chemical space of ionic liquids

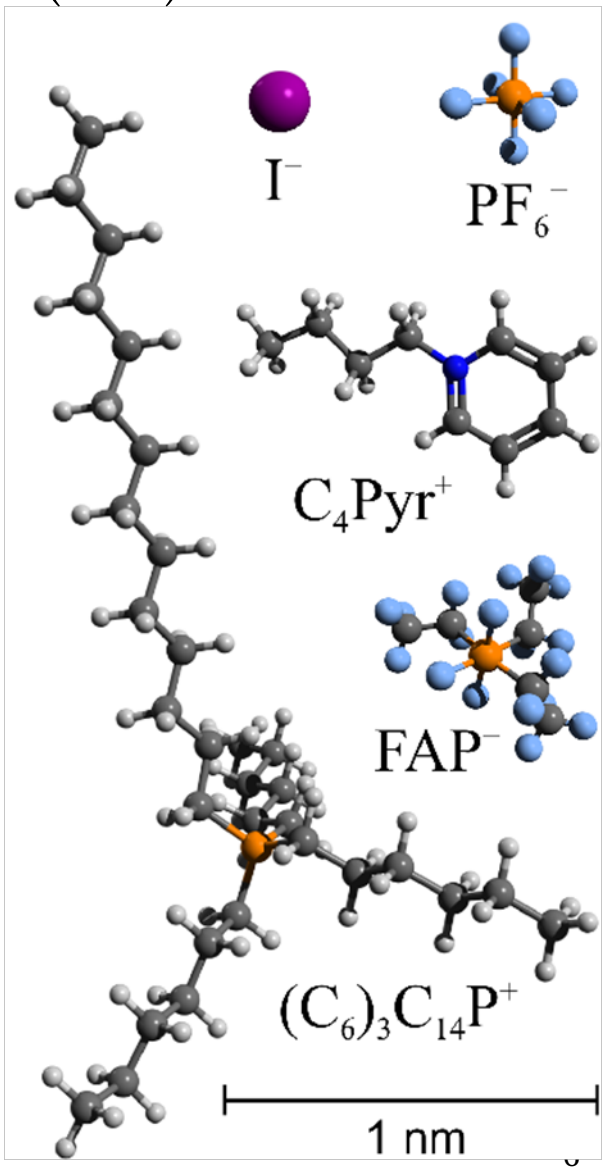
M.V. Fedorov, A.A. Kornyshev, Chem. Rev. 114 (2014) 2978.





Atomistic model →

← Coarse grained model



Matrix of electrolyte compositions

$$
\begin{array}{c} \\ [BF_4]^- \\ [DCA]^- \\ [FSI]^- \\ [TFSI]^- \end{array}
\begin{array}{c}
\begin{array}{ccc} [BMIm]^+ & [BMPyr]^+ & [BPy]^+ \end{array} \\
\begin{pmatrix} c_{11} & c_{12} & c_{13} \\ c_{21} & c_{22} & c_{23} \\ c_{31} & c_{32} & c_{33} \\ c_{41} & c_{42} & c_{43} \end{pmatrix}
\end{array}
\times
\begin{array}{c} \\ F^- \\ Cl^- \\ Br^- \\ I^- \end{array}
\begin{array}{c}
\begin{array}{ccc} Li^+ & Na^+ & K^+ \end{array} \\
\begin{pmatrix} h_{11} & h_{12} & h_{13} \\ h_{21} & h_{22} & h_{23} \\ h_{31} & h_{32} & h_{33} \\ h_{41} & h_{42} & h_{43} \end{pmatrix}
\end{array}
$$

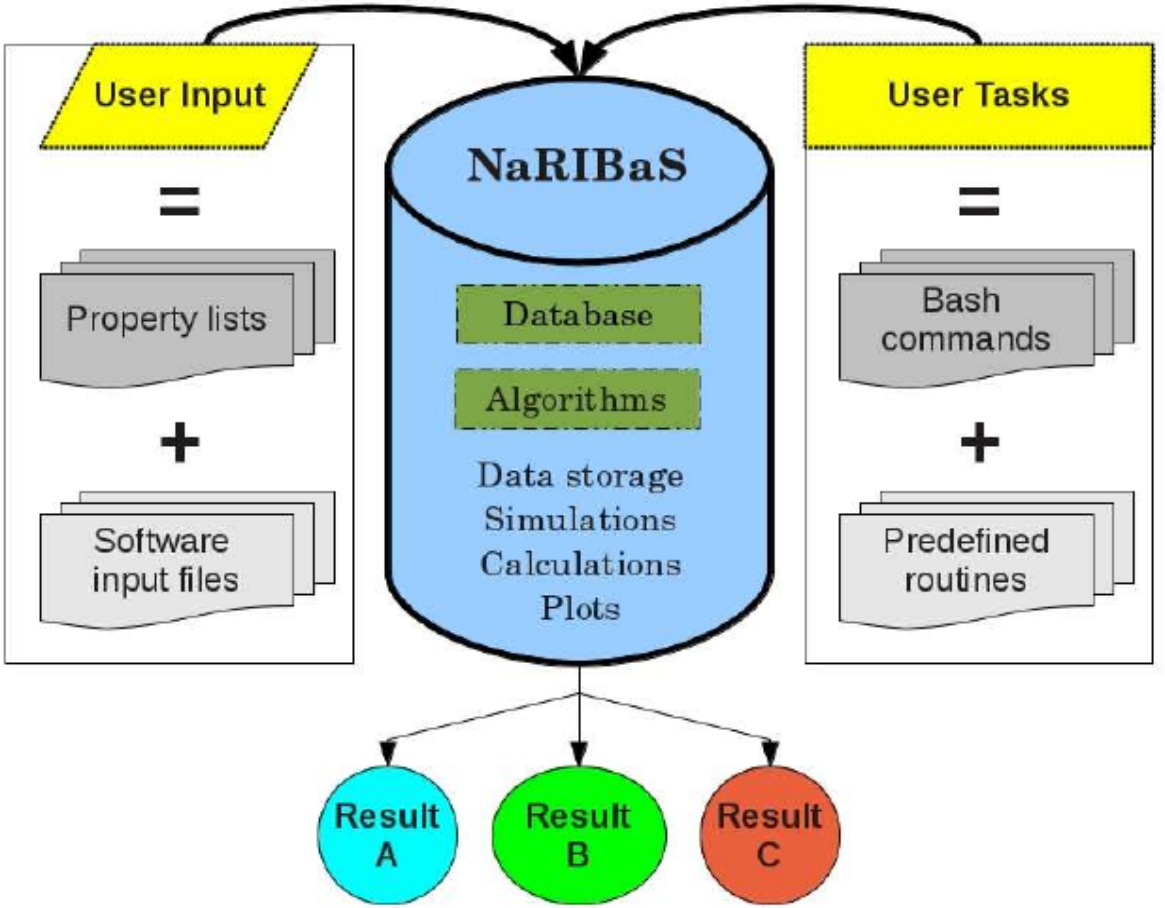
+

Variables:
Electrode material
Surface charge
Temperature & Pressure

NaRIBaS: A scripting framework for computational modelling of Nanomaterials & Room Temperature Ionic Liquids in Bulk and Slab

NaRIBaS workflow:

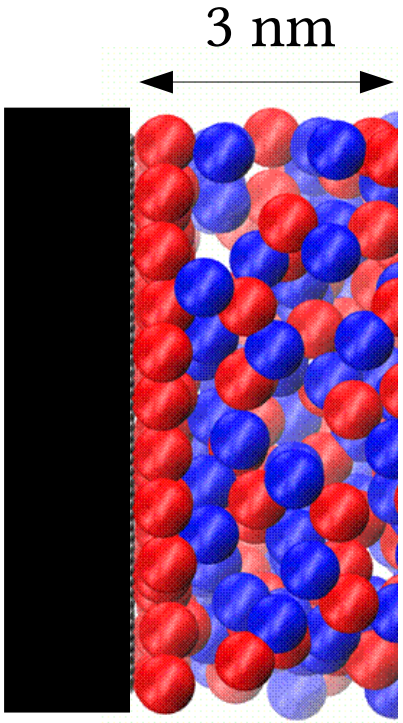
1. System preparation
2. Equilibration
   10 ns
3. Production run
   2 ns × n replica
4. Data management
5. Analysis



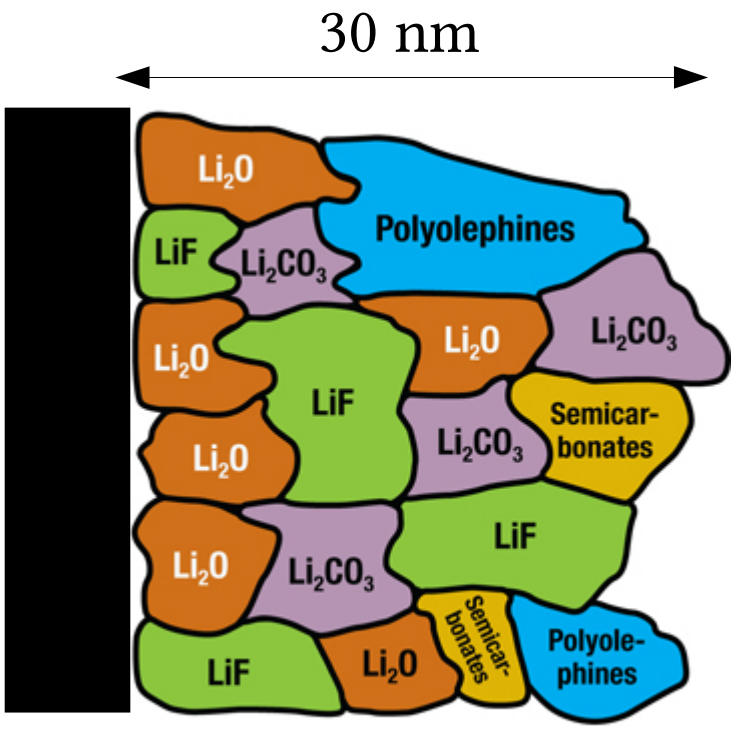
sourceforge.net/projects/naribas

Figure 1: General composition of NaRIBaS scripting framework.

A naive view on the interface

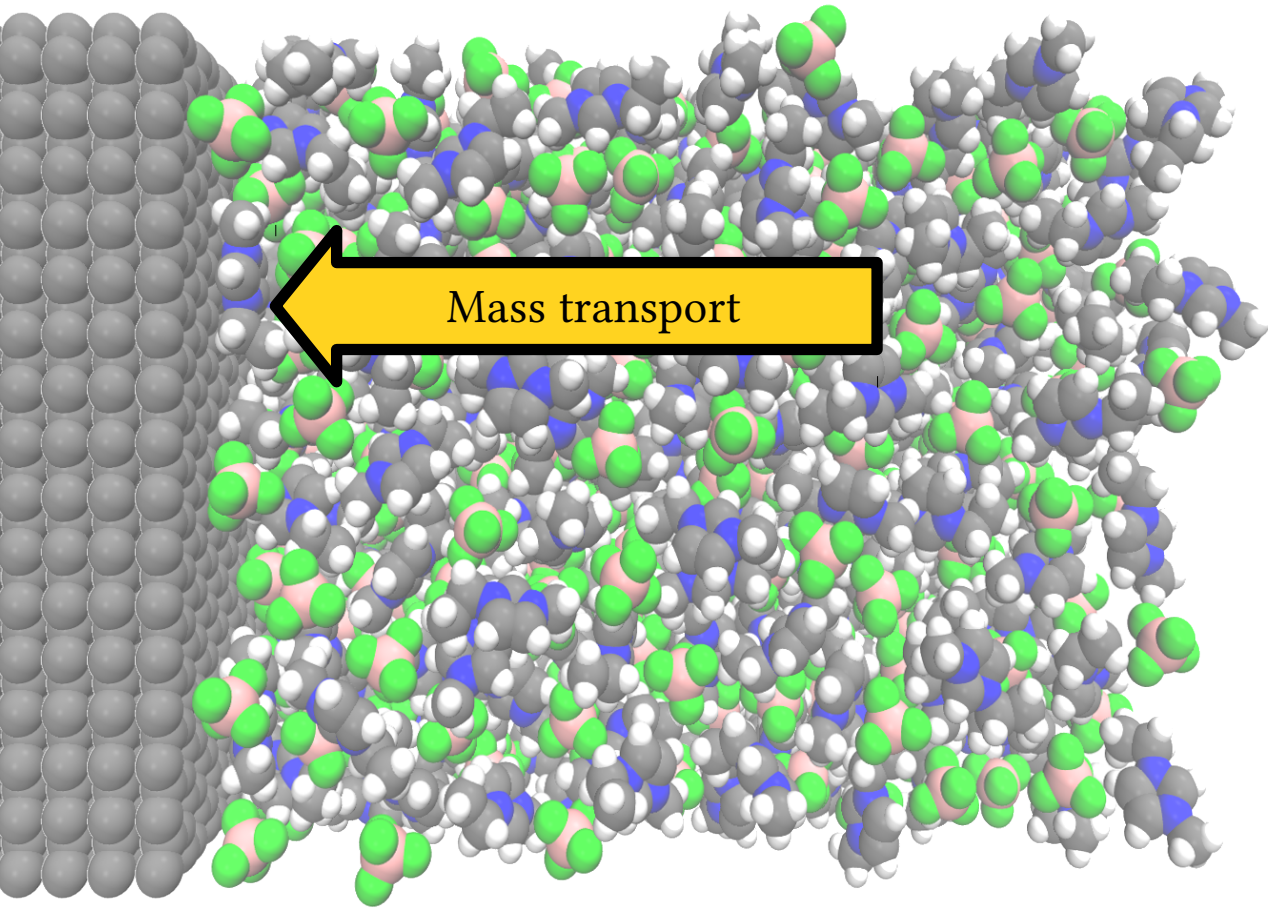


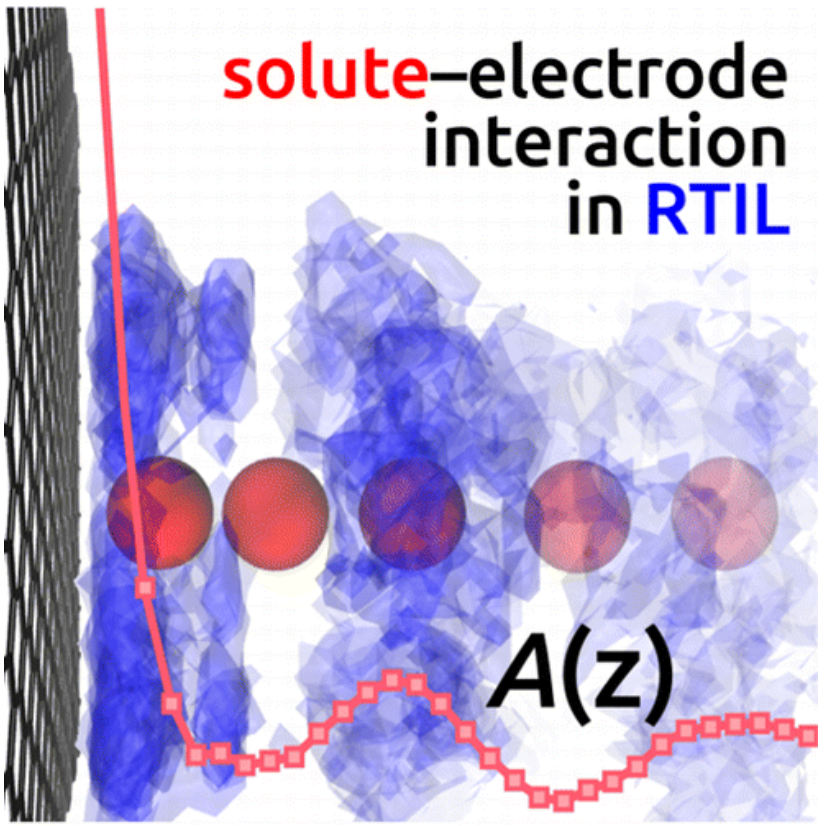
Model interface

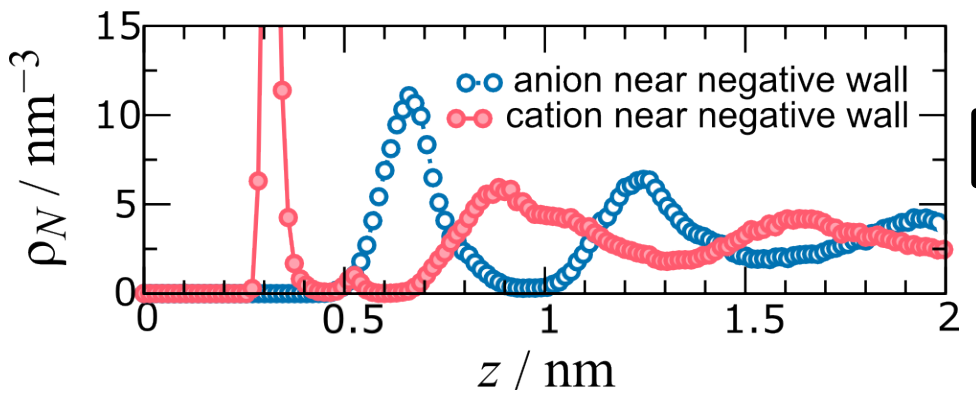


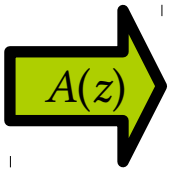
Realistic interface

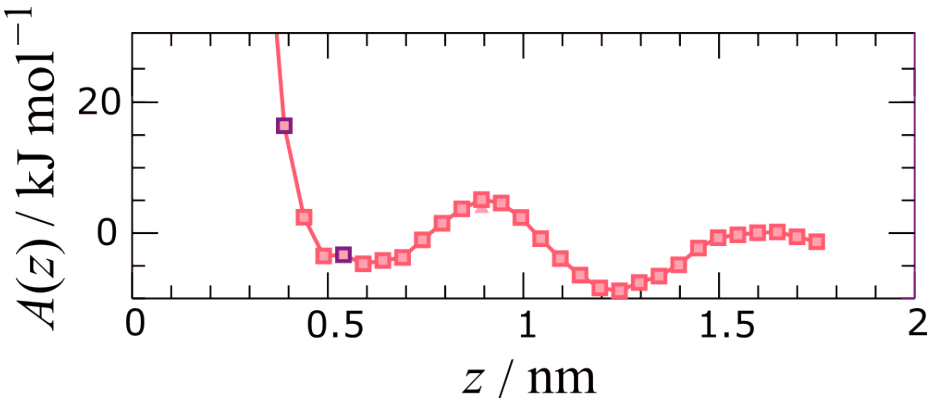
Mass transport and Free energy profiles











Mass transport and Free energy profiles

- Probability method

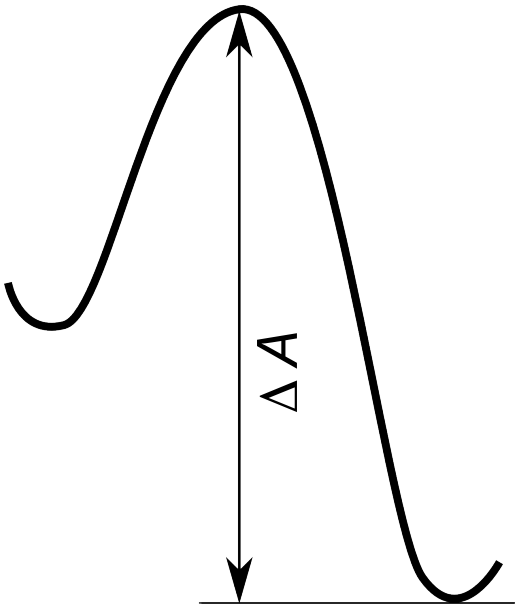
$$\rho(z) = \rho_{bulk} e^{-\beta A(z)} \Rightarrow$$

$$A(z) = -k_B T \ln \frac{\rho(z)}{\rho_{bulk}}$$

- Potential of mean force method

$$\langle F(z) \rangle = -\frac{dA(z)}{dz} \Leftrightarrow$$

$$A(z) = -\int_0^z \langle F(z') \rangle dz'$$

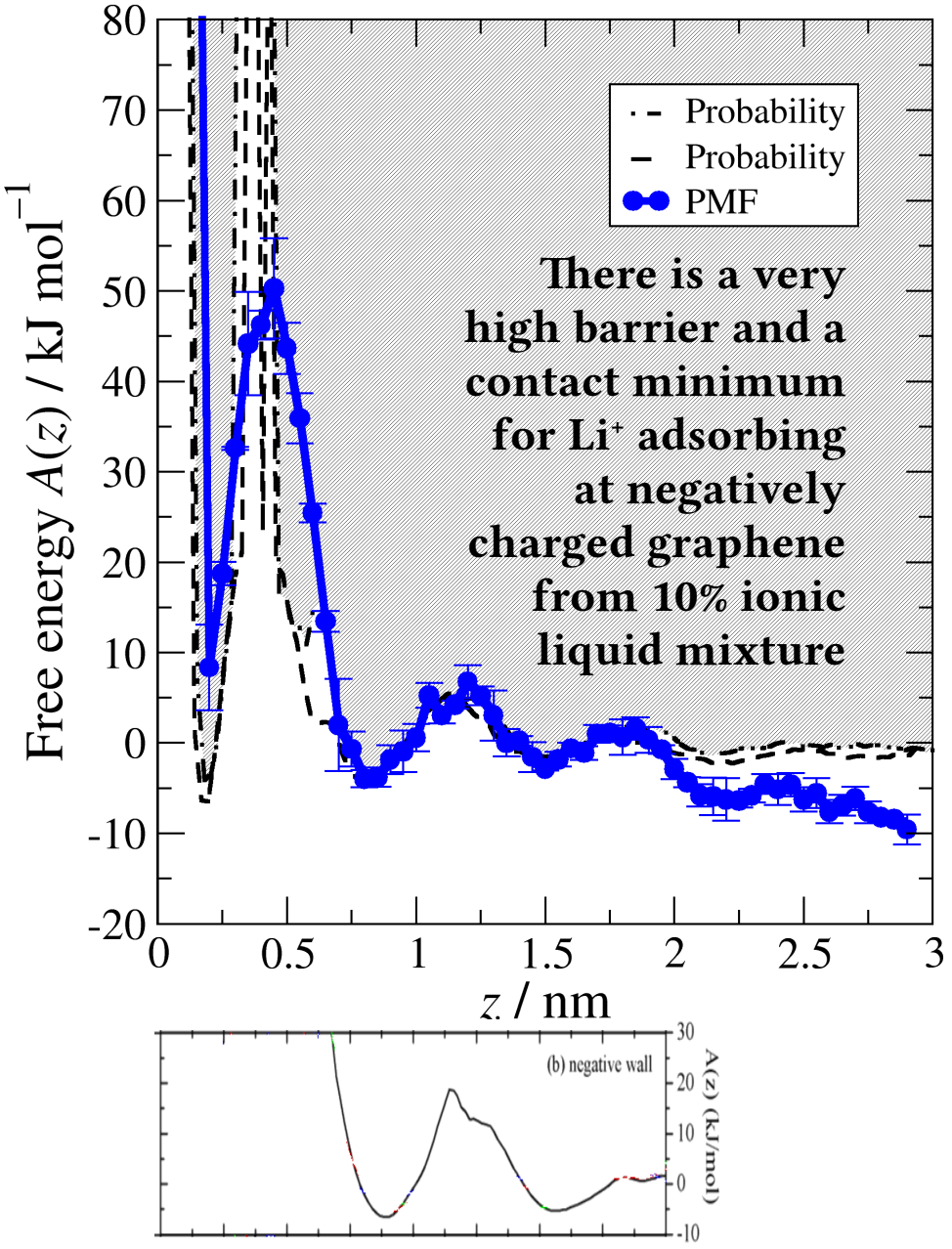


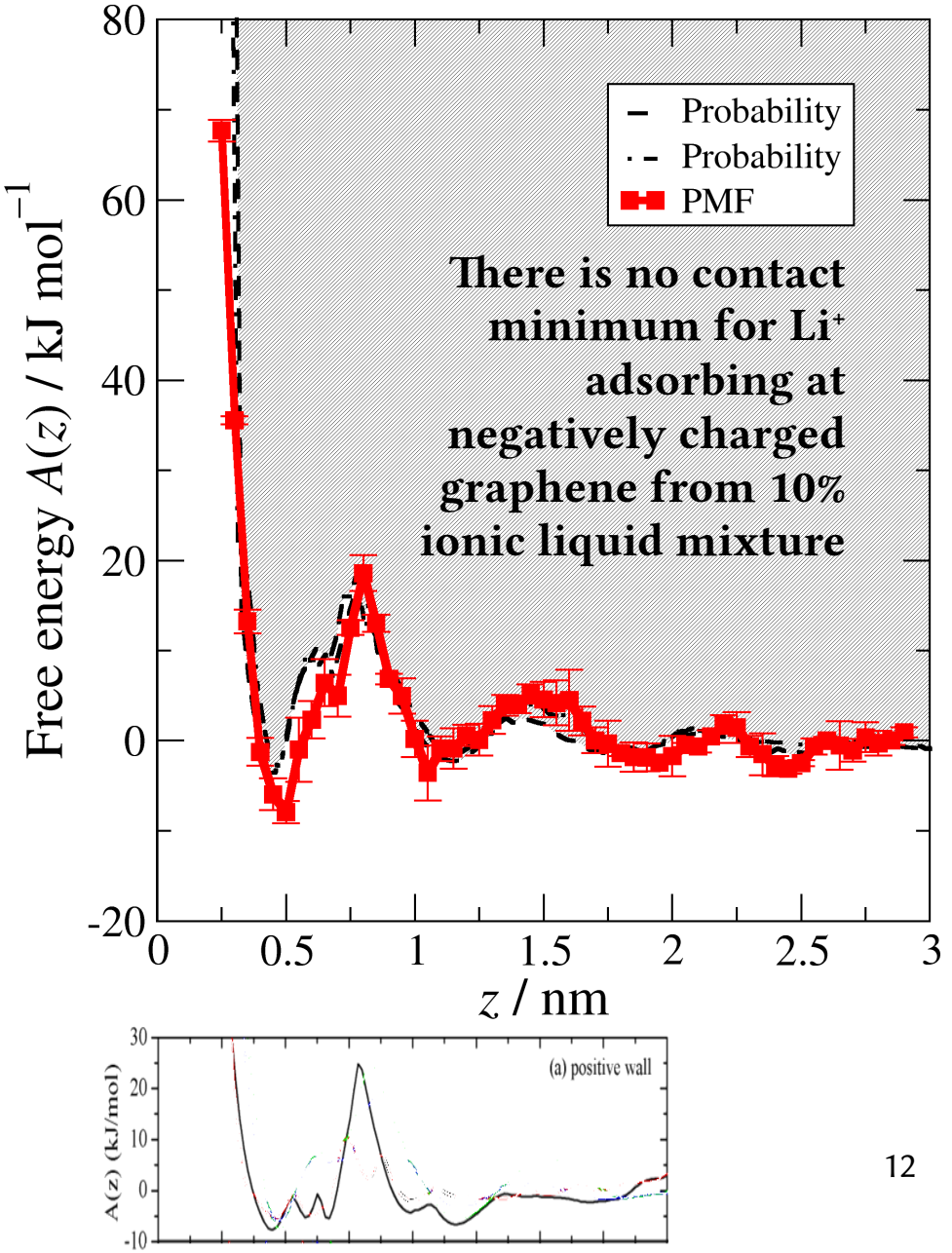
$$k = B \exp\left(-\Delta A / RT\right)$$

Li^+ ion approaching *negative* (left) and *positive* (right) graphene walls

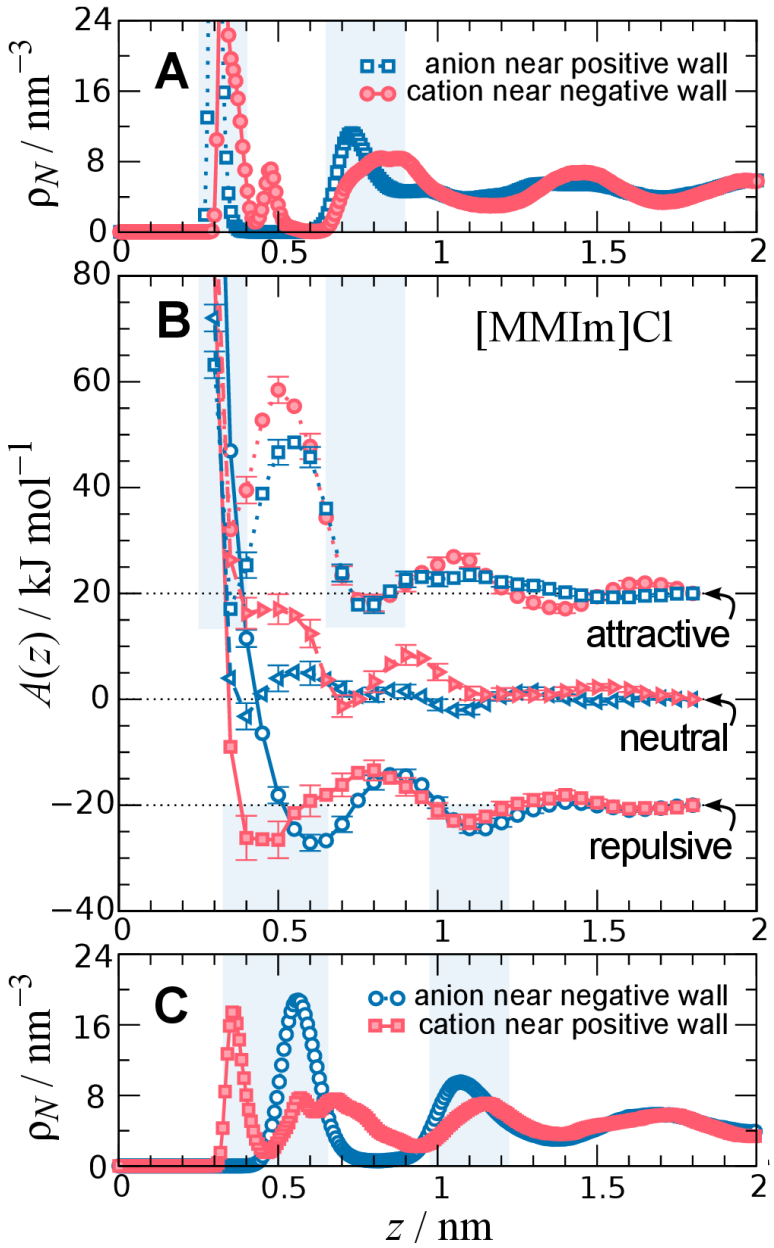
$\sigma = \mp 1$ e nm^{-2}, $c_{mol} = 10\%$

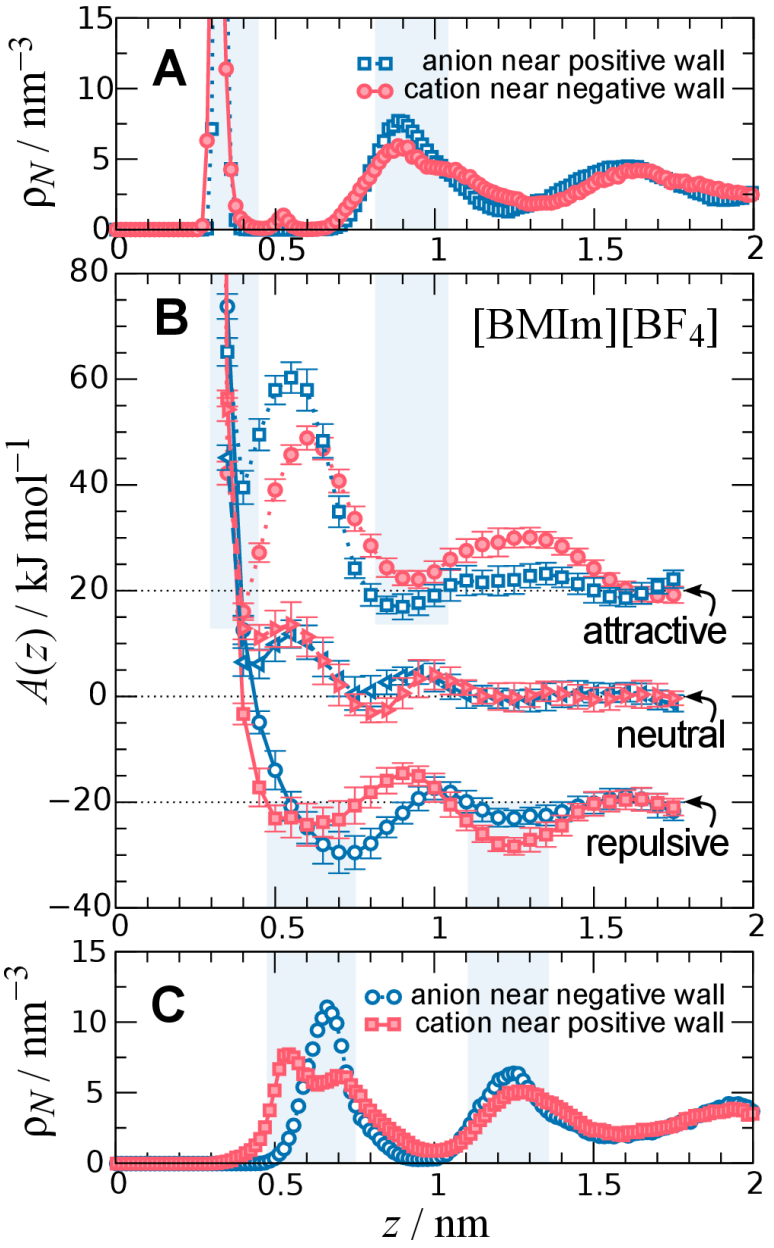
dashed line – $A(z)=-RT\ln(c/c_0)$; solid line – from the pulling results





Charged probe in [MMIm]Cl and $[BMIm]BF_4$



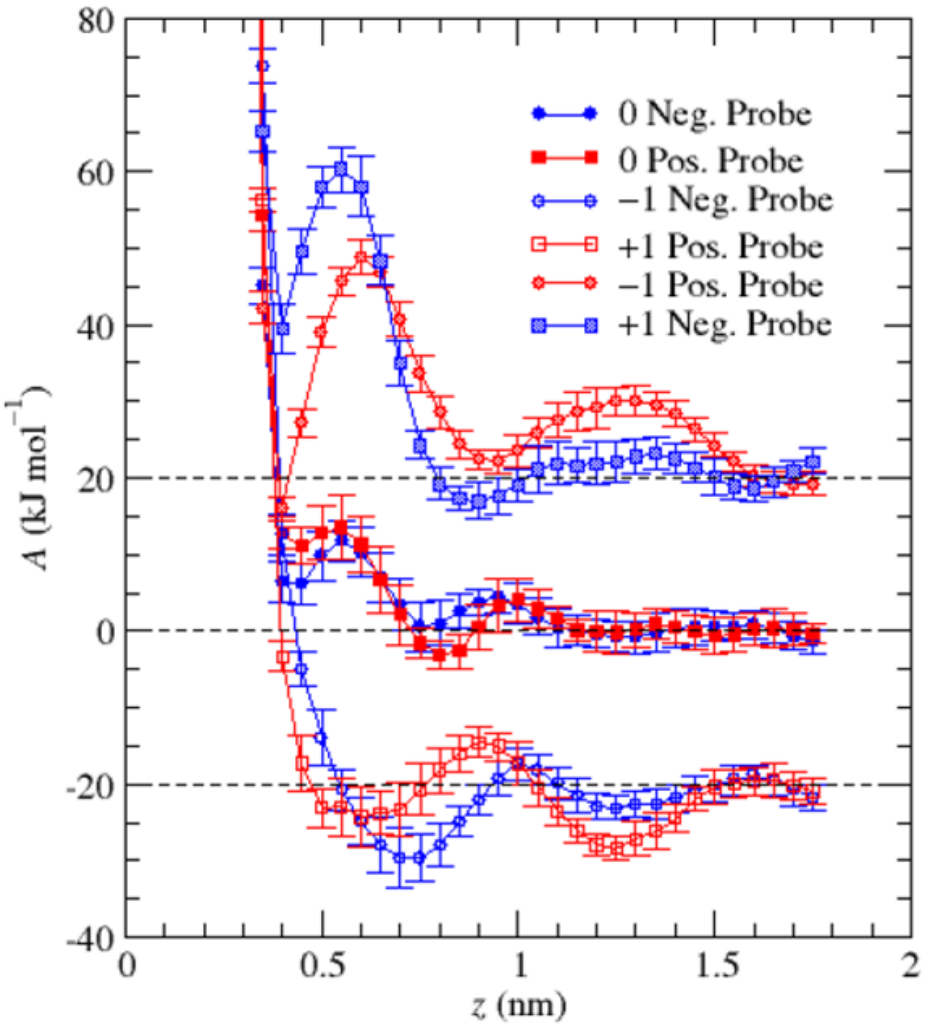


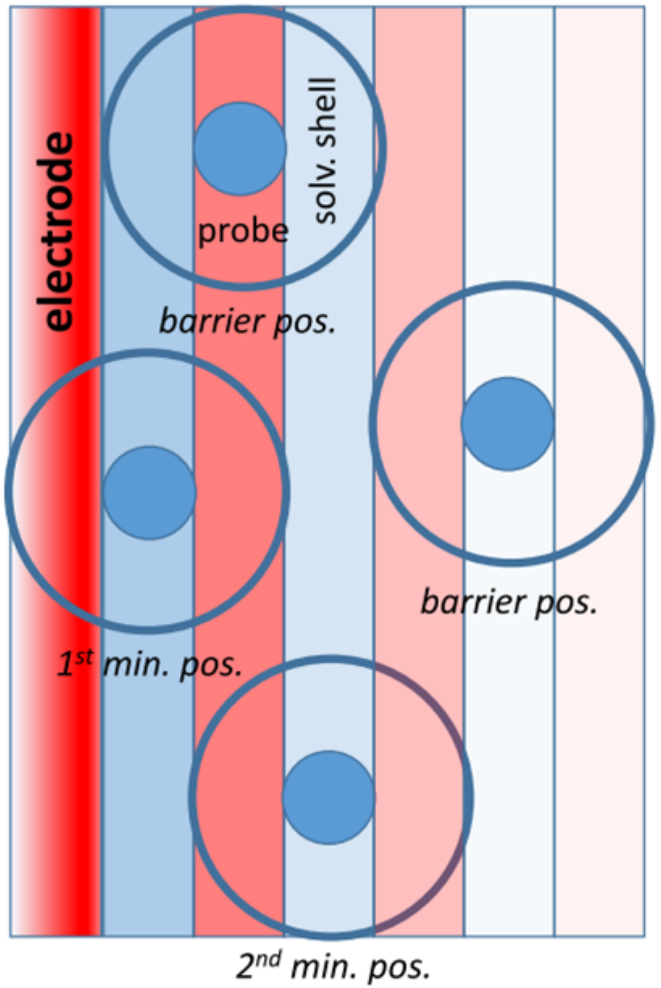
Probe charge × Surface charge

$$\begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix} \times \begin{pmatrix} +1 \\ 0 \\ -1 \end{pmatrix}$$

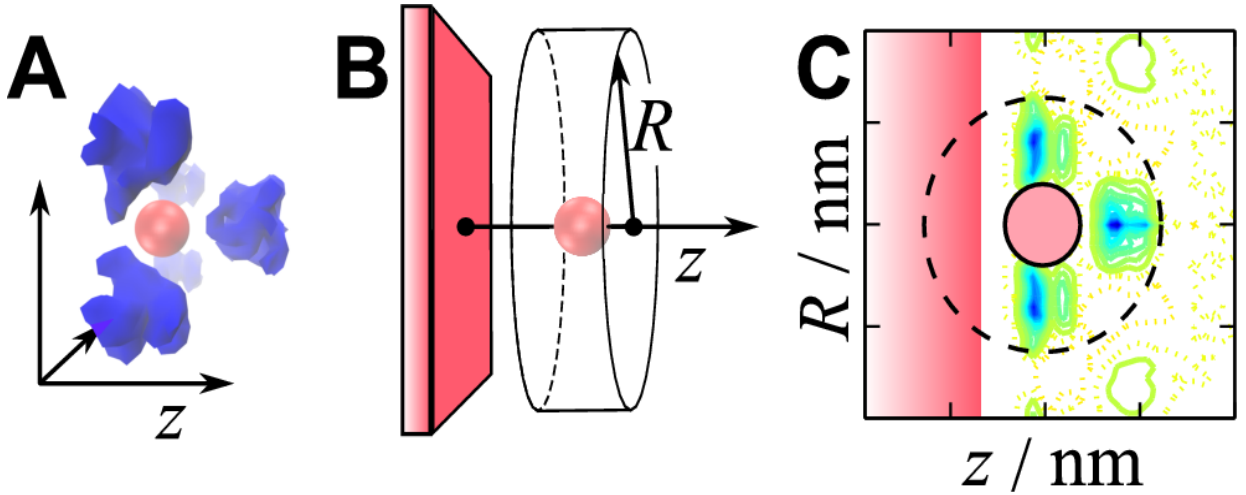
	$[A]^-$	$[C]^+$
anode	−	+
cathode	+	−

Solvation layers and the solvation shell

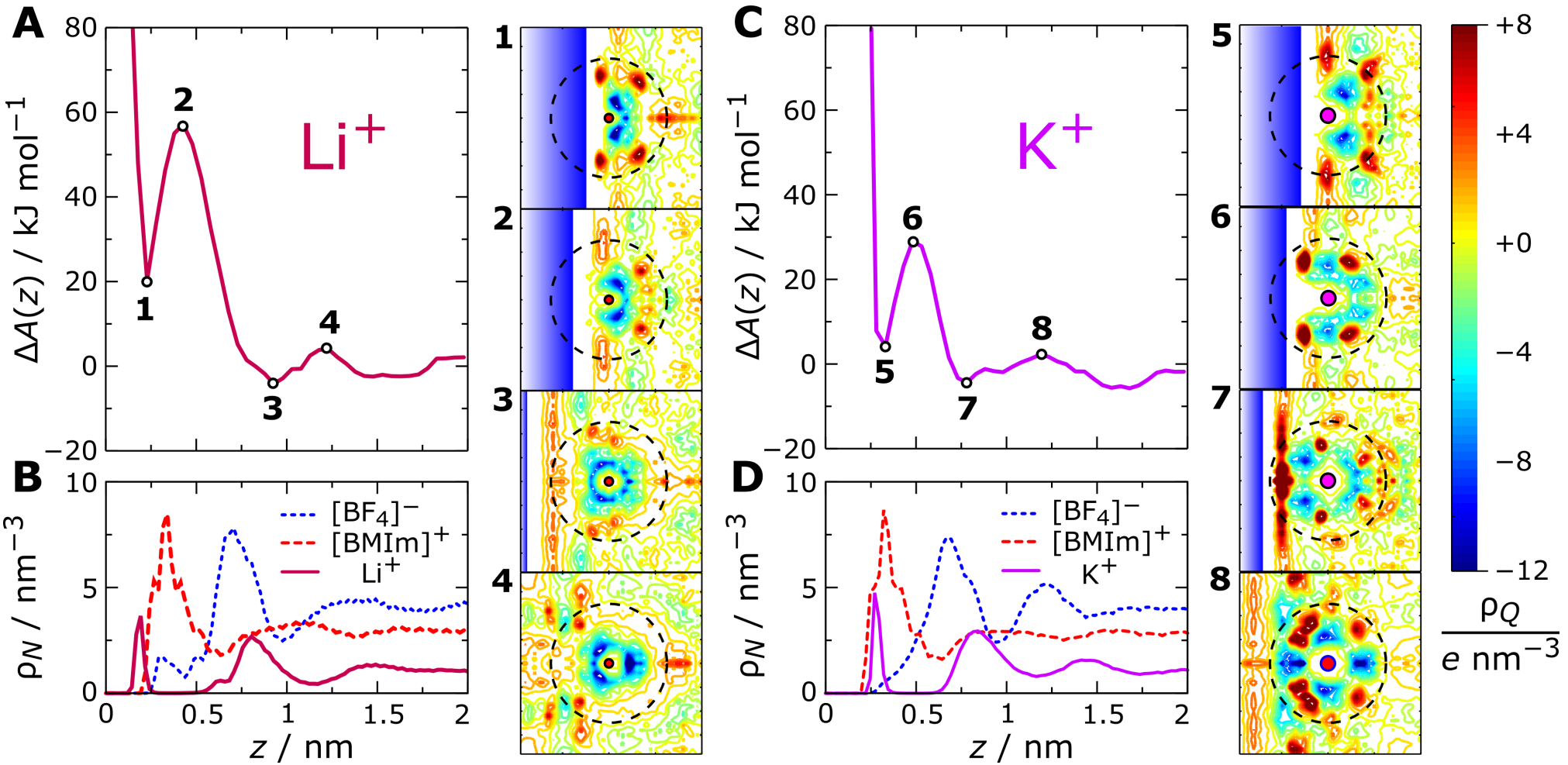




Cylindrically averaged charge density



Li^+ and K^+ at Graphite | $BMImBF_4$ interface



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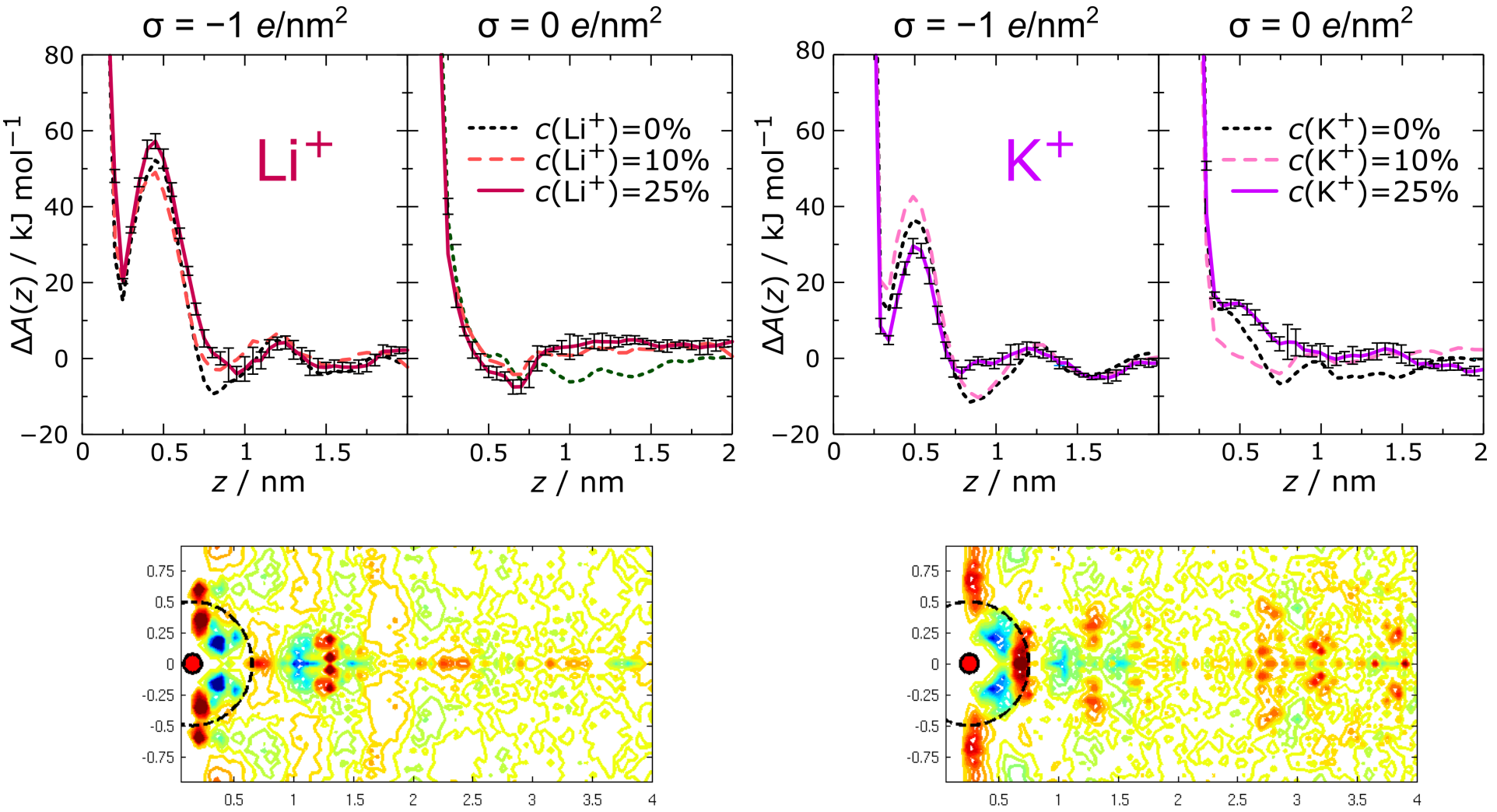
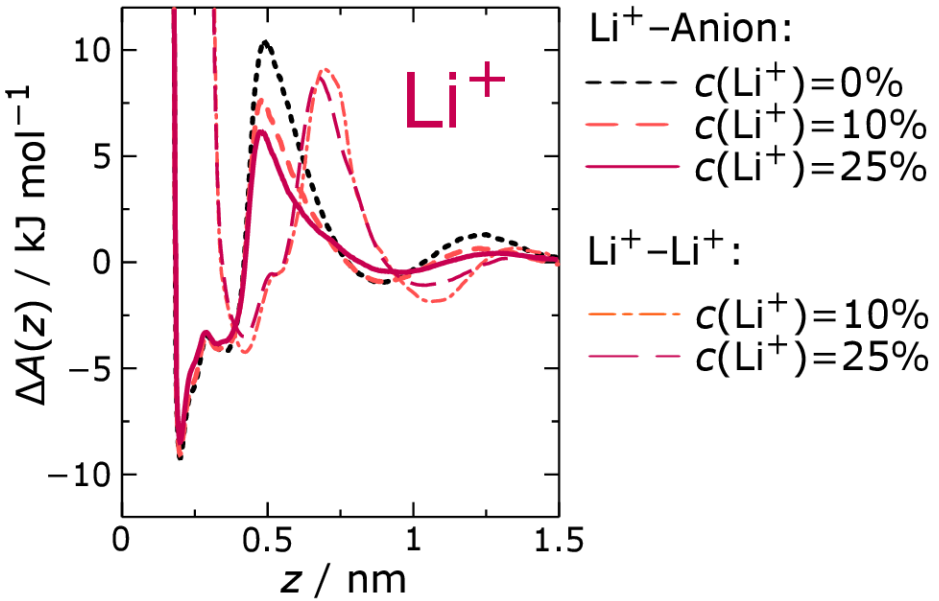
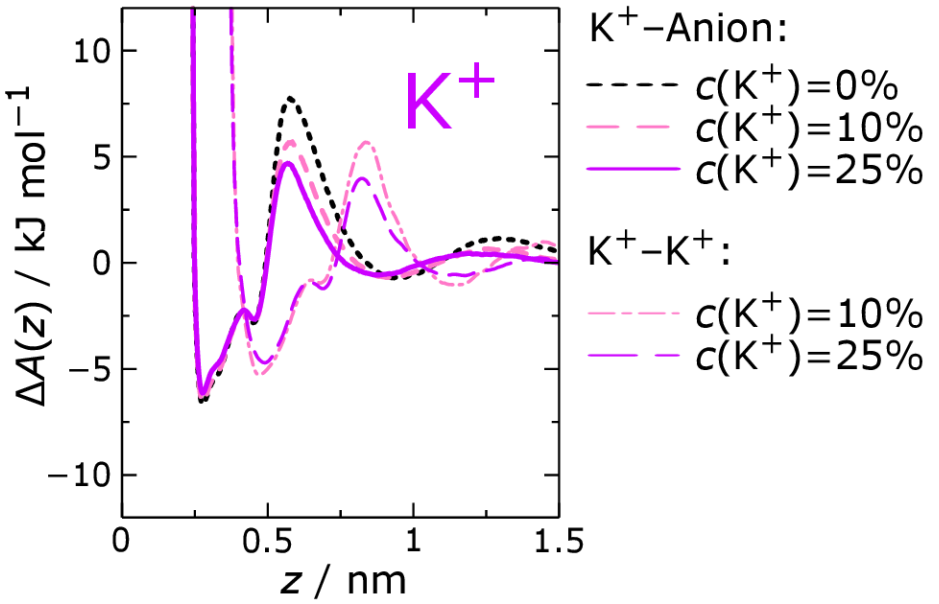
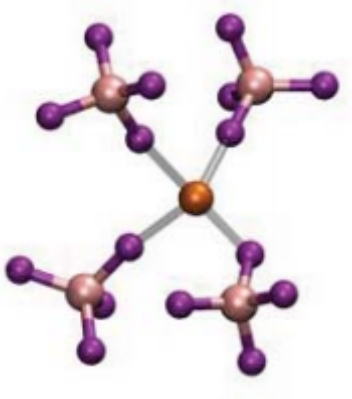


Li^+ and K^+ at Graphite | $BMImBF_4$ interface







metal-ion–anion binding
anion size
electrolyte density

J.B. Haskins, et al., J. Phys. Chem. B 118 (2014) 11295.

Conclusions

- The interfacial mass-transport of a probe ion (Li^+, K^+) is related to the free energy profiles fom translation of the ion in direction perpendicular to the surface.
- The structure of solvation layers at the electrodes determines the positions of the minima and maxima on the free energy profiles.
- At those positions where these solvation structures enhance each other, the free energy profile is lower, whereas at those positions where they distort each other, the free energy is higher.
- Barrier for K^+ is lower than for Li^+ in $BMImBF_4$ + $MeBF_4$ mixtures.
- The method presented can be applied for ionic liquids screening.

Some preliminary results

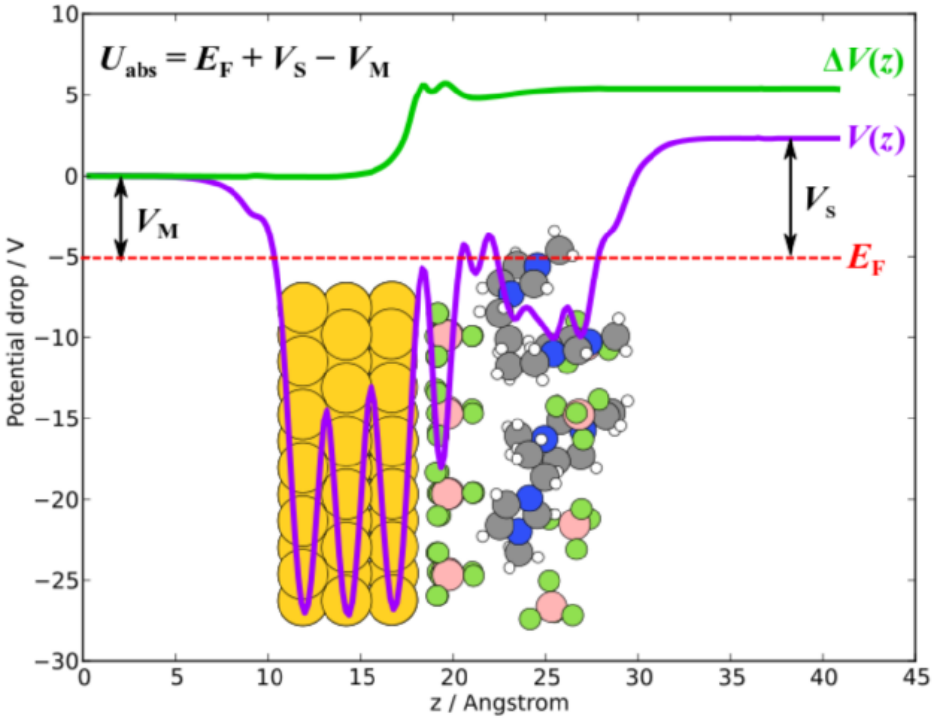
Unpublished results

Challenges

Potential scale

Polarisable force fields

Constant potential simulations



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- T. Méndez-Morales, J. Carrete, M. Pérez-Rodríguez, Ó. Cabeza, L.J. Gallego, R.M. Lynden-Bell, L.M. Varela, Phys. Chem. Chem. Phys. 16 (2014) 13271.

See also

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- V. Nikitina, S.A. Kislenko, R.R. Nazmutdinov, M.D. Bronshtein, G.A. Tsirlina, J. Phys. Chem. C 118 (2014) 6151.
- V. Ivaništšev, S. O'Connor, M.V. Fedorov, Electrochem. Commun. 48 (2014) 61.

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Thank you for your attention!

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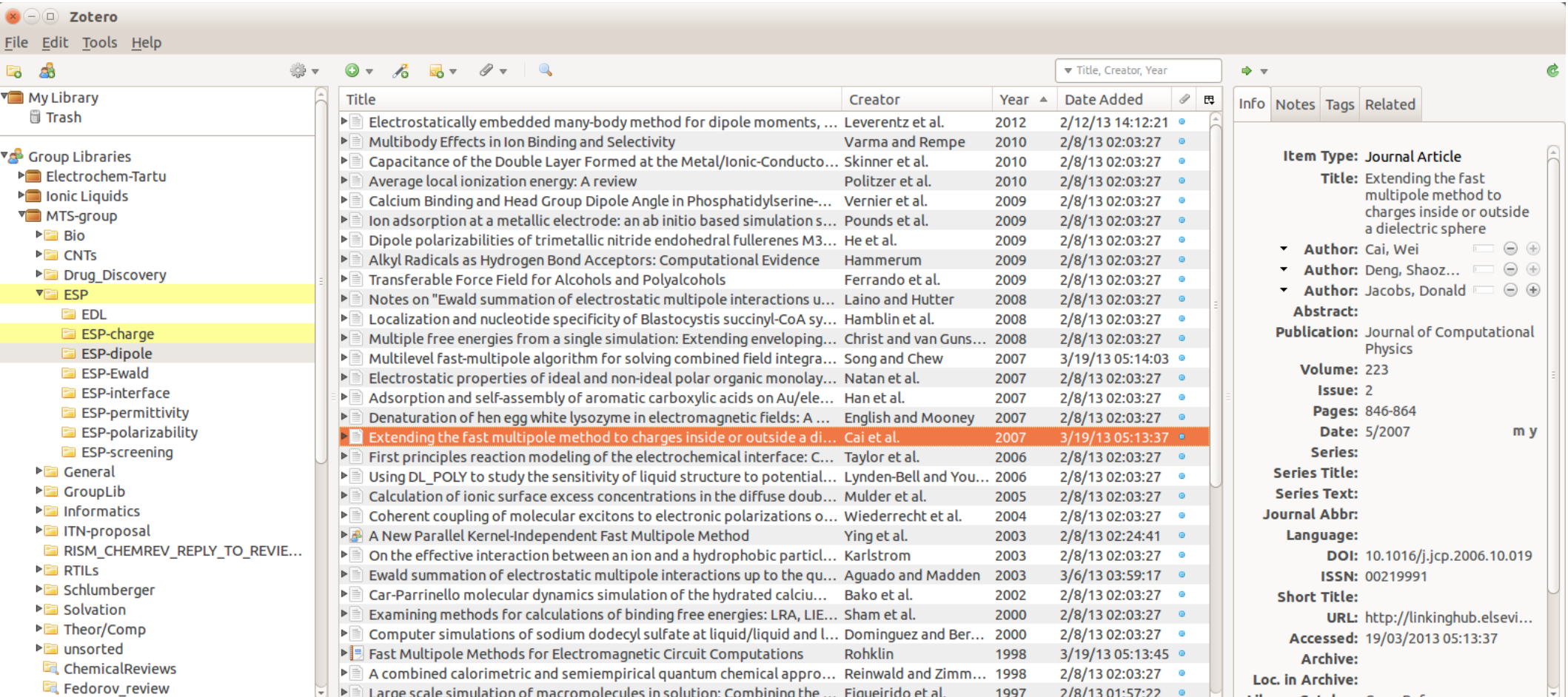
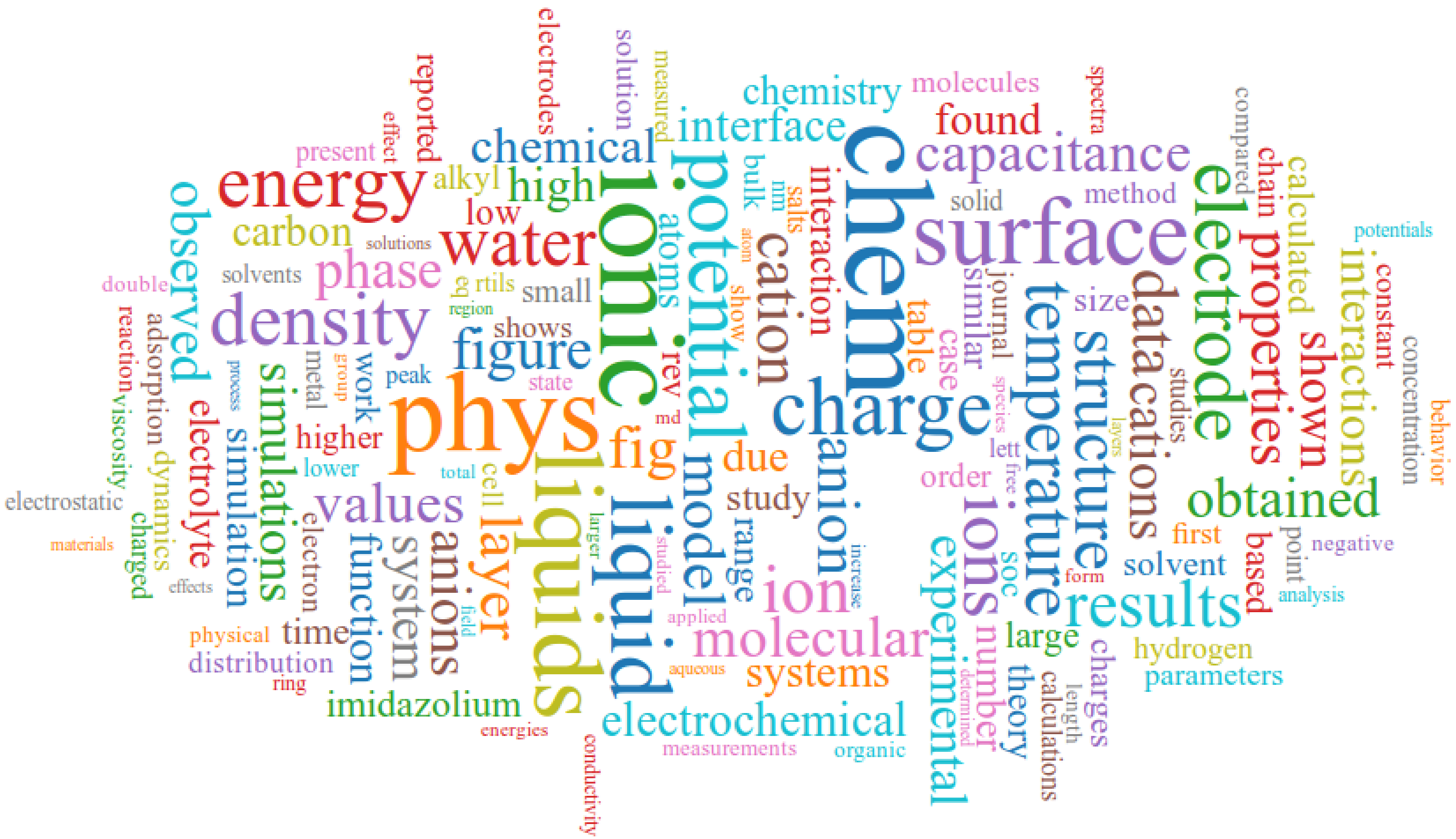


World cloud



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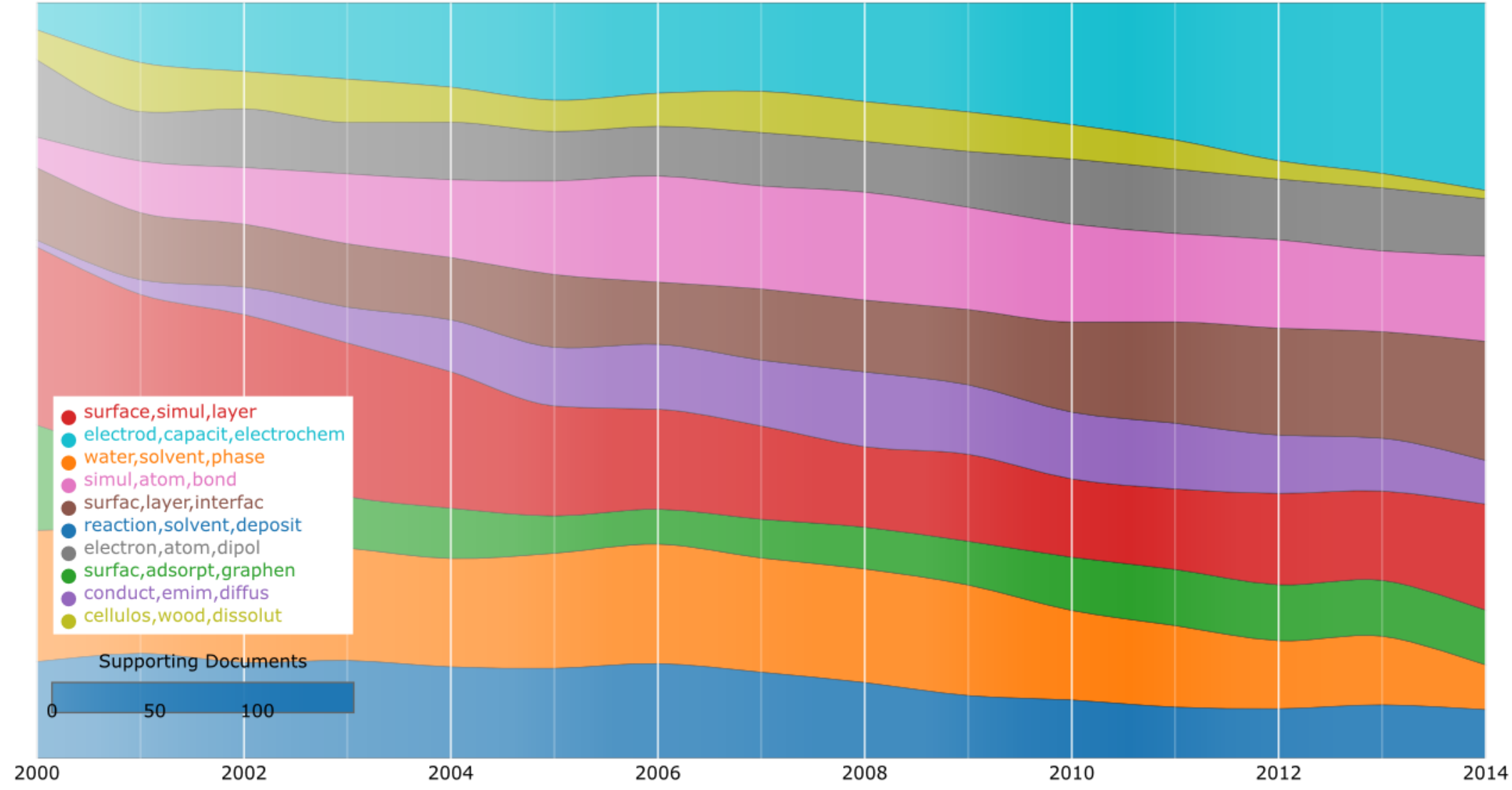

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