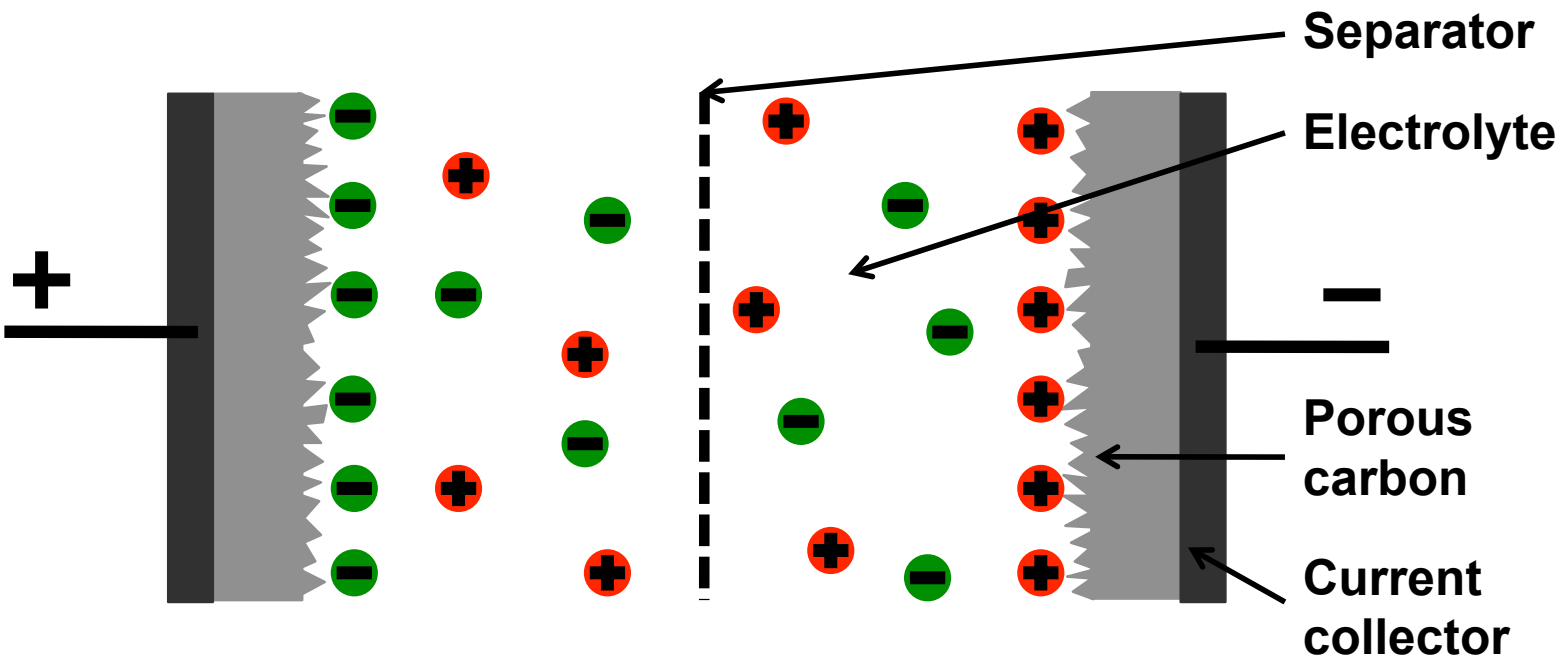
Modelling high energy density supercapacitors by molecular dynamics simulations

Mathieu Salanne

Laboratoire PHENIX, Université Pierre et Marie Curie
&
Maison de la Simulation
CEA, CNRS, INRIA, U. Paris-Sud, U. Versailles

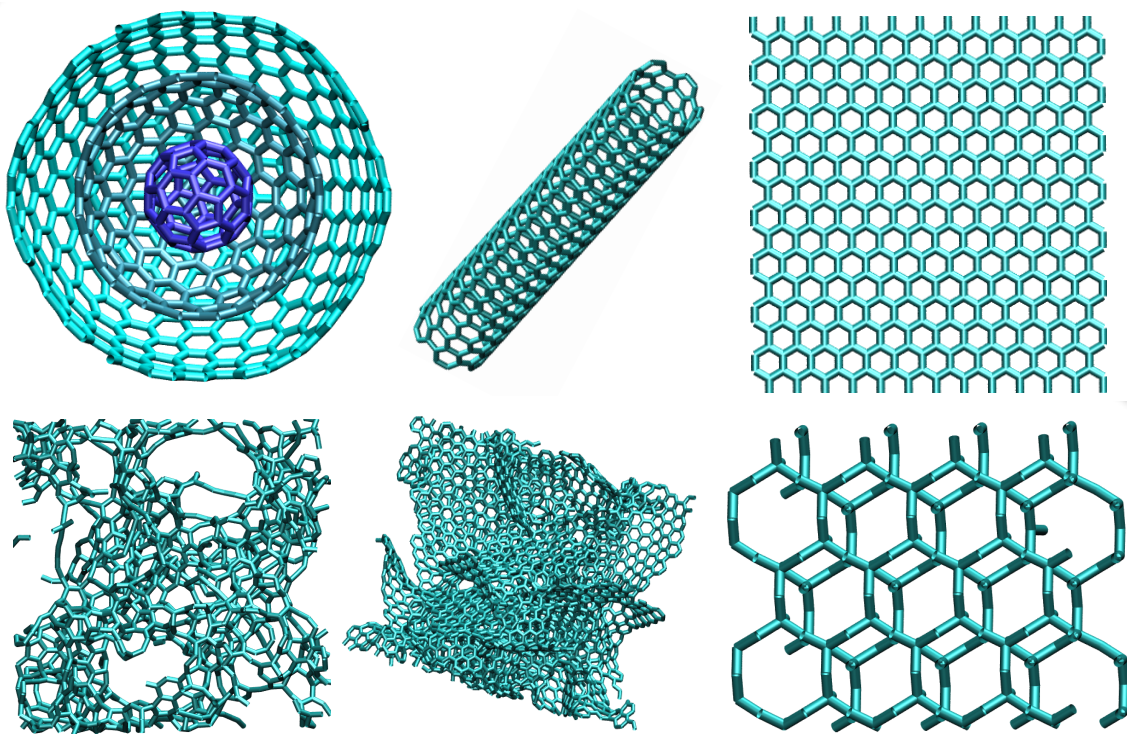
Forum de l'ORAP - 15 Octobre 2014

Supercapacitors: electricity storage devices



- Also called Electrochemical Double Layer Capacitors
- Charge stored through adsorption of ions at the surface of electrode
- No redox reaction in the bulk material $\rightarrow$ different from batteries
- $E = \frac{CU^2}{2}$ & $P = \frac{U}{4R}$

Electrode materials



- Commercial devices: carbon materials
- 1D, 2D, 3D materials
- Various porosities, surface area, chemical activation
- Efficiency measured with the capacitance

Simon & Gogotsi, *Nature Materials* **7**, 845 (2008)

Electrolytes

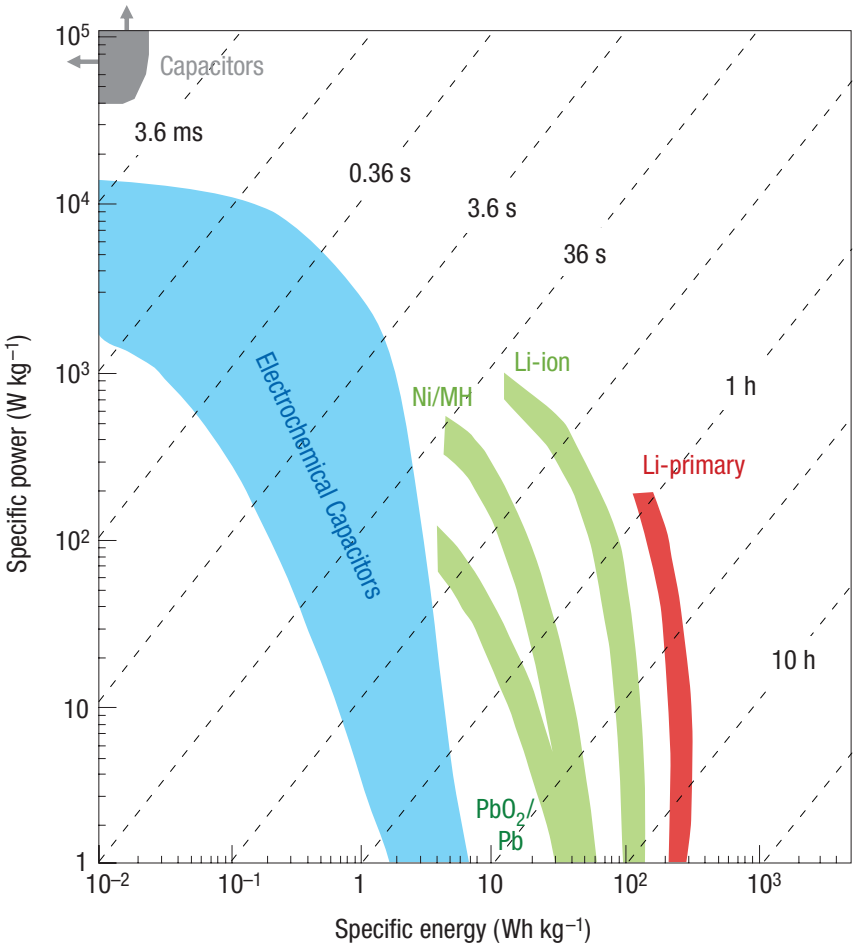
Need to find a good compromise between:

- Large electrochemical window
- High conductivity
- Good adsorption of ions on (porous) carbon materials
- Toxicity, safety...

Depending on the application:

- Ionic liquids
- Organic electrolytes (acetonitrile + organic salts)
- Aqueous electrolytes (inorganic salts)
- Solid electrolytes (ionic liquids + polymers)

Supercapacitors in the electricity storage landscape

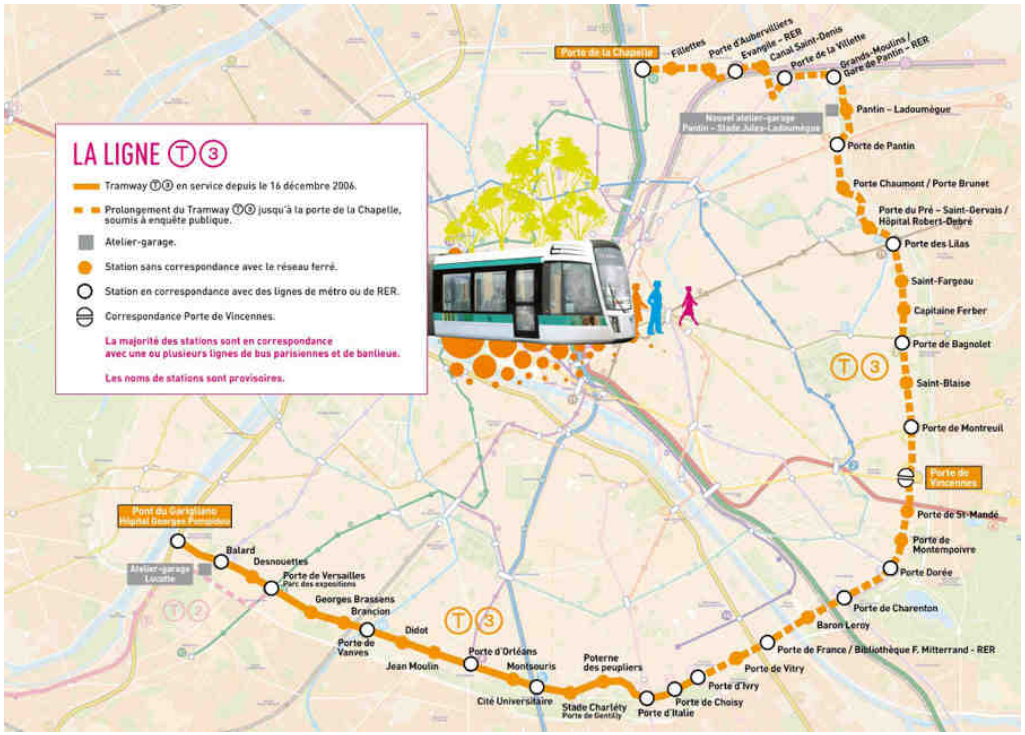


Intermediate performances between conventional capacitors and Li-ion batteries.

- High specific power
- Correct specific energy
- Rapid charge/discharge (a few seconds)
- High cyclability (1 million cycles)

Applications

Collaboration Alstom / Batscap

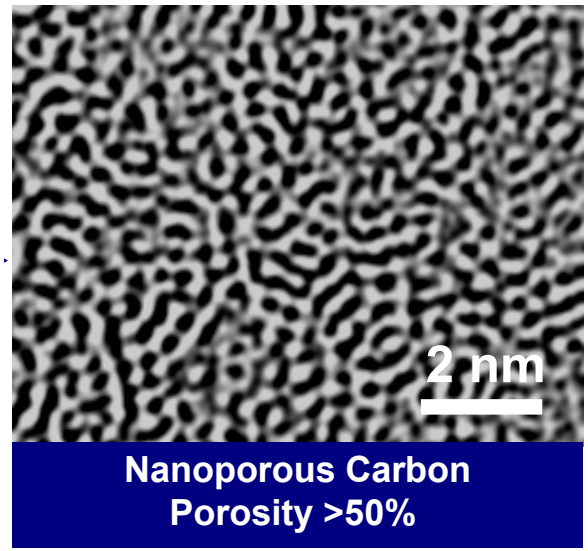


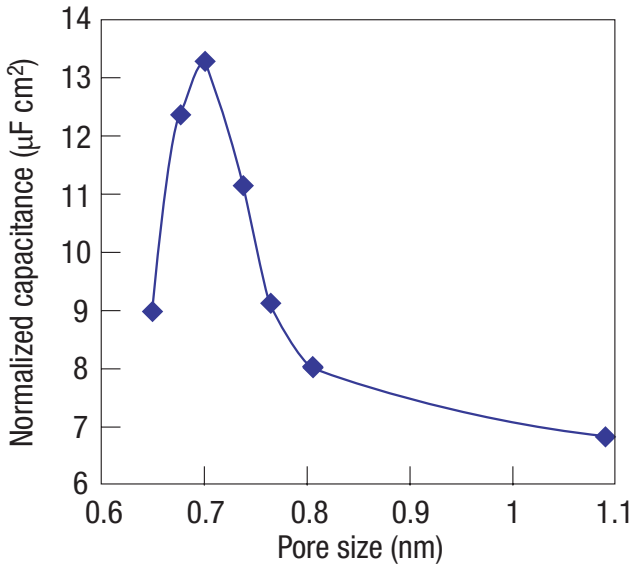
Tramway in Paris: braking energy is stored in a supercap (allows for a traction of more than 100 m)

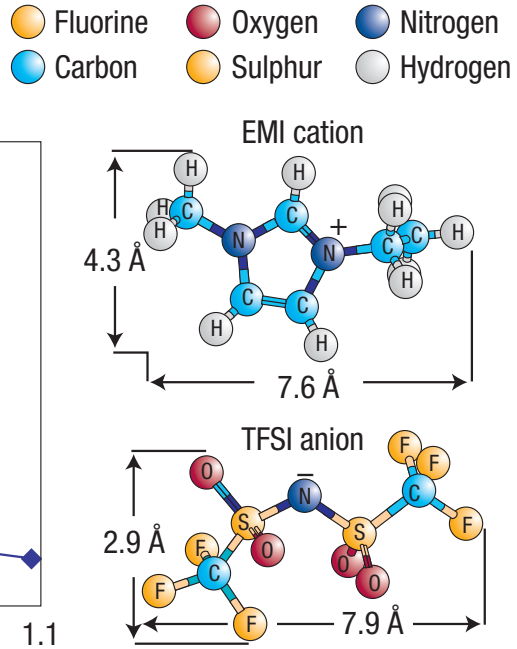
Applications

- Peugeot 308 e-HDI: 5V supercapacitor
- Stop-start system $\rightarrow$ lower fuel consumption (-15 %)
- Also in Formula One: KERS

Experimental discovery (Gogotsi & Simon)







- CDC: narrow pore size distribution
- Increase of the capacitance by +50 %!
- Optimum when pore size = ion size

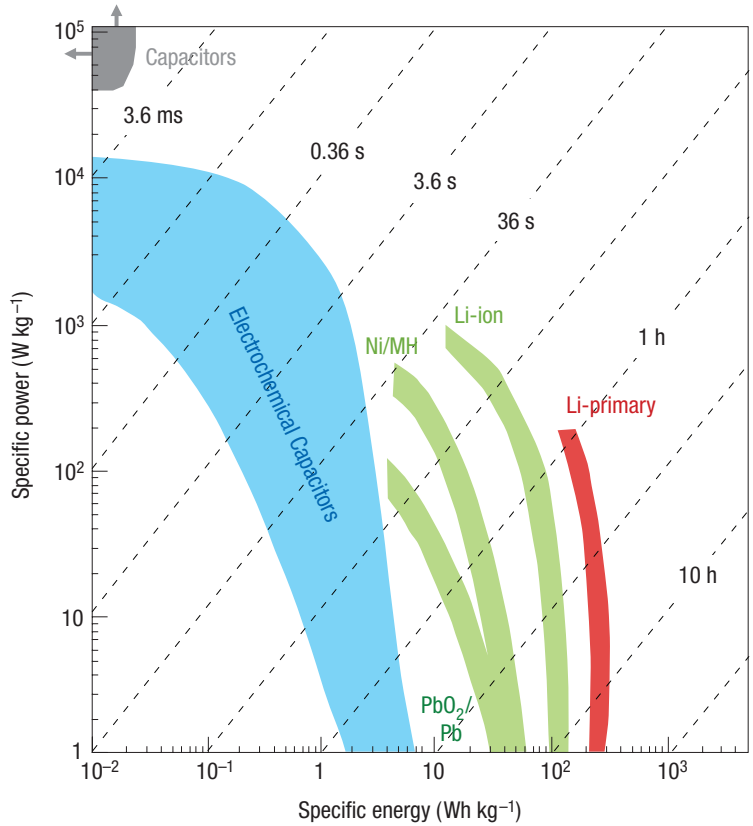
Chmiola *et al.*, *Science*, 313, 1760 (2006)

Largeot *et al.*, *J. Am. Chem. Soc.*, 130, 2730 (2008)

Challenges

Need for improvements:

- Increase of capacitance
  $\rightarrow$ design of new carbon materials
- Electrolytes with high potential window
- Electrolytes with high conductivity
  at low temperature (-40°C)



Much research work to be done in materials and electrochemistry, but...

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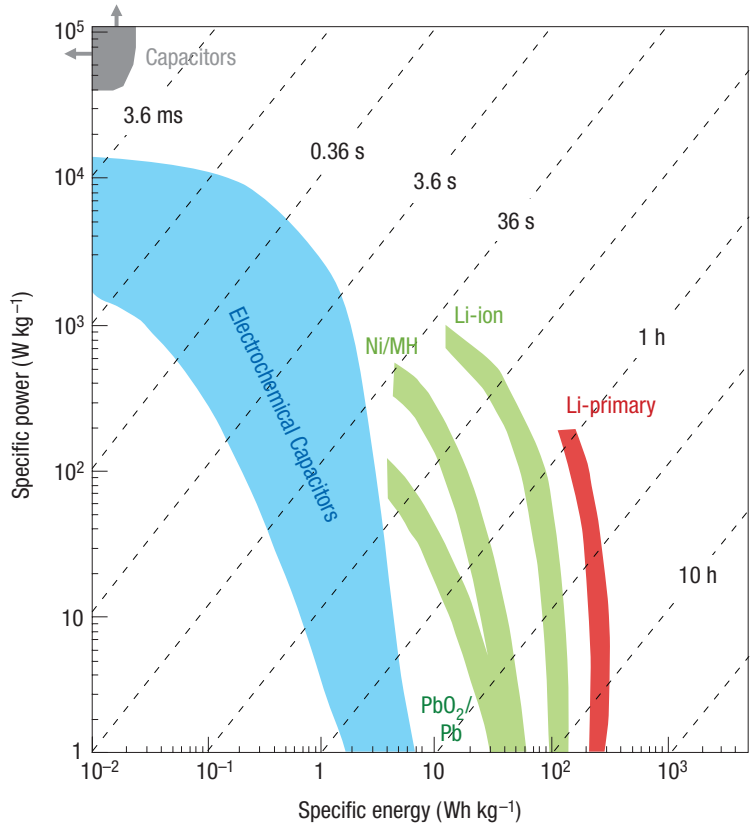


Much research work to be done in materials and electrochemistry, but...

- Local structure of the liquid inside the nanopores is unknown
- Very difficult to probe it experimentally

$\rightarrow$ Simulation can help!

Simulation method: molecular dynamics

- System of N classical atoms/molecules interacting together
- Periodic boundary conditions
- Iterative integration of Newton's equation

$$m^i \frac{\partial^2 \vec{r}^i}{\partial t^2} = \sum_{j \neq i} \vec{F}^{j \to i} = -\frac{\partial V}{\partial \vec{r}^i}$$

  where V is the interaction potential

- Numerical resolution
- Trajectory of the atoms over several nanoseconds
- Determination of structural, thermodynamic and transport properties

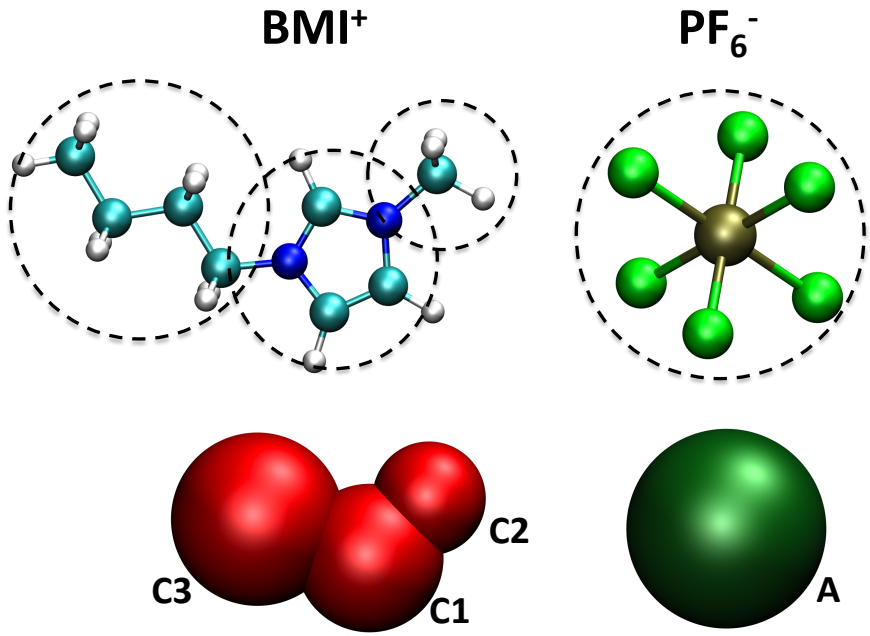
Electrolyte: coarse-grained model

BMI^+: 1-butyl-3-methylimidazolium

$\rightarrow$ 3 sites

PF_6^-: hexafluorophosphate

$\rightarrow$ 1 site



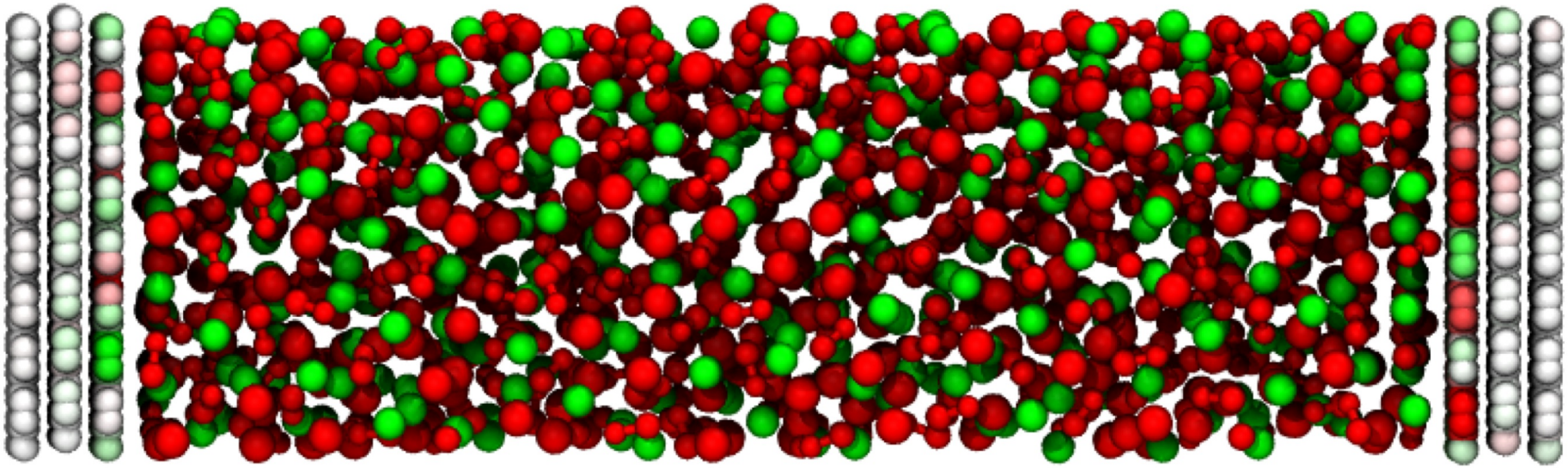
Interaction potential:

$$V = \sum_{i,j>i} \left[4\varepsilon_{ij} \left((\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^{6} \right) + \frac{q_i q_j}{r_{ij}} \right]$$

Roy & Maroncelli, *J. Phys. Chem. B* **114**, 12629 (2010)

Merlet, Salanne & Rotenberg, *J. Phys. Chem. C* **116**, 7687 (2012)

Simulating constant voltage electrodes



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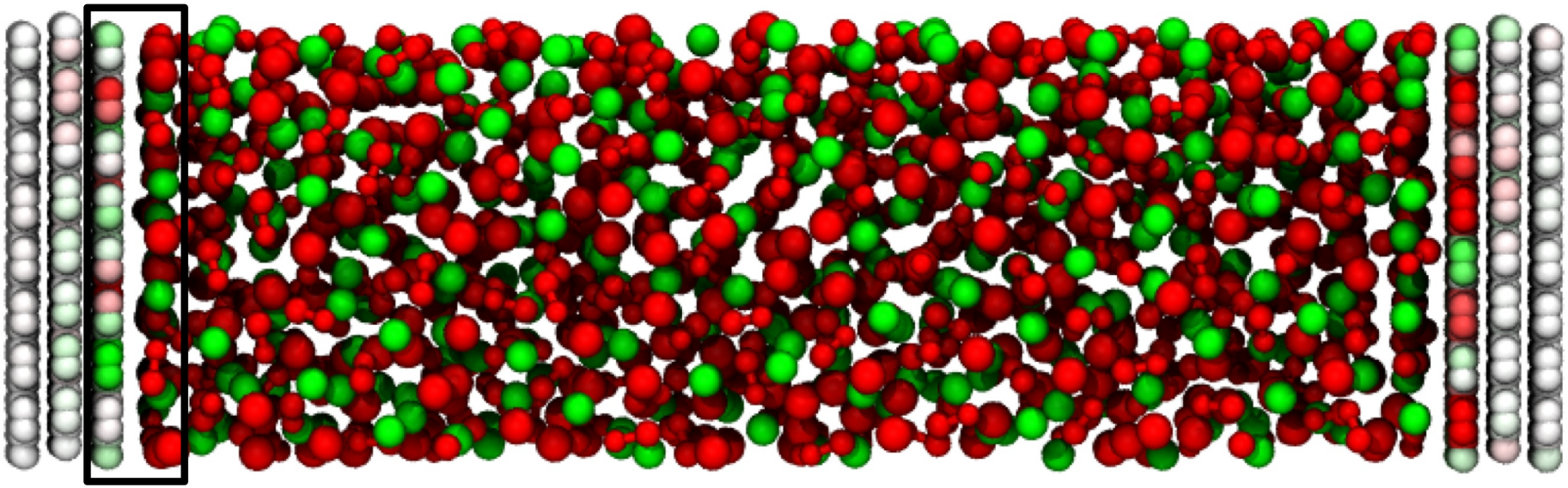

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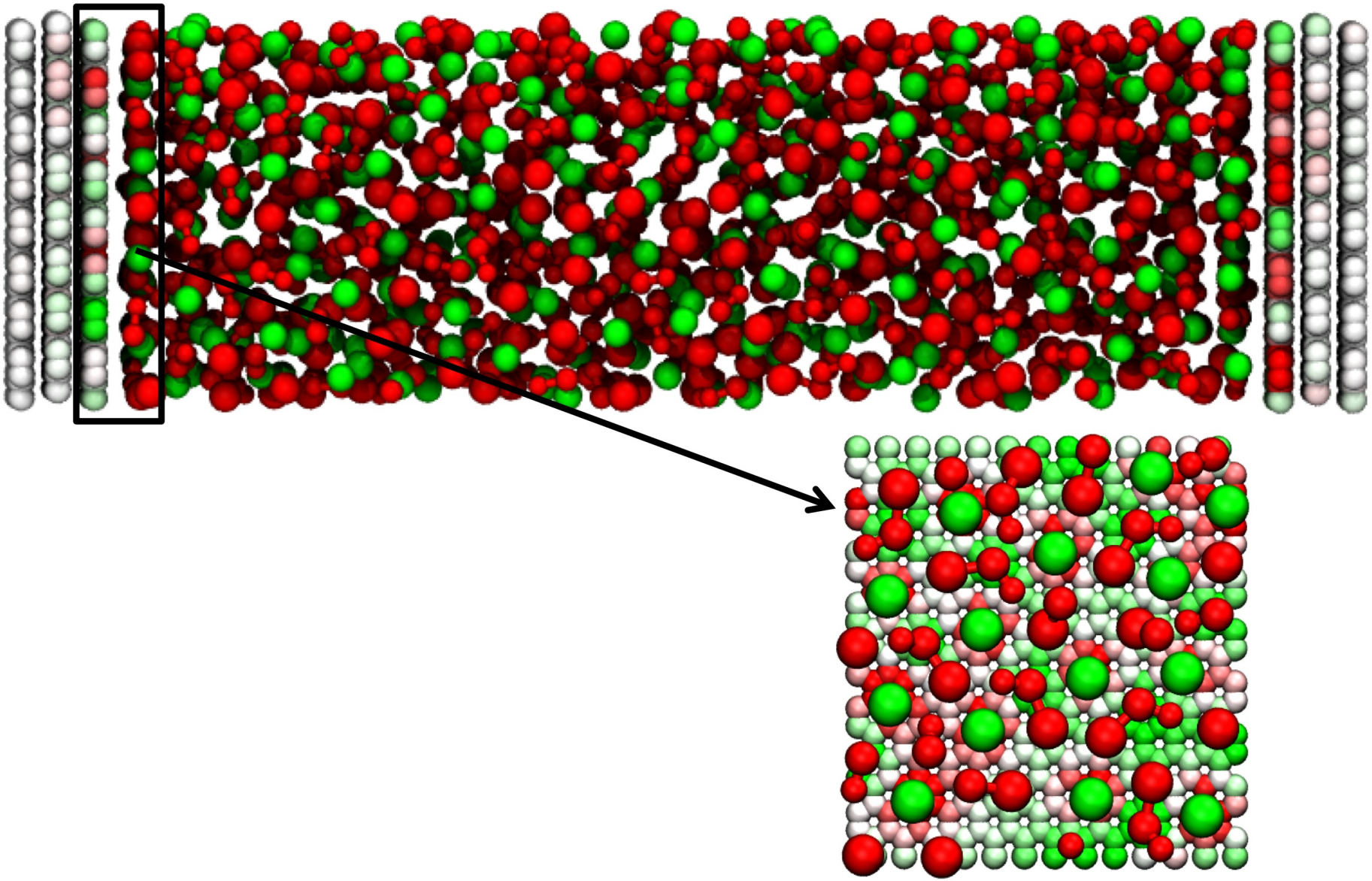

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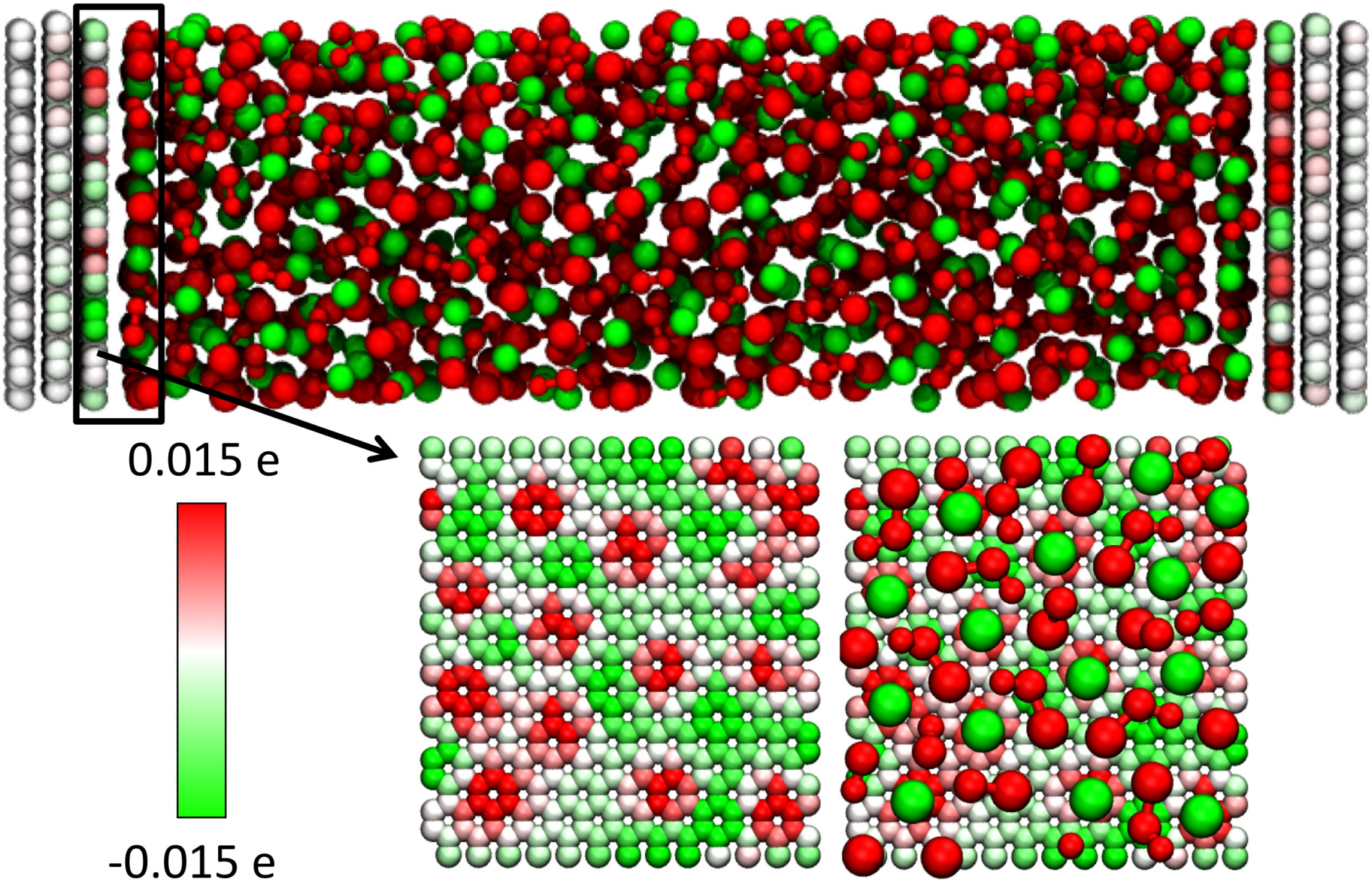
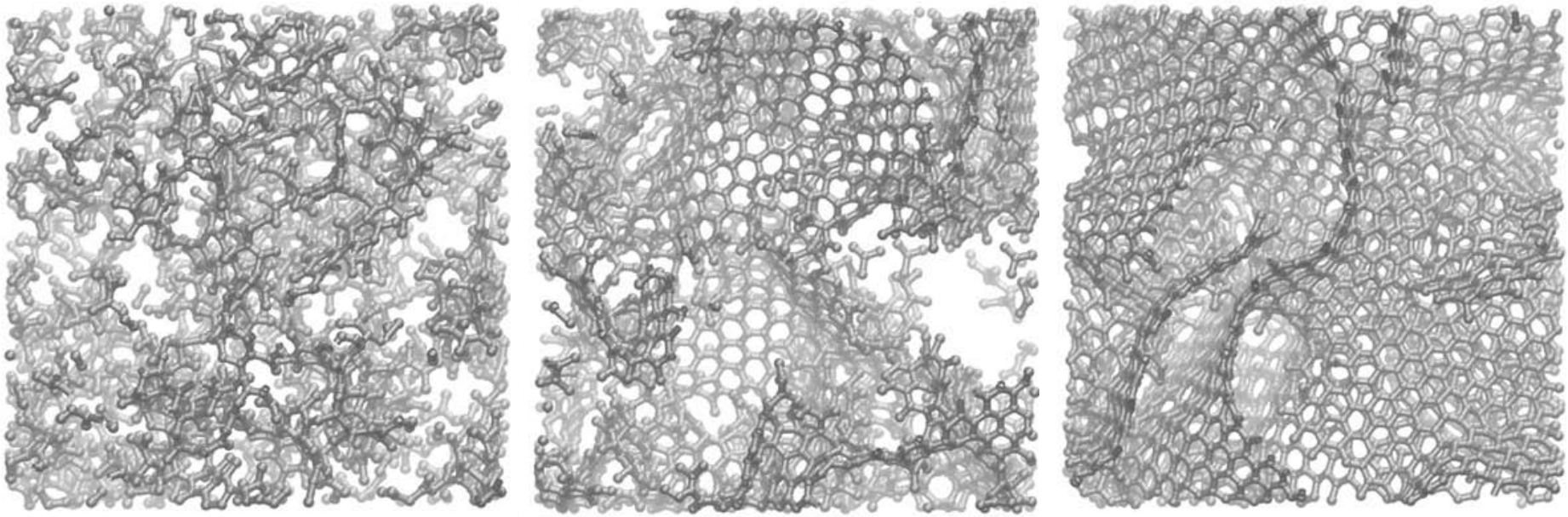


Porous electrodes: CDC model structures



- Obtained from quenching a liquid carbon (ReaxFF)
- Different quenching rates: changes in the pore shape and size distribution
- Mimics CDC structures obtained at different temperatures

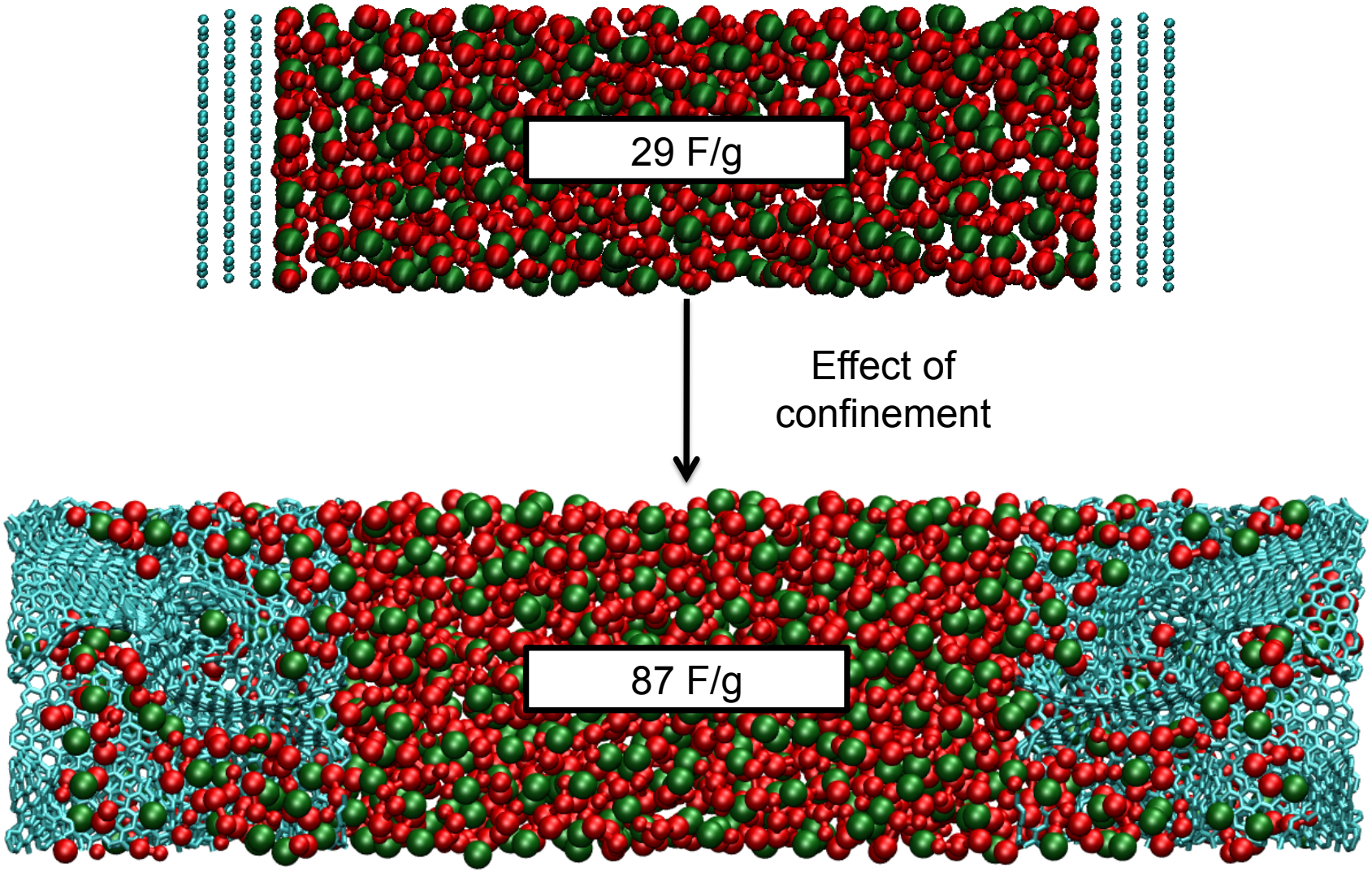
Palmer *et al.*, *Carbon* **48**, 1116 (2010)

Example of trajectory

Loading movie

Simulation cell with 2-Dimensional periodic boundary conditions

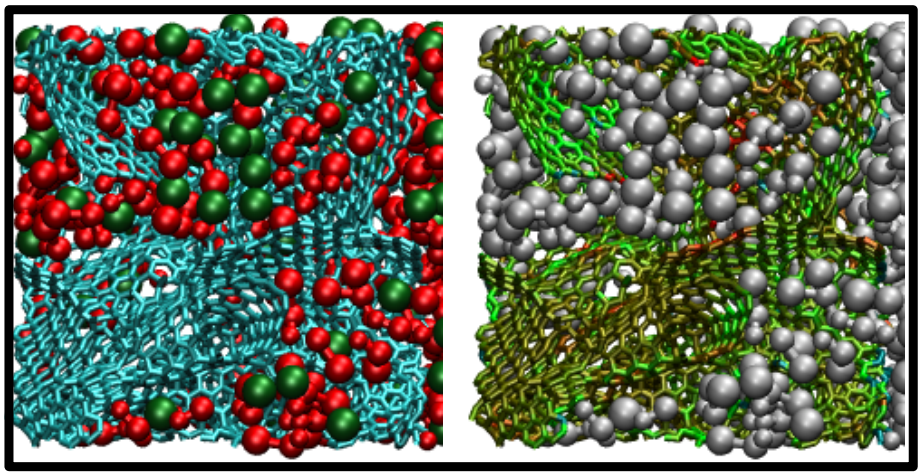
Increase of the capacitance in nanoporous carbons



Merlet *et al.*, *Nature Materials*, 11, 306 (2012)

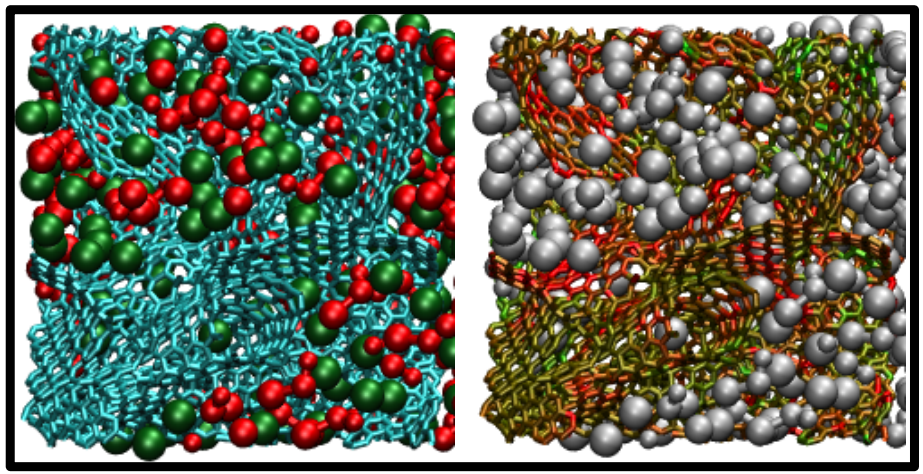
Superionic state

Ψ = – 0.5 V



N_+ = 104
N_- = 55

Ψ = + 0.5 V

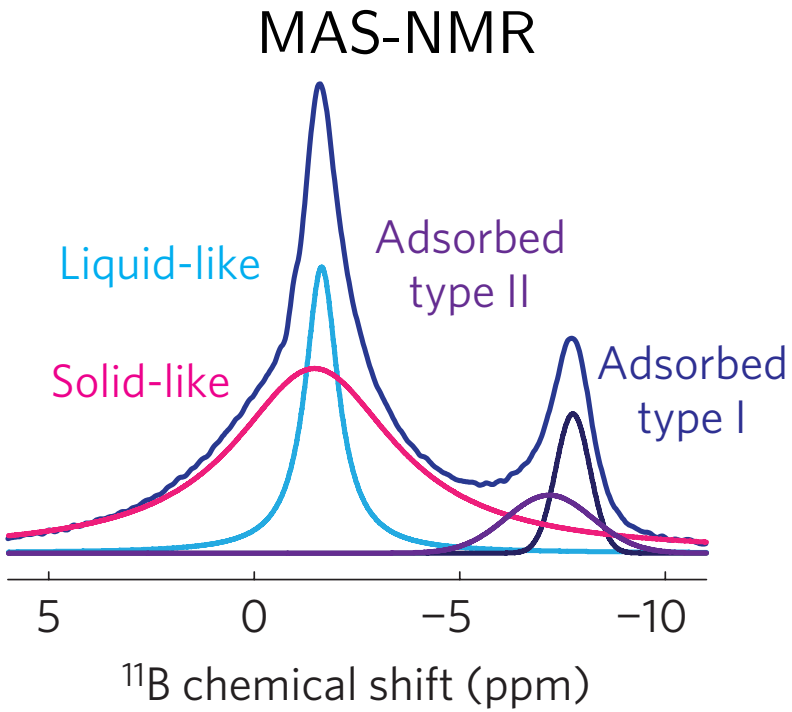


N_+ = 66
N_- = 115

Like-like ions interactions screened by the metallic walls
$\rightarrow$ superionic state

Merlet *et al.*, *Nature Materials*, 11, 306 (2012)

NMR experiments on supercapacitors

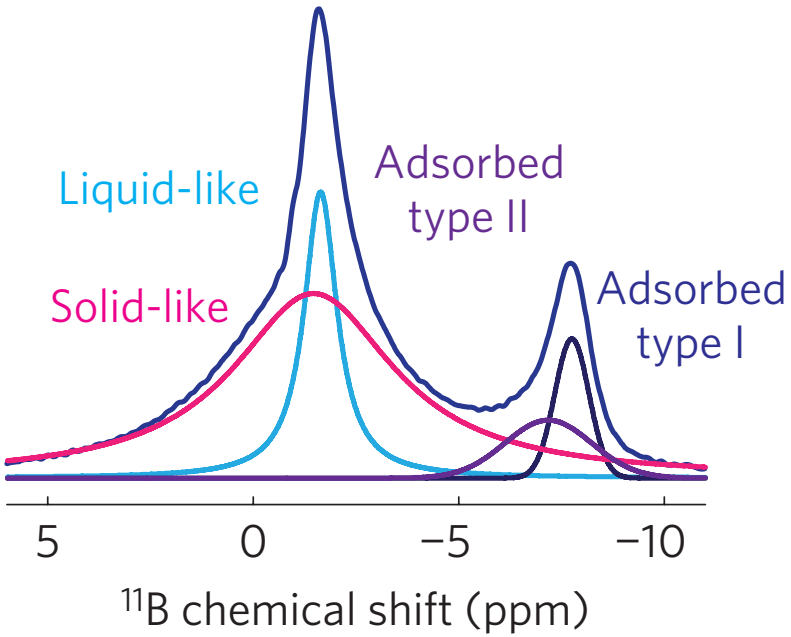


- Several adsorption modes

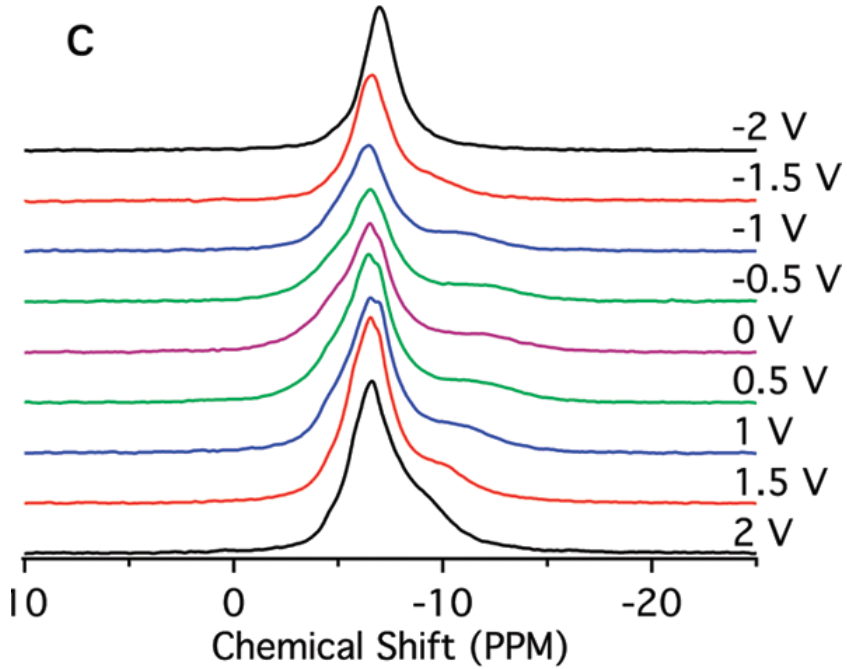
Deschamps *et al.*, *Nature Materials* **11**, 306 (2013)

NMR experiments on supercapacitors

MAS-NMR



in situ NMR

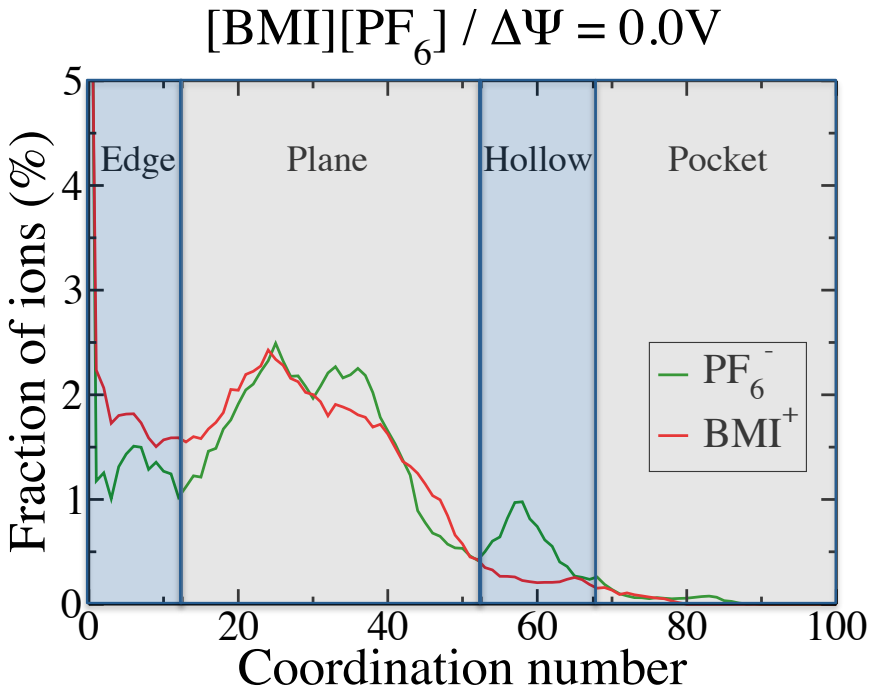


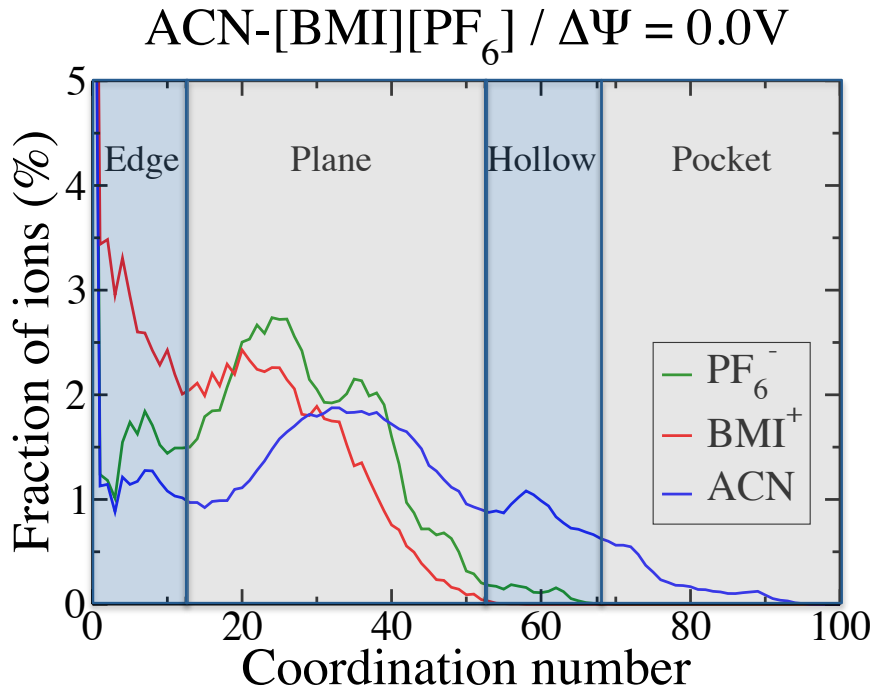
- Several adsorption modes
- Evolution with applied potential

Deschamps *et al.*, *Nature Materials* **11**, 306 (2013)

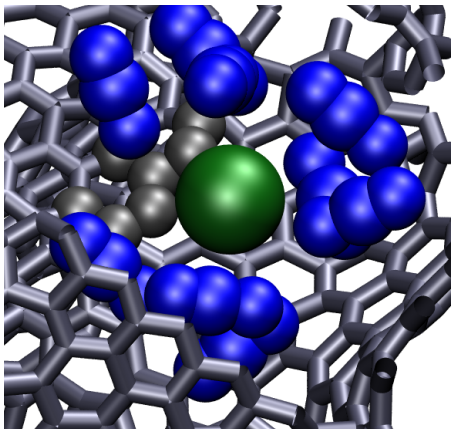
Wang *et al.*, *J. Am. Chem. Soc.* **133**, 19270 (2011)

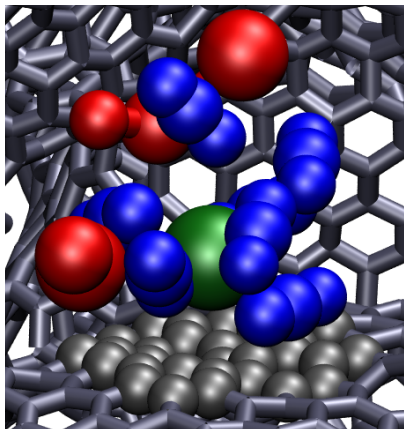
A variety of adsorption sites

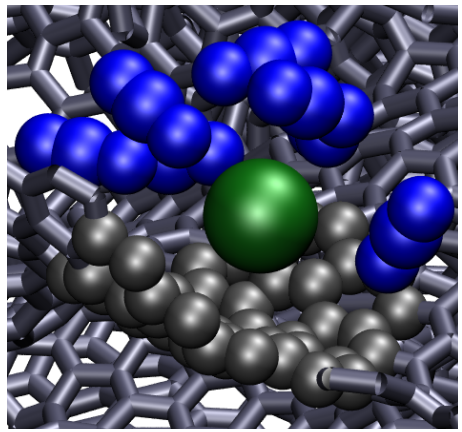


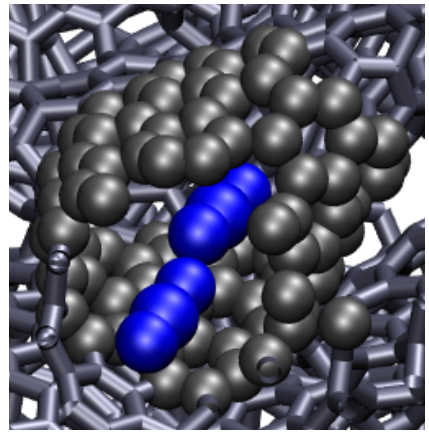


Edge **Plane** **Hollow** **Pocket**

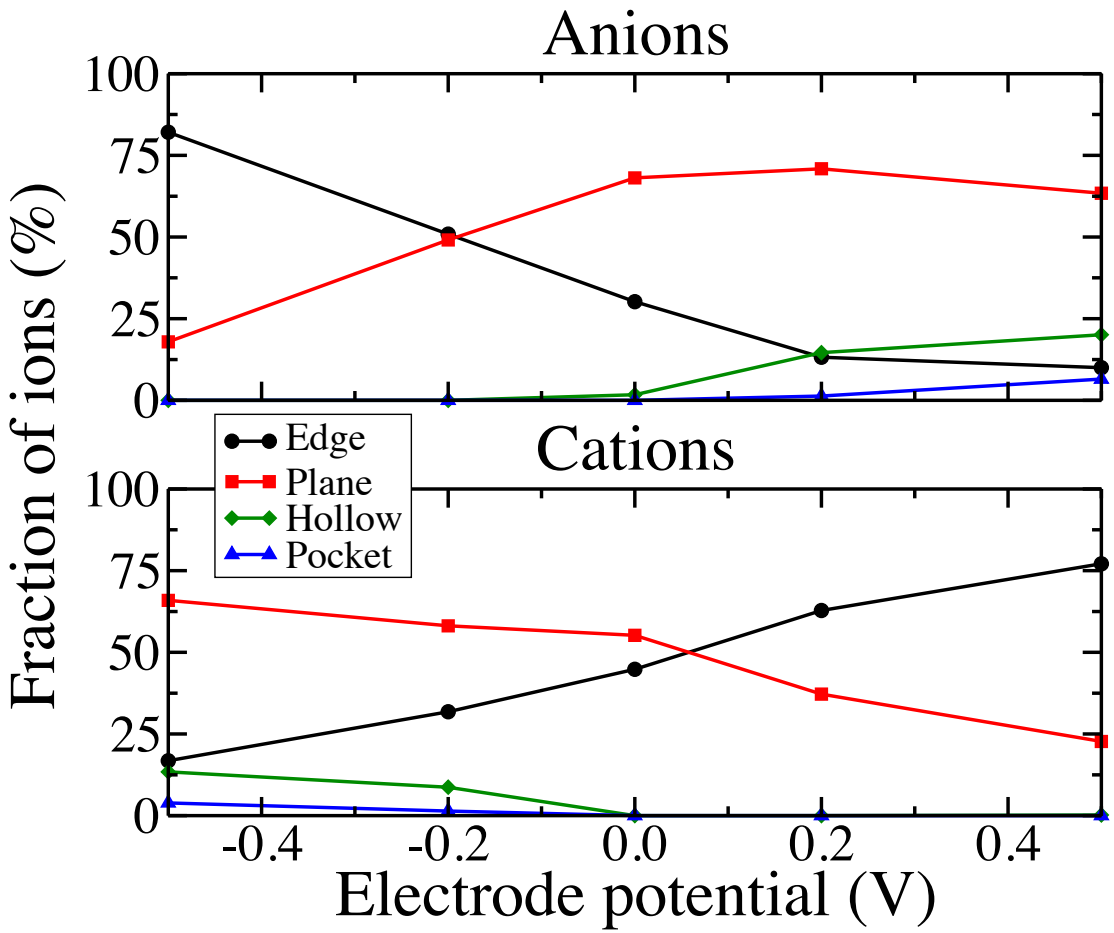






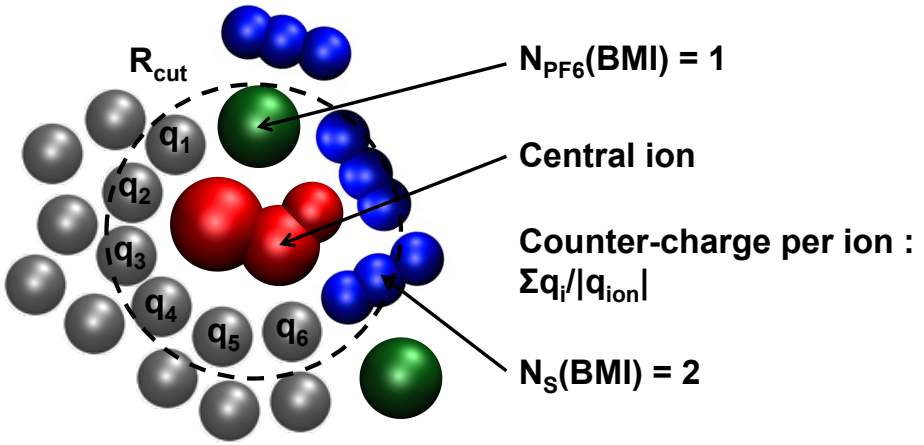


Evolution with applied potential

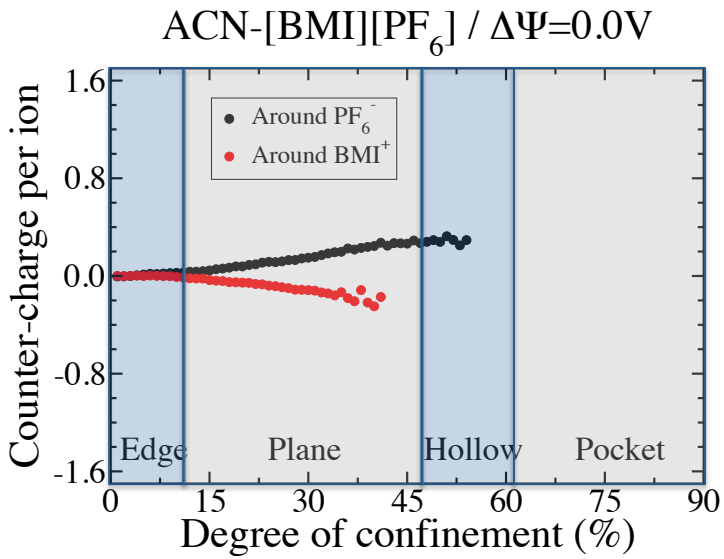


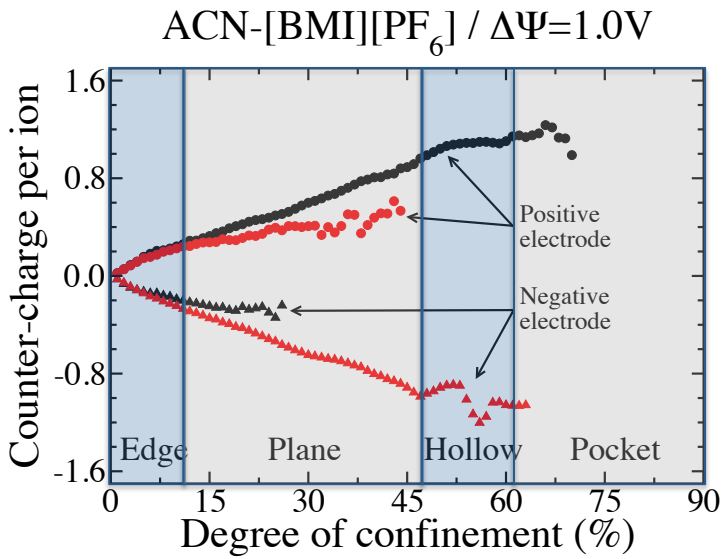
- Counter-ions migrate in confined sites...
- ... While other ions (and the solvent) leave them

Impact of local morphology on supercapacitor properties



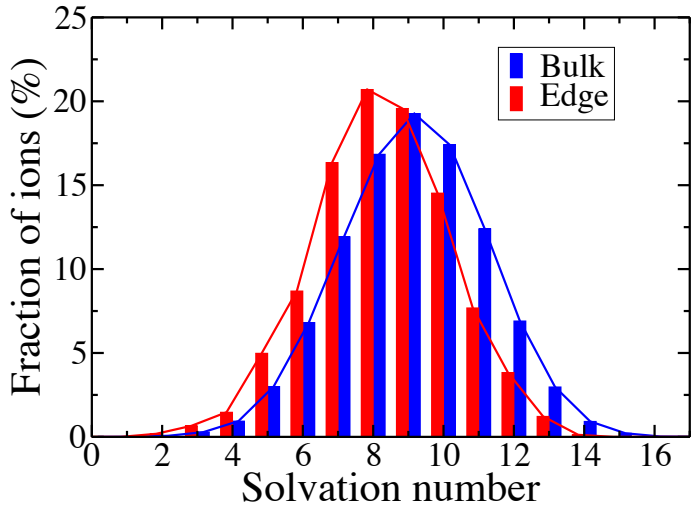
The local charge on the electrode is greater in highly confined sites

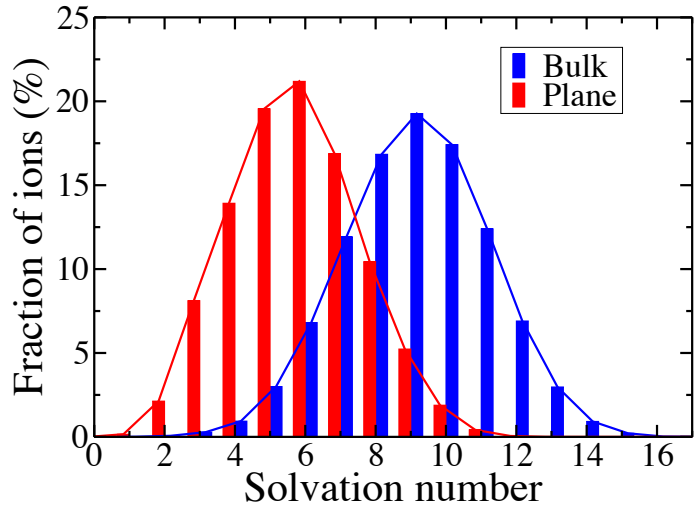


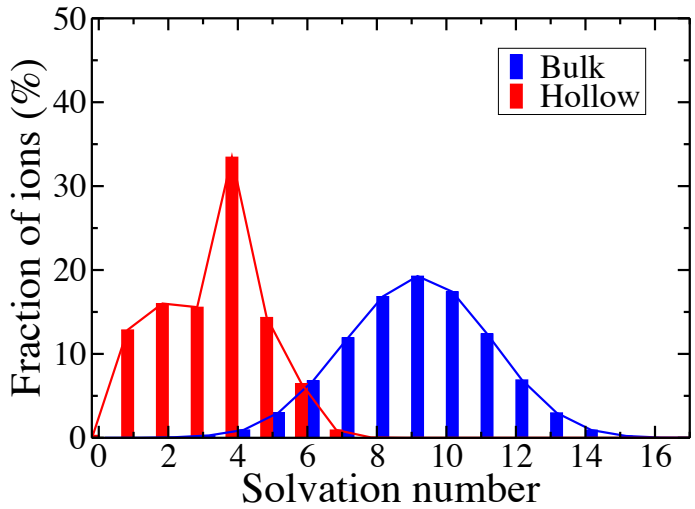


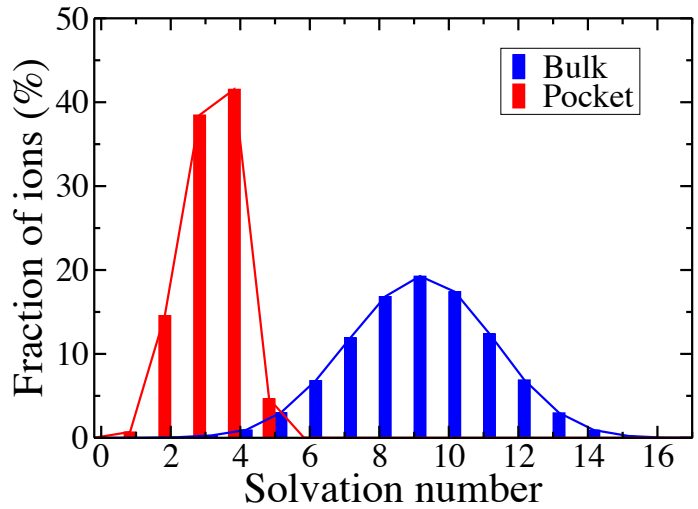
Merlet *et al.*, *Nature Communications*, 4, 2701 (2013)

Desolvation of ions in nanoporous carbons









Merlet *et al.*, *Nature Communications*, 4, 2701 (2013)

Conclusion & Perspectives

- Simulations performed at constant applied potential
- Realistic structures of CDCs
- Nanoporous carbons:
  -screening by the metallic walls $\rightarrow$ superionic state
  -absence of overscreening due to confinement $\rightarrow$ better efficiency
  -role of the local morphology
- Simulations of charge/discharge processes

- Influence of the ionic sizes (development of new models)
- Porous carbon structure (evaluation of new models)
- Ionic liquids dissolved in other solvents

Acknowledgements

- Céline Merlet, Clarisse Péan, Benjamin Rotenberg (PHENIX)
- Paul Madden (Oxford University)
- Patrice Simon (Université Paul Sabatier)
- Yury Gogotsi (Drexel University)
- French National Research Agency
- European Research Council (P. Simon project)
- CINES (project c2013096728)
- PRACE (project 2012071287)