THE UNIVERSITY OF MELBOURNE

Melbourne Energy Institute

Cross-scale modelling of ion transport in nanoporous electrodes towards digital design of high efficiency ionic devices

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Research Fellow

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Content

- Challenges for high efficiency of porous electrodes
- Why we need an across-scale modelling in the engineering strategy
- Case study
  a. Importance of nanoscience: reviewing solvent effect in EDL theory
  b. Engineering electrode macrostructure in practical supercapacitor system
- Outlook
  How to in-time monitor and interactive with practical system?

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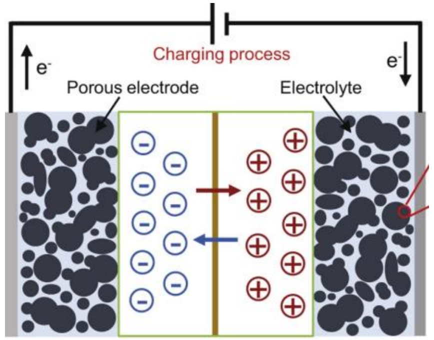
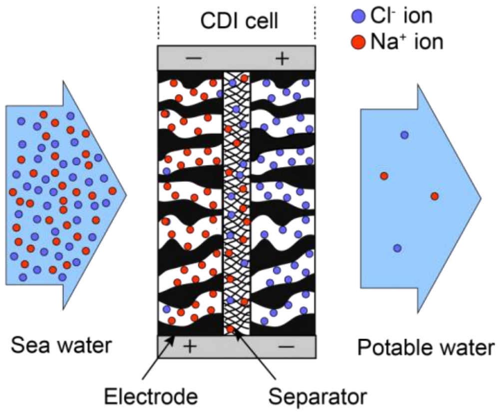
Wide applications of electrolyte-filled porous electrode

Electrochemical energy storage



Green Energy & Environment 5 (2020) 303–321

Water treatment



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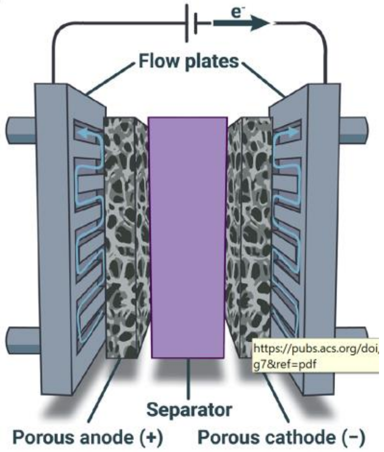
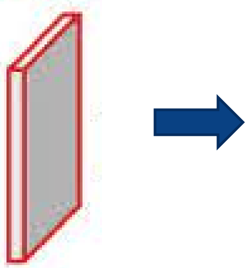
Electrochemical synthesis



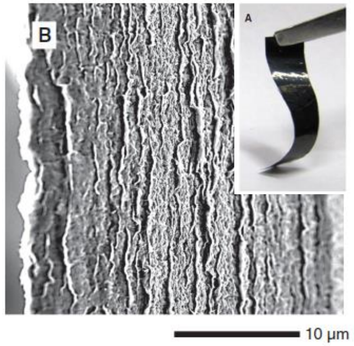
Bulk and dense porous electrode:

- Interconnected pore/voids in bulk electrode
- High ion-accessible surface area
- Practical/device level priority

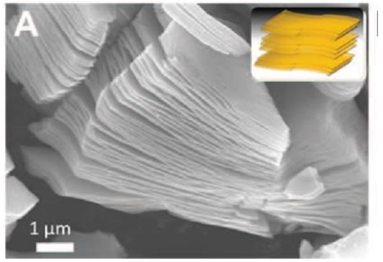
Plate electrode



Bulk and dense porous electrode



Graphene membranes



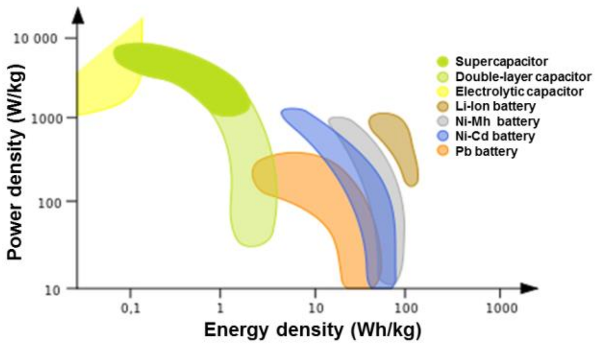
MXene layers

Challenges for high efficiency of porous electrodes

Trade-off between performance metrics

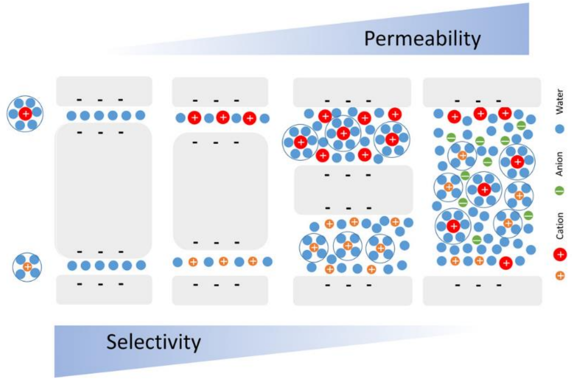
Performance varied on multiple characteristics

Power density *vs.* Energy density



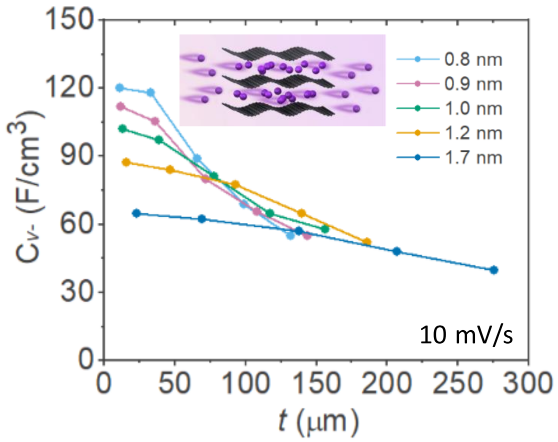
Adv. Energy Mater. 9, 1901457 (2019)

Permeability *vs.* Selectivity



J. Appl. Phys. 2020, 128, 131102 (2020)

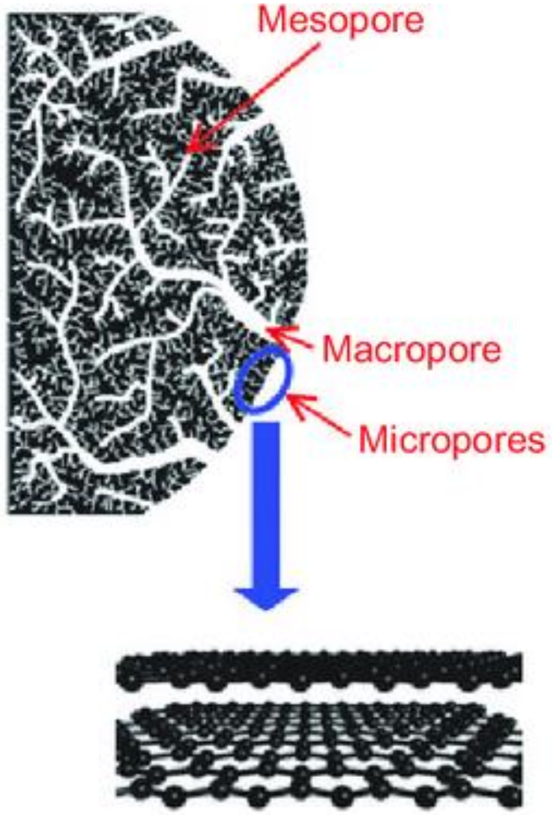
Pore size effect at varied thickness



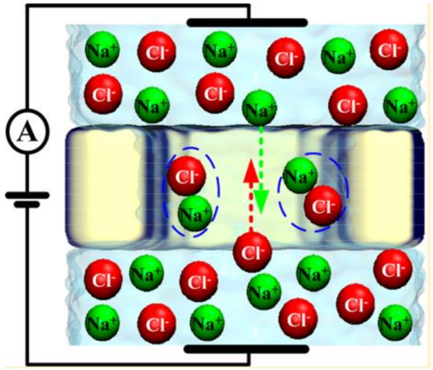
Future on-demand design, real-time monitor, prediction is difficult!

Multiscale, multi-component, and dynamic system

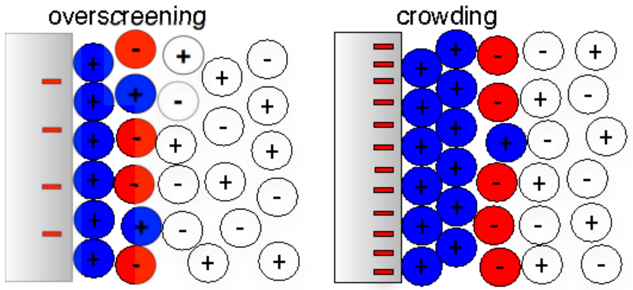
Highly hierarchical structure



New nanoscience



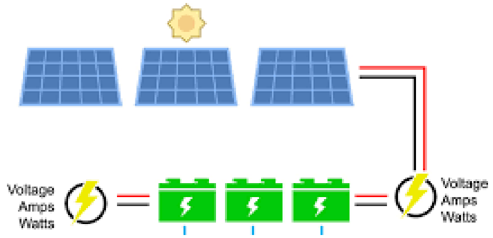
J. Am. Chem. Soc. 141, 4264−4272 (2019)



PRL 106, 046102 (2011)

- Ion pairing
- Superionic
- Coulombic blockage

Dynamic working conditions



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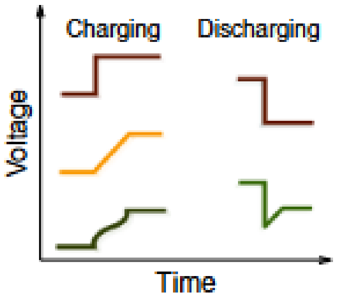

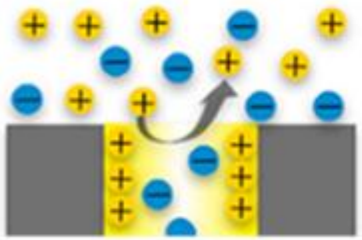

J. Am. Chem. Soc. 141, 8658−8669 (2019)

- Unpredictable

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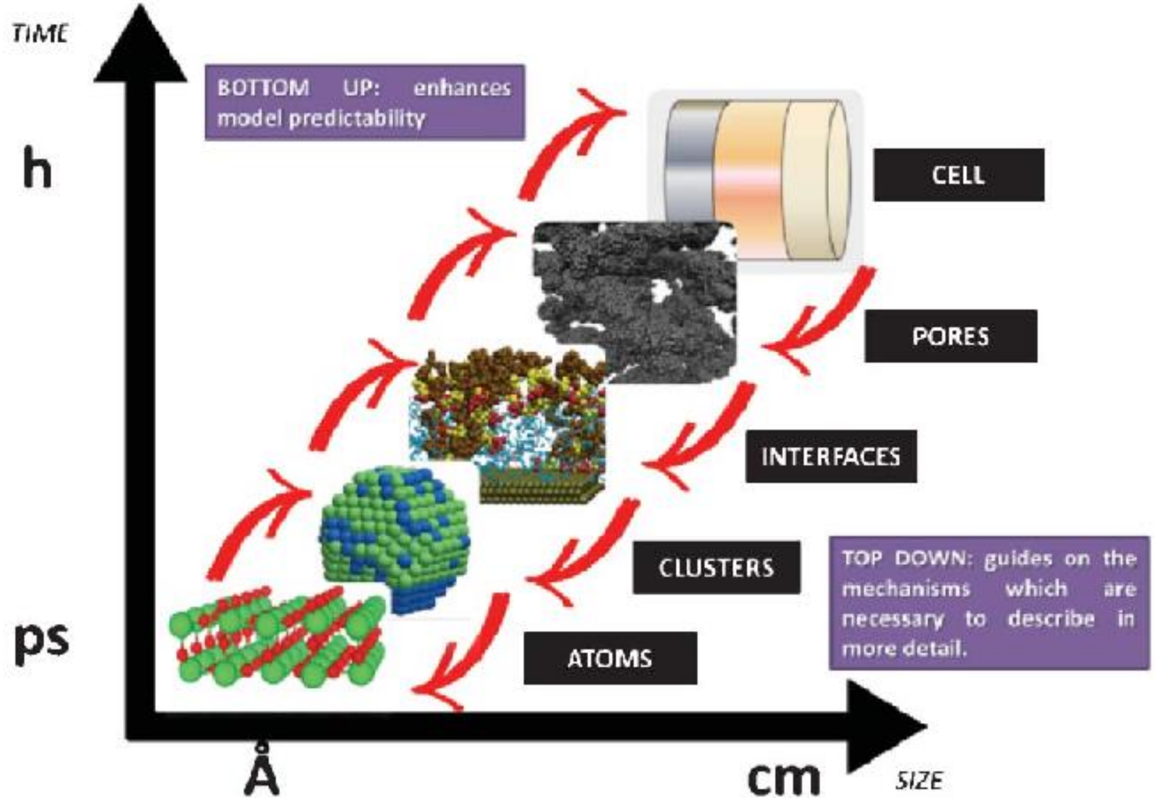
Why we need a across-scale modelling?

A across-scale digitalization platform

Quantitative/semiquantitative description, engineering and prediction of nano science involved ion transport from nanoscale upscaling to bulk nanoporous electrodes towards target application



Continuum

MD

DFT

Overlooked new physics?

How to develop/bridge the models?

It is a pathway to quantitatively compare, engineer, and design practical system

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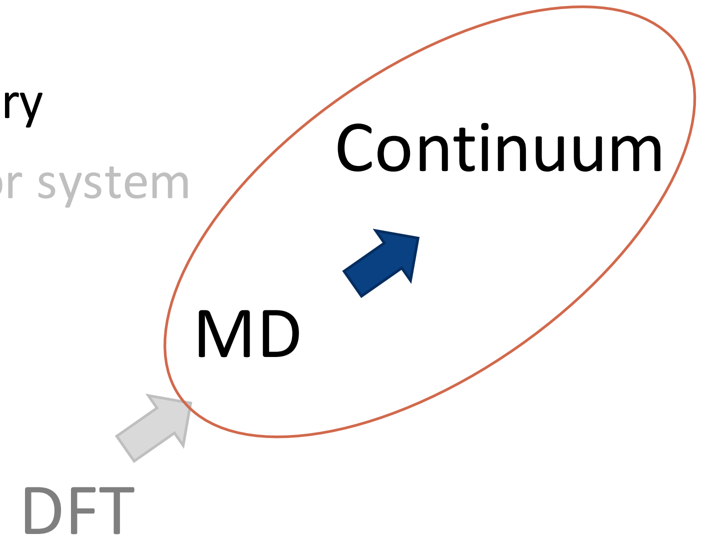
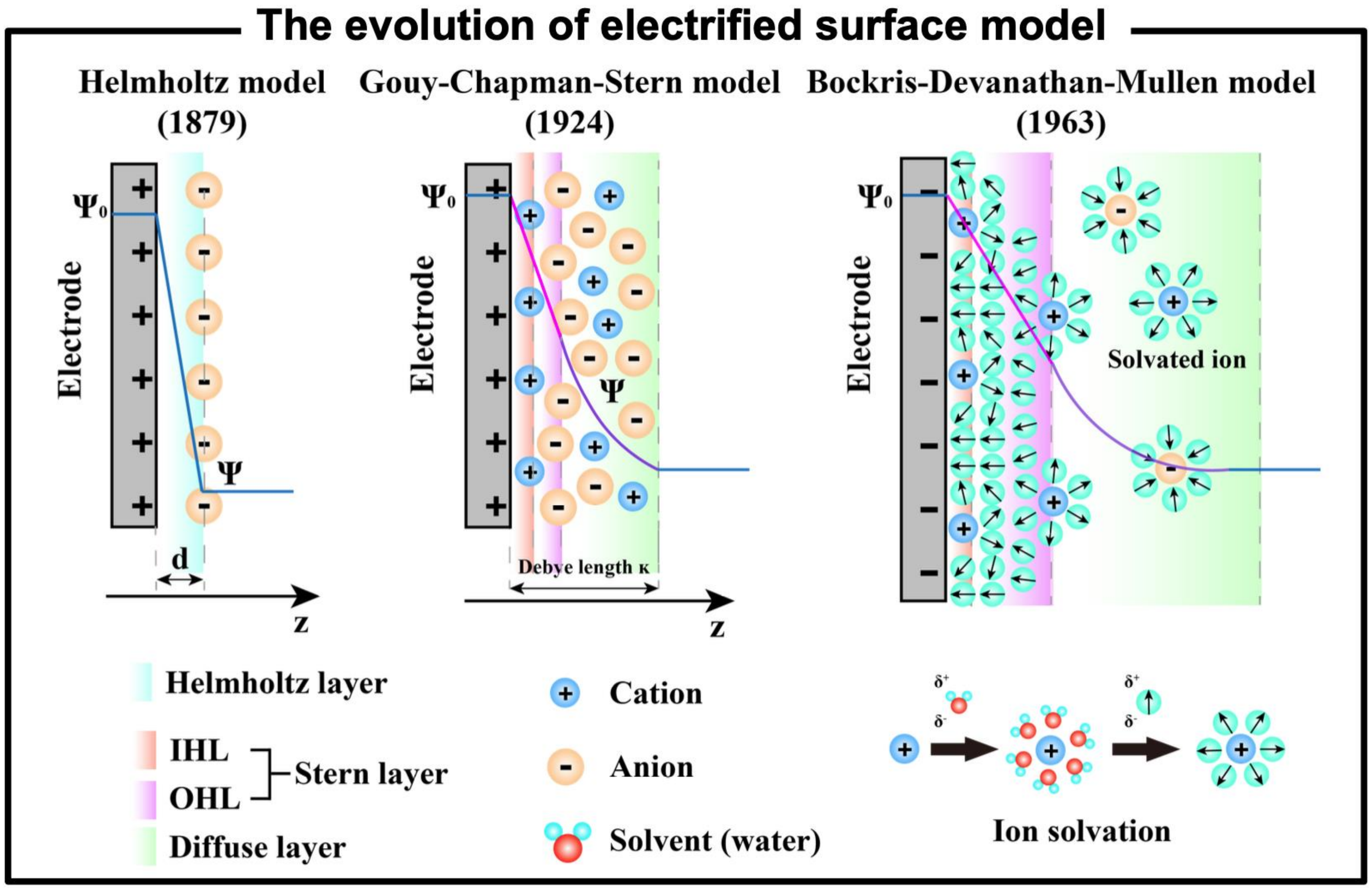


Case-1 : Modern EDL theory



Helmholtz model

- Ions concentrate at interface
- Linear potential drop
- Describe the screening effect

Gouy-Chapman-Stern model

- Introduction of diffuse layer
- Linear + exponential potential drop

Bockris-Devanathan-Mullen model

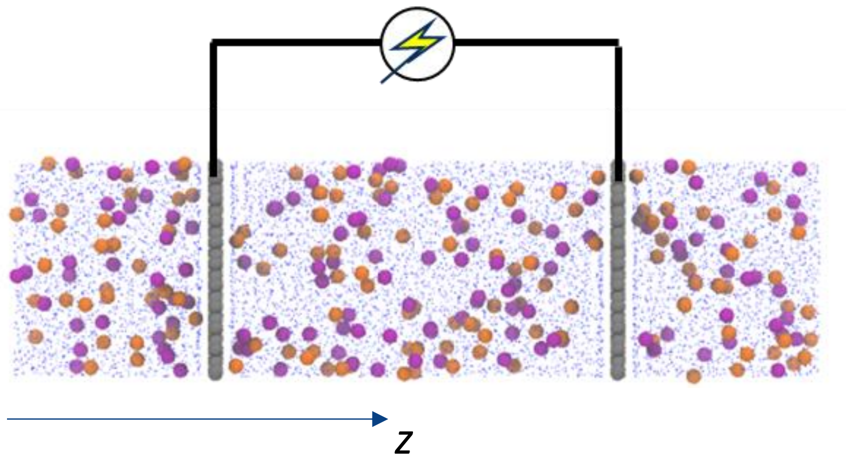
- Consider the hydration of ion
- Show fluctuations in potential drop

- Diffusion layer well verified in experiments.
- Poor description of the molecular structures next to the interface.

Case-1 : Modern EDL theory

Simulation method and systems

A schematic of two graphene sheets in an aqueous electrolyte reservoir

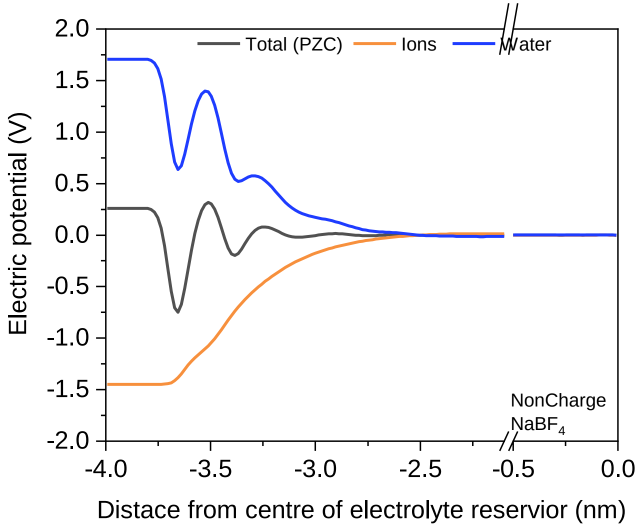


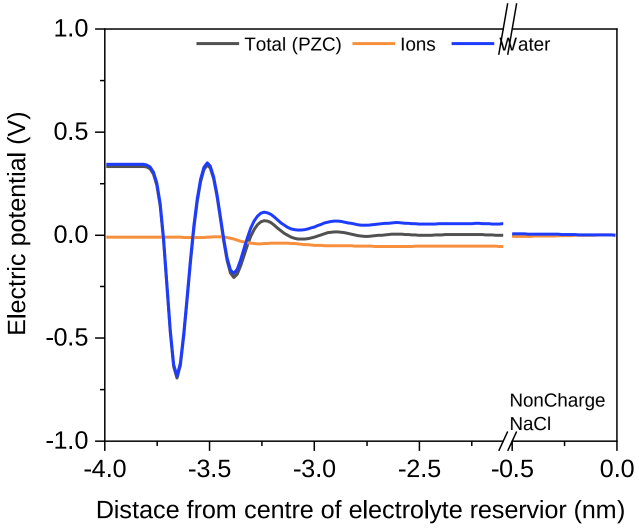
- Graphene sheets: $z = \pm 4$ nm & x-y plane dimension: 4.156×4.254 nm^2
- Aqueous electrolytes: 0.8 M $NaBF_4$ and NaCl
- 9052 water molecules & 132 cation-anion pairs
- Charging densities: $\sigma_s = \pm 0.00938$ e/C-atom (i.e., 6.0 μC/cm^2) and 0
- NVT ensemble; 300K; LAMMPS code
- The electric potential profiles: calculated by double integrating the spatial charge distributions via the Poisson equation

Crucial surface water on PZC values of electrode

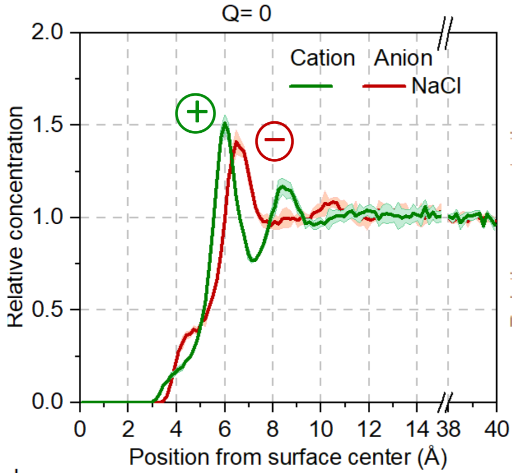
**PZC: Potential of Zero Charge*

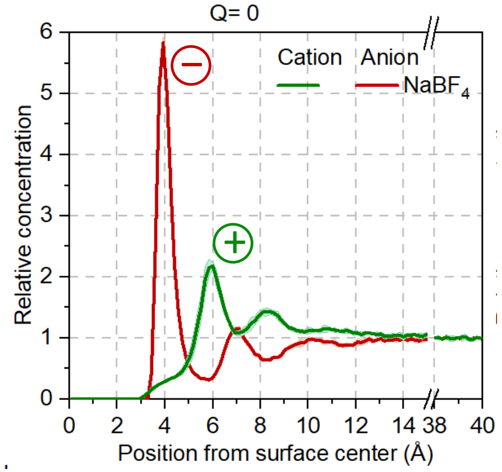
Dominated contribution of water on electric potentials





Ion interfacial distribution



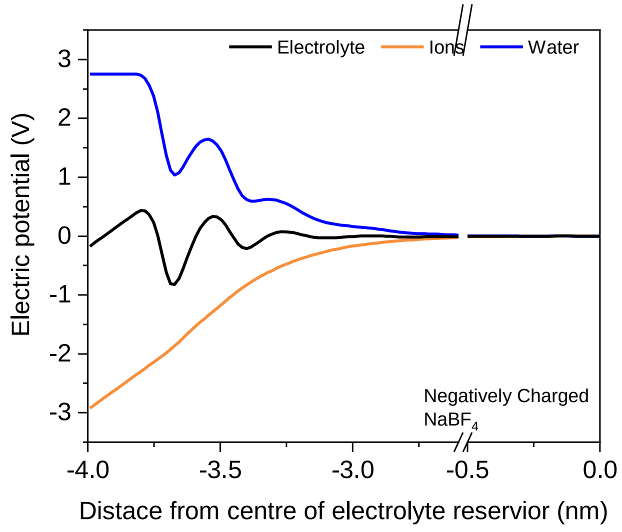


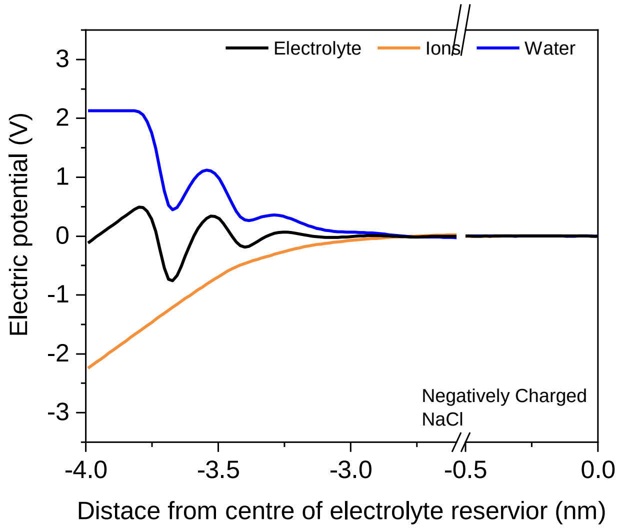
Surface potentials

$\varphi_{PZC@NaBF4}$	$\varphi_{ion@NaBF4}$	$\varphi_{water@NaBF4}$	$\varphi_{PZC@NaCl}$	$\varphi_{ion@NaCl}$	$\varphi_{water@NaCl}$
0.26 V	−1.45 V	1.71 V	0.33 V	-0.01 V	0.34 V

Crucial surface water on electrode capacitance

Comparable water electric potentials to ion electric potentials





$NaBF_4$ electrolyte

$\Delta\varphi_{electrolyte}$	$\Delta\varphi_{\text{ion}}$	$\Delta\varphi_{\text{water}}$
-0.43 V	−1.47 V	1.04 V

NaCl electrolyte

$\Delta\varphi_{electrolyte}$	$\Delta\varphi_{ion}$	$\Delta\varphi_{water}$
-0.45 V	-2.24 V	1.79 V

$$C = \frac{Q}{\Delta\varphi_{electrolyte}} = \frac{Q}{\Delta\varphi_{ion} + \Delta\varphi_{water}}$$

Electrode capacitance

$NaBF_4$ electrolyte: **6.98** $\mu F/cm^2$

NaCl electrolyte: **6.67** $\mu F/cm^2$

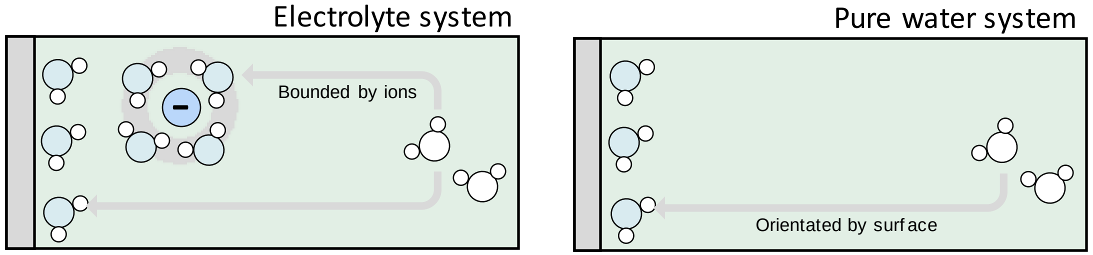
If without considering surface water:

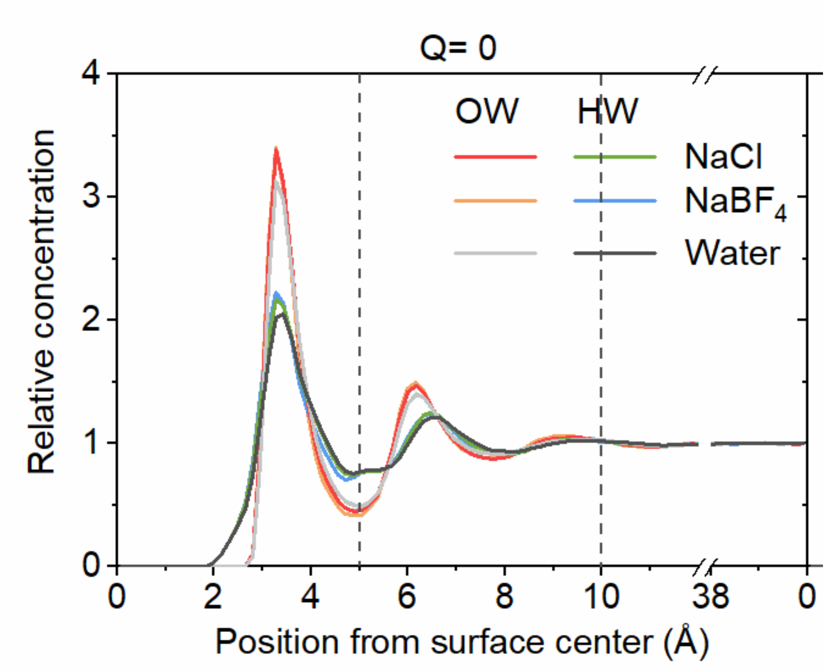
$NaBF_4$ electrolyte: **2.04** $\mu F/cm^2$

NaCl electrolyte: **1.34** $\mu F/cm^2$

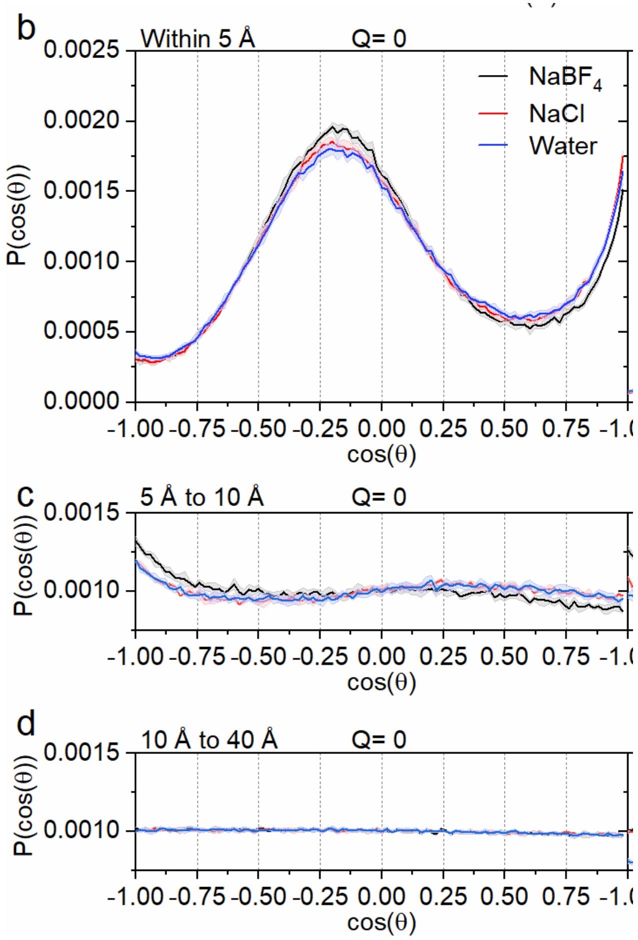
Particular water interfacial properties counter in bulk solution

Surface water with enhanced density and layering structure

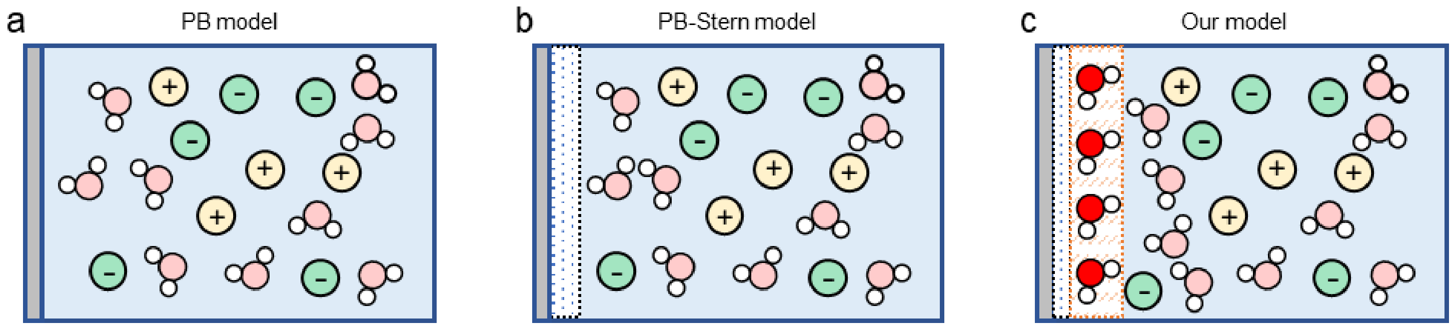




Orientated surface water



Our developed modern EDL model



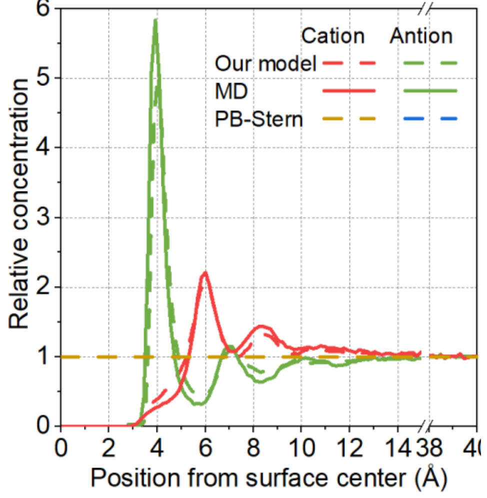
Orientated surface water region

$$\nabla\varphi = E_0 + \frac{\sigma}{L_O C_w}$$

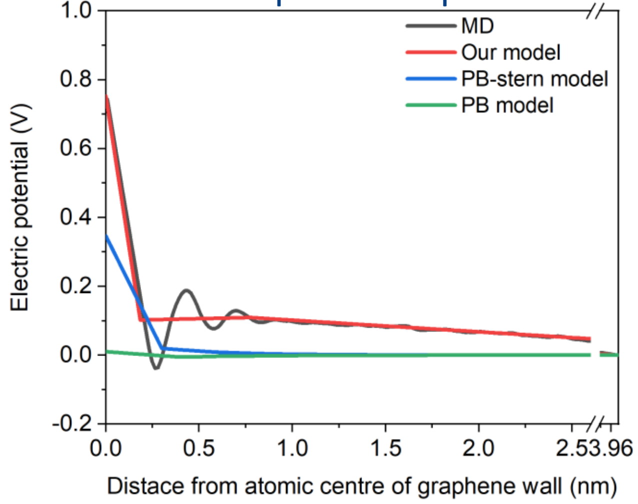
Electrolyte diffuse region

$$\epsilon_{r,s}\epsilon_0\nabla^2\varphi = -\sum_i q_i\, c_\infty\, e^{-\frac{[V_i^{PMF}+q_i\varphi]}{k_B T}}$$

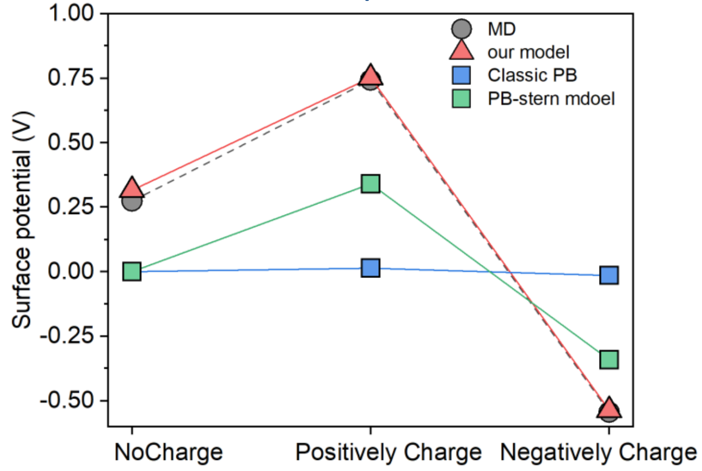
Ion distribution



Electric potential profile



Surface potential



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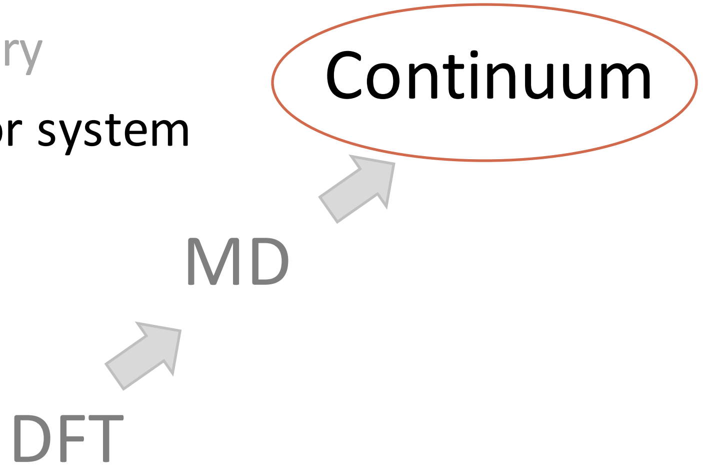
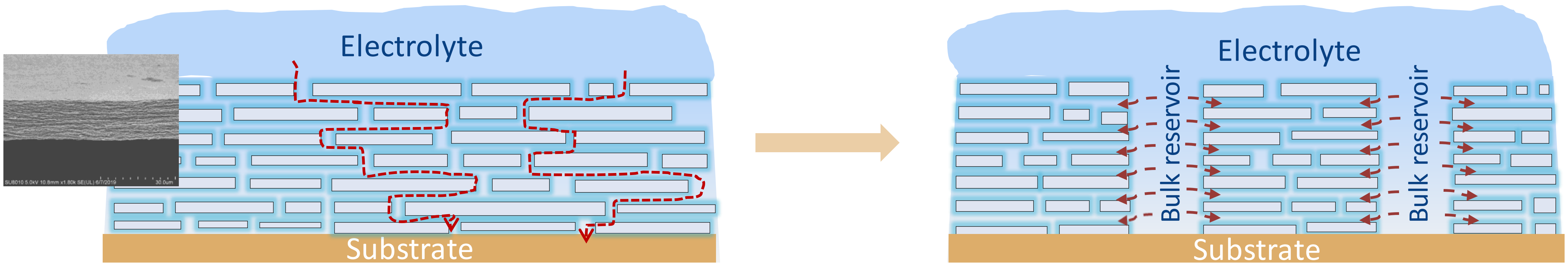


Case-2: Engineering electrode structure in practical supercapacitor system

Background: the tortuous ion transport pathway in 2D laminate electrode, particularly dense and thick, compromise the rate performance

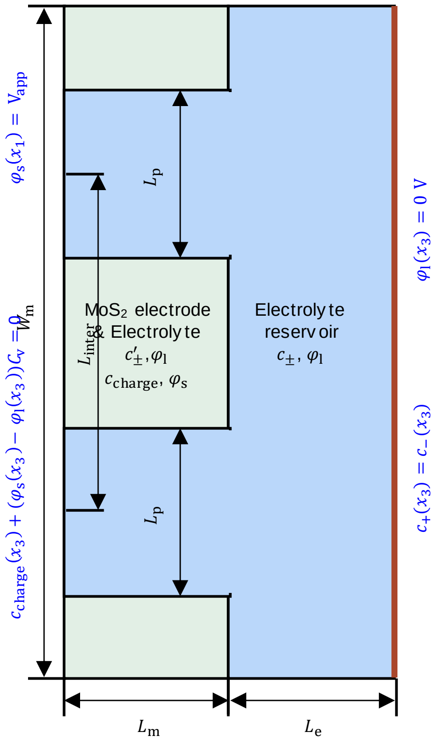


Vertical pore promote ion transport, but the accessible electrode surface would be sacrificed

How to balance the hole density and size for improving rate performance of supercapacitor

Case-2: Engineering electrode structure in practical supercapacitor system

Simulation methods and systems



For electrolyte accessible region

$$\frac{\partial \alpha c_i}{\partial t} = -\nabla N_i = \alpha(D_i \nabla^2 c_i + \nabla(c_i \mu_i \nabla(z_i e \varphi_l)) + \frac{D_i \nabla(c_i \nabla(c_+ + c_-))}{c_{max} - (c_+ + c_-)})$$

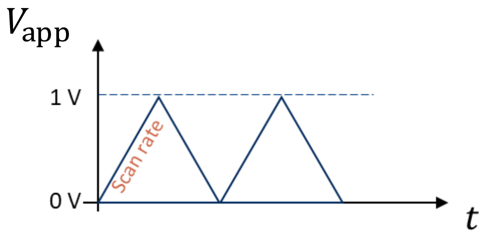
$$D_{i,\perp} = \eta D_{i,\parallel}$$

$$\epsilon \epsilon_0 \nabla^2 \varphi_l = F(z_+ c_+ \alpha + z_- c_- \alpha + z_{charge} c_{charge})$$

For the MoS_2 phase/part in the electrode

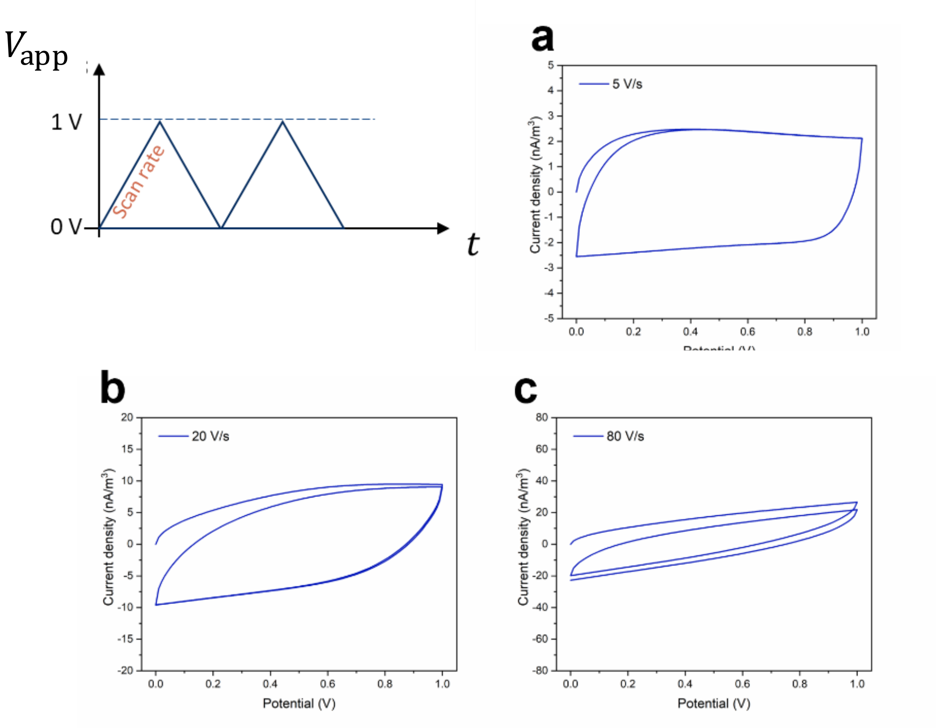
$$\nabla(\sigma_s \nabla \varphi_s) = 0$$

$$z_{charge} c_{charge} = -C_v(\varphi_s - \varphi_l)/F$$



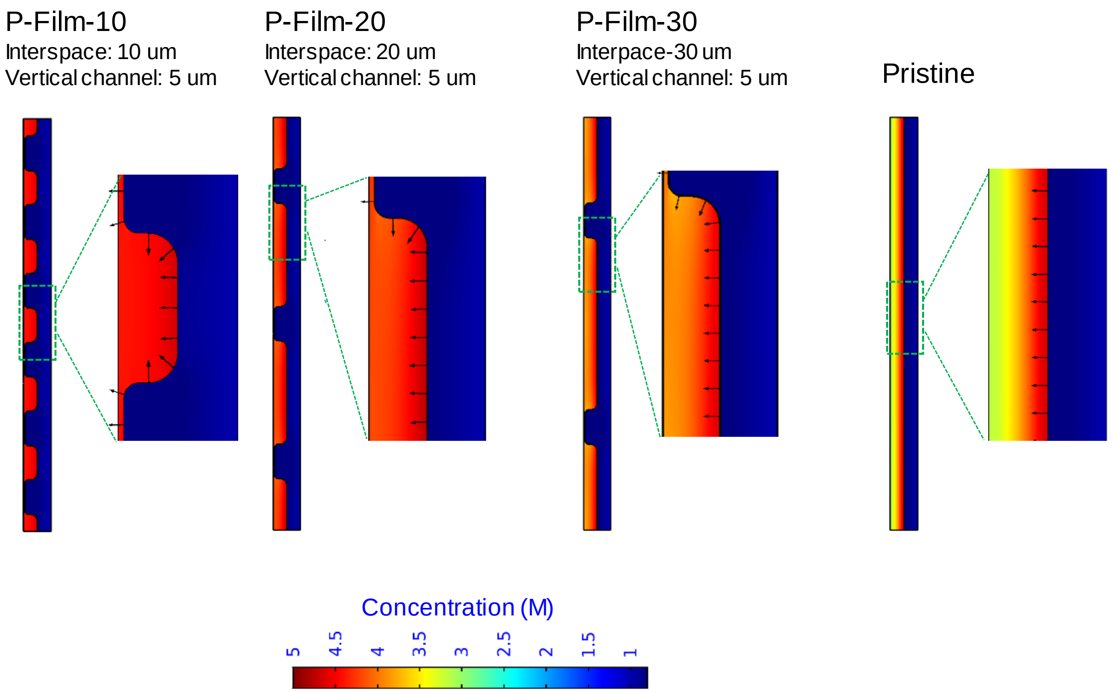
Case-2: Engineering electrode structure in practical supercapacitor system

Typical charging rate dependent CV curves



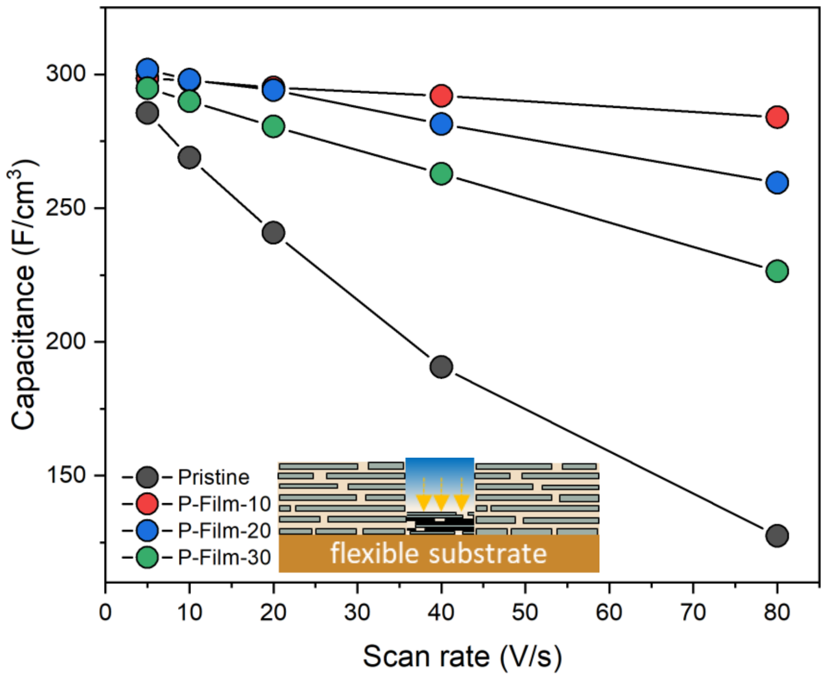
Ion accessibility in varied electrode structures

Thickness: 2 µm, height: 60 µm, hole size: 5 µm/100 nm

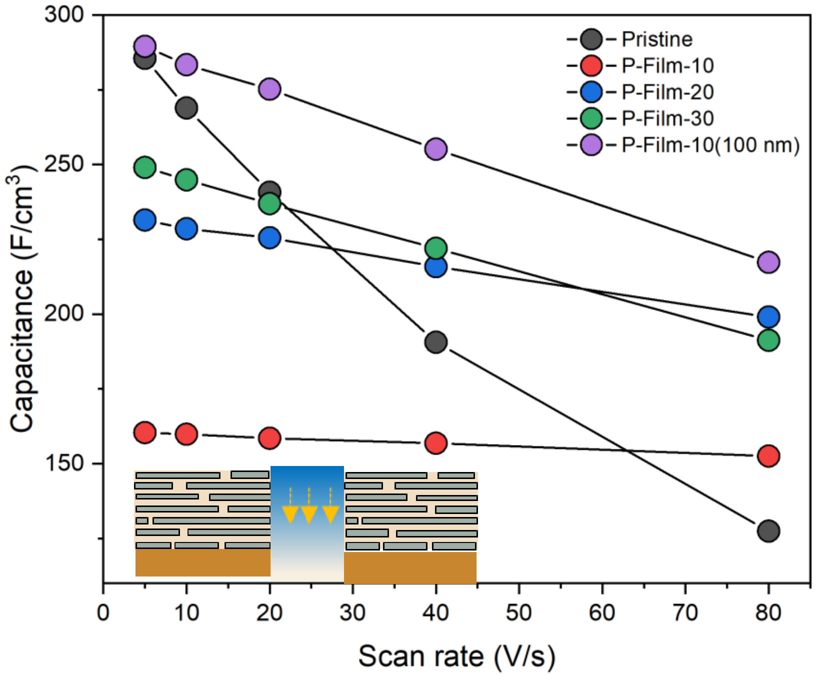


Case-2: Engineering electrode structure in practical supercapacitor system

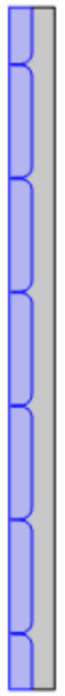
If electrode without mass loading loss



If electrode has mass loading loss



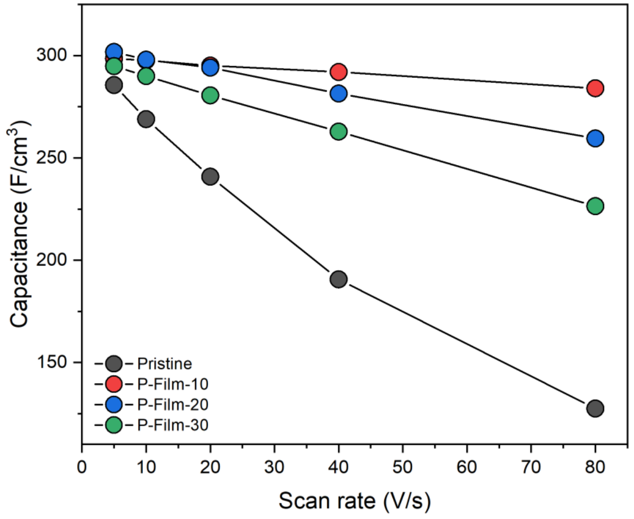
P1-100nm
Interspace: 10 um
Vertical channel: 100 nm



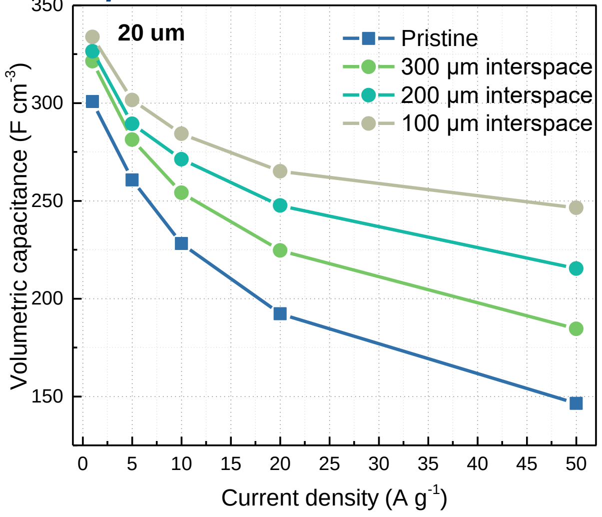
Case-2: Engineering electrode structure in practical supercapacitor system

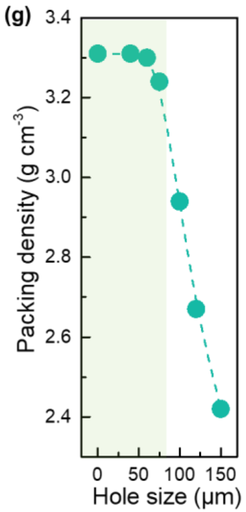
Verified by experimental results

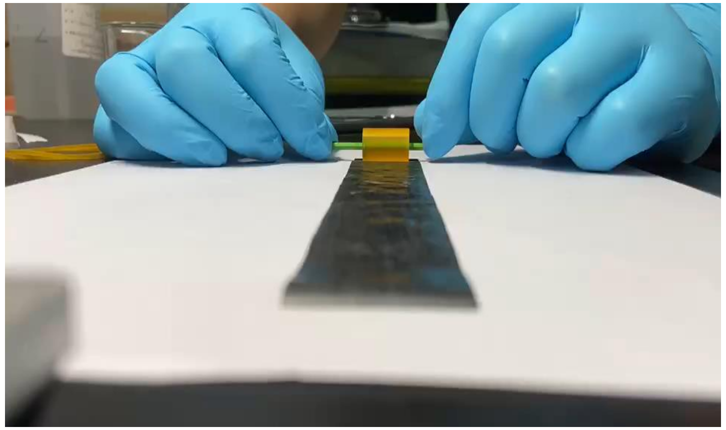
Our model result



Experimental result







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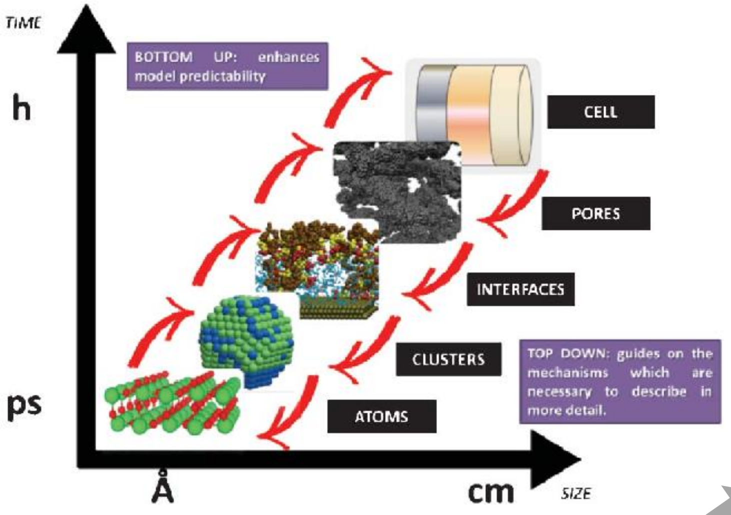
How to in-time monitor and interactive with practical system?

A future digital twin of porous electrode based applications

with combination of data science, IOT techniques, and experimental system



DFT

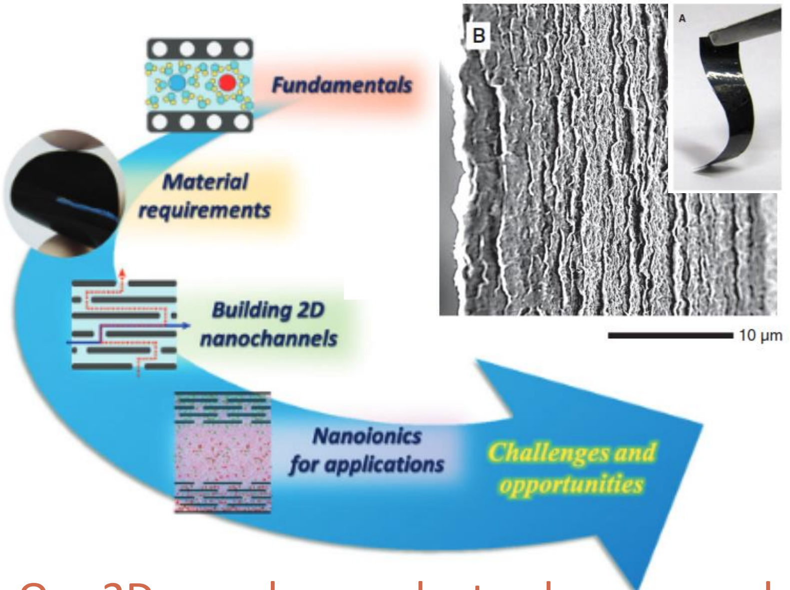
MD

Continuum

Circuitry

IOT techniques

Data science



Our 2D membrane electrode as a good experimental platform

Adv. Mater. 2019, 190456

Conclusion

- We proposed a digital engineering strategy for porous electrode based applications towards high energy efficiency

- A across-scale model is introduced, which considering the crucial surface water for improved description of surface potentials and ion interfacial distributions, transferring the nanoscale features into macroscopic framework.

- A mesoscale dynamic model is introduced, which can simulate the pore structure and charging rate dependent ion storage process in supercapacitor systems. This model demonstrates a capability to assist porous structure engineering for high rate performance of supercapacitors.

Acknowledgement

All my group members and my two supervisors:

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The collaborators involved in the reported projects:

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A/Prof. Qiu Ling (Tsinghua University, China)

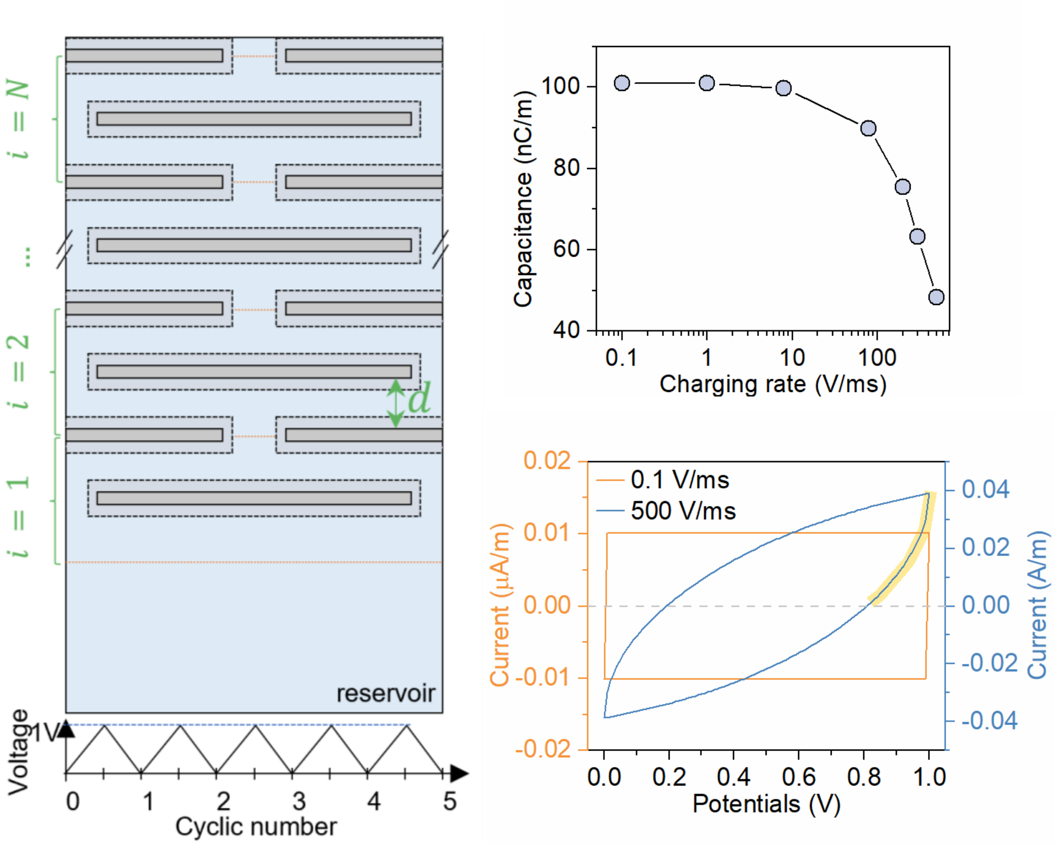
Supercomputer sources:

Spartan (University of Melbourne)

Pawsey Supercomputing Centre

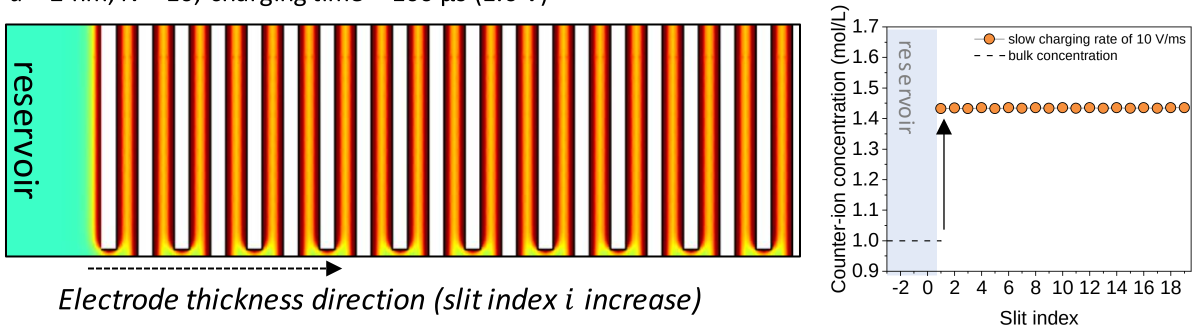
Thank you for your attention!!!

Our recent works: Spatiotemporal probing ion distribution in supercapacitor system



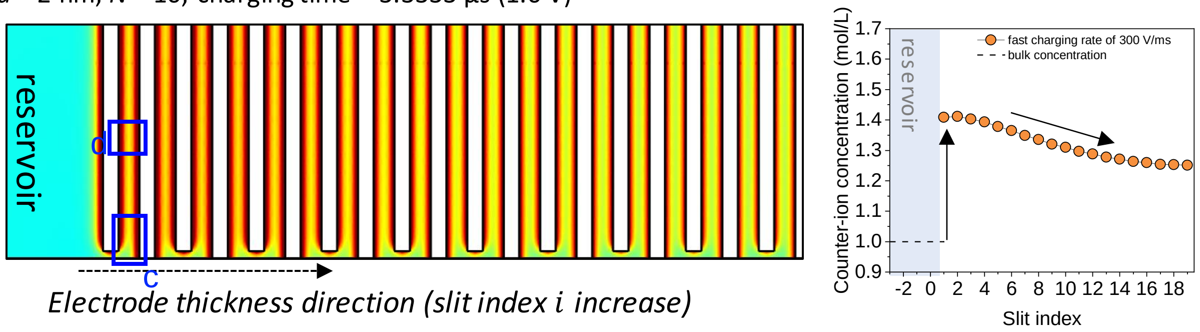
a Counter ion distribution at 1/2 charging cycle and slow charging rate of 10 mV/s

d = 2 nm; *N* = 10; charging time = 100 μs (1.0 V)



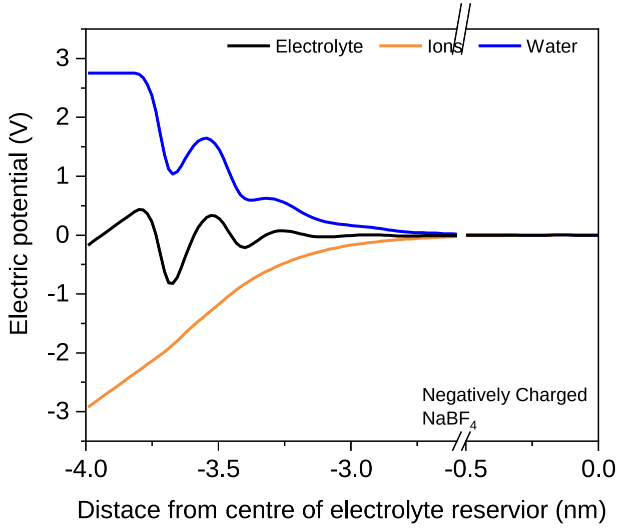
b Counter ion distribution at 1/2 charging cycle and fast charging rate of 300 mV/s

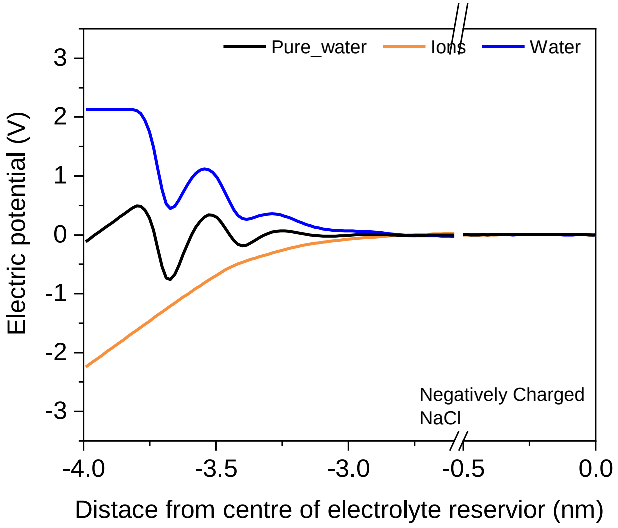
d = 2 nm; *N* = 10; charging time = 3.3333 μs (1.0 V)



Crucial surface water on electrode capacitance

Electric potential profiles





$\varphi_{PZC@NaBF4}$	$\varphi_{ion@NaBF4}$	$\varphi_{water@NaBF4}$
-0.17 V	−2.92 V	2.75 V

$\varphi_{PZC@NaCl}$	$\varphi_{ion@NaCl}$	$\varphi_{water@NaCl}$
-0.12 V	-2.25 V	2.13 V