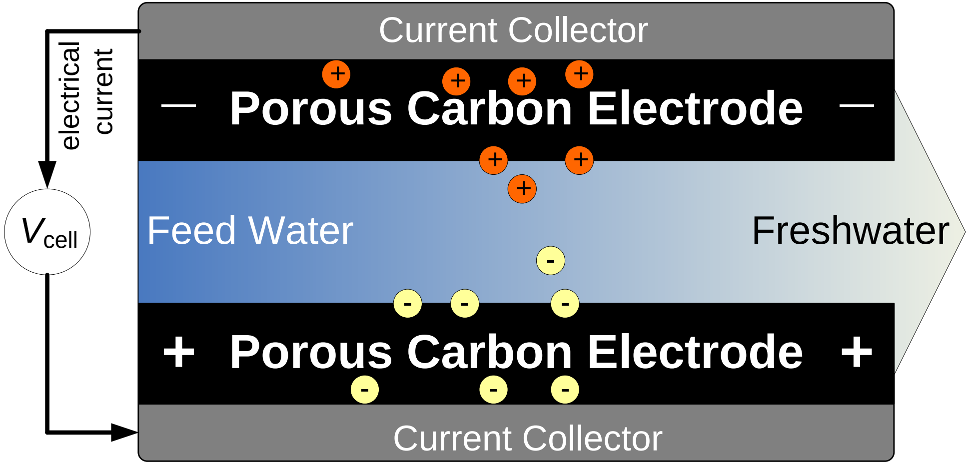
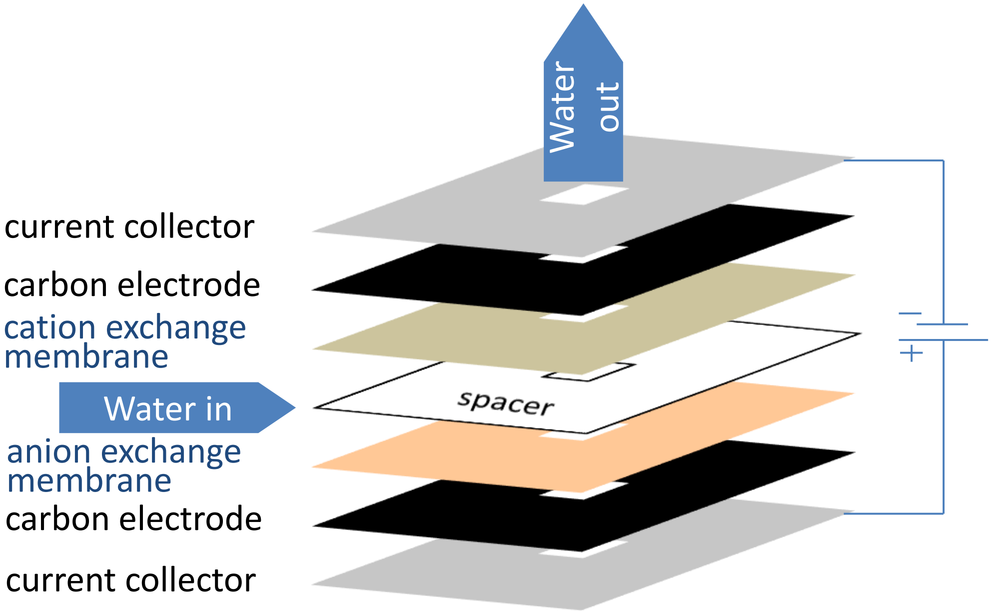
Porous electrodes for energy storage, desalination and CO_2 cycling

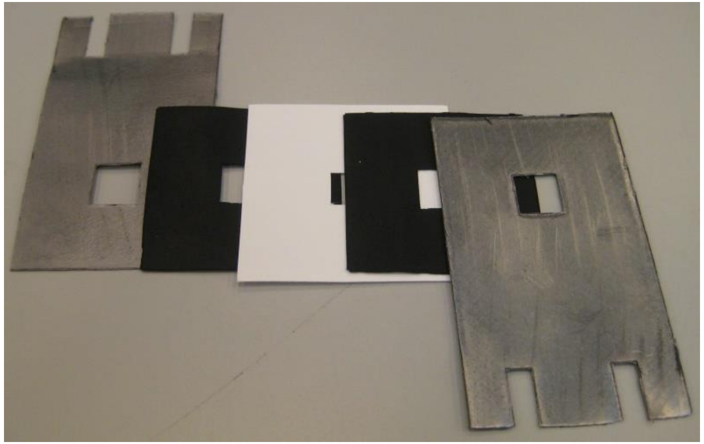


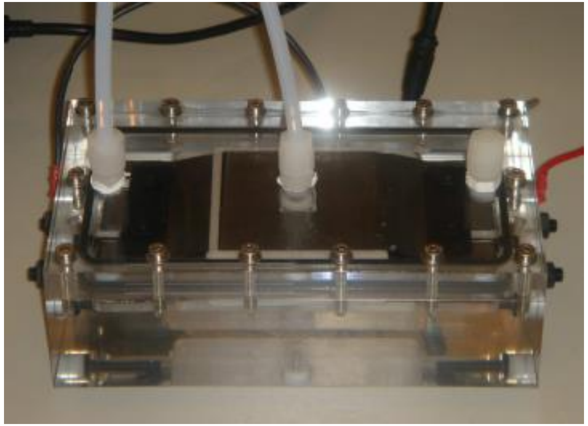
wetsus
european centre of excellence for sustainable water technology

Maarten Biesheuvel

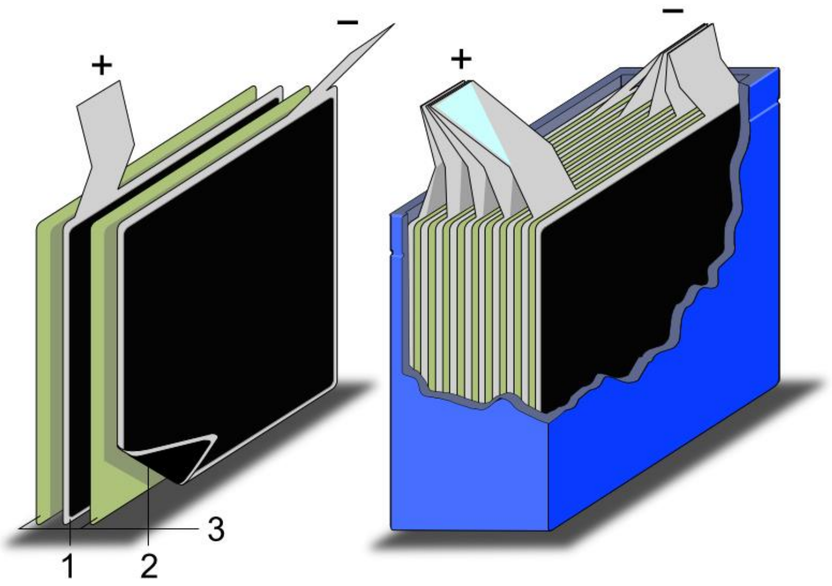
What does such an electrochemical cell look like?



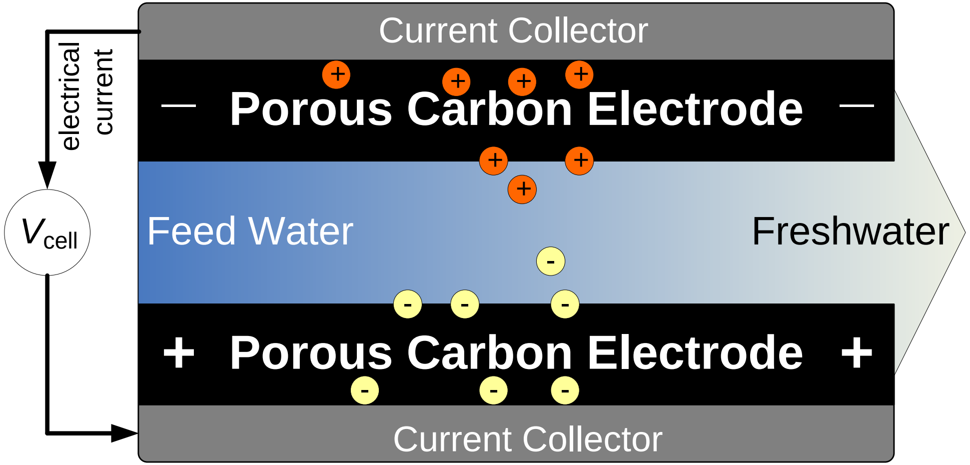




EDL-“super”-capacitors and Capacitive Deionization



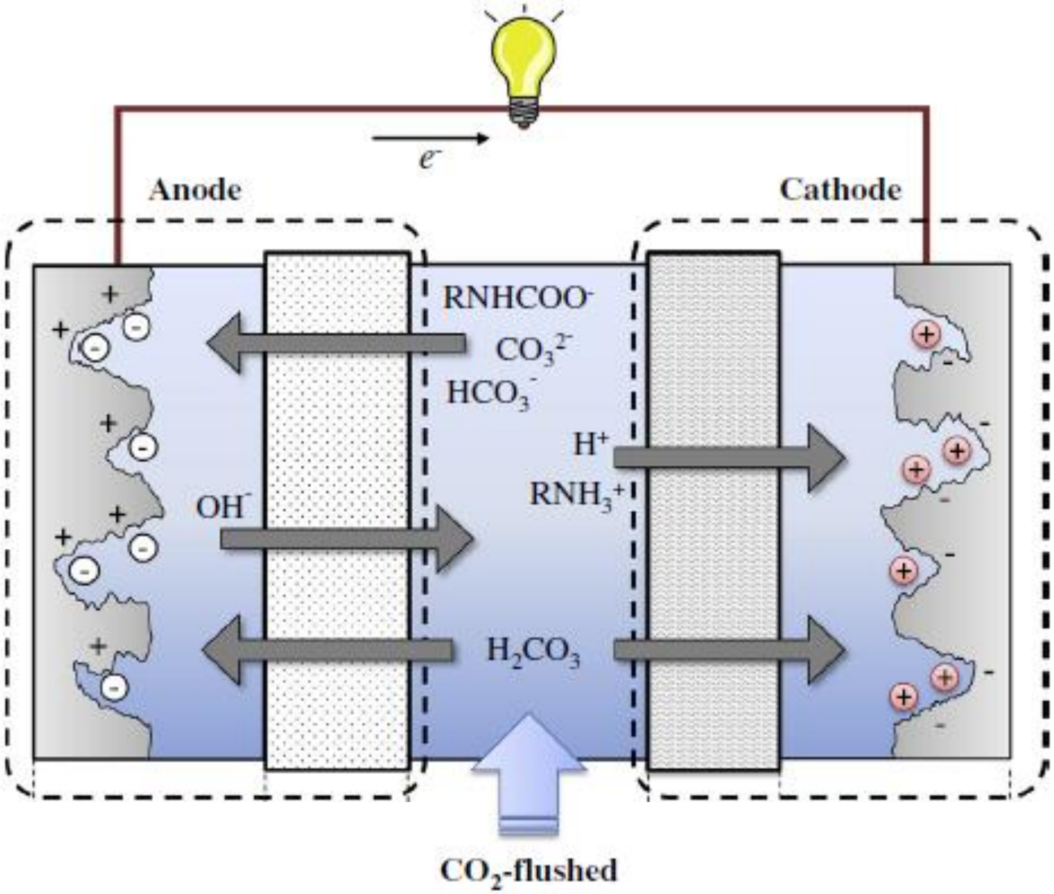
“super”-capacitors



Capacitive Deionization (CDI)

3rd option: osmotic energy , or blue energy

CO2 cycling



Methods of water desalination

Distillation

Reverse Osmosis

Electrodialysis

Capacitive Deionization

Capacitive Deionization

Classical CDI (with carbons)

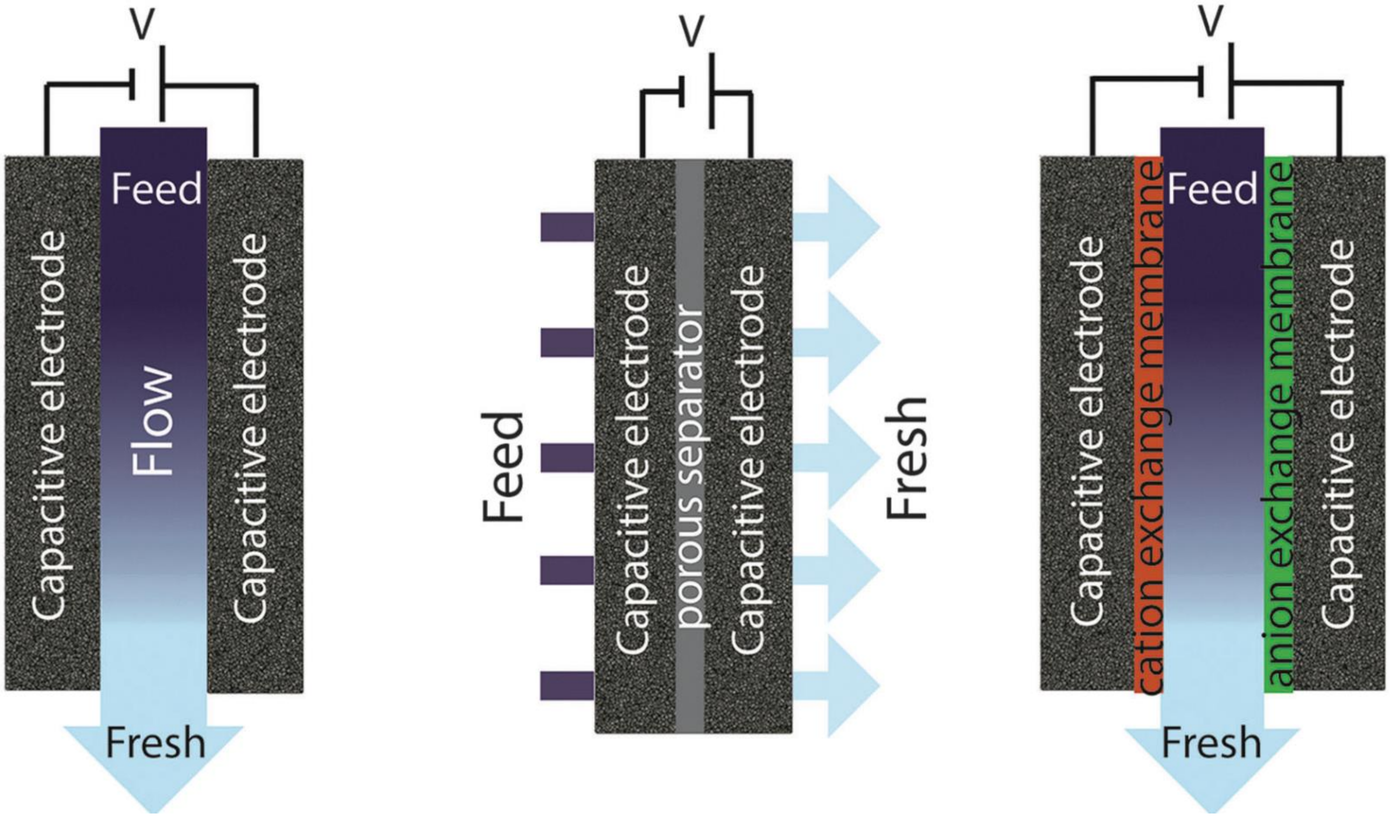
CDI with non-carbon materials*

Membrane CDI

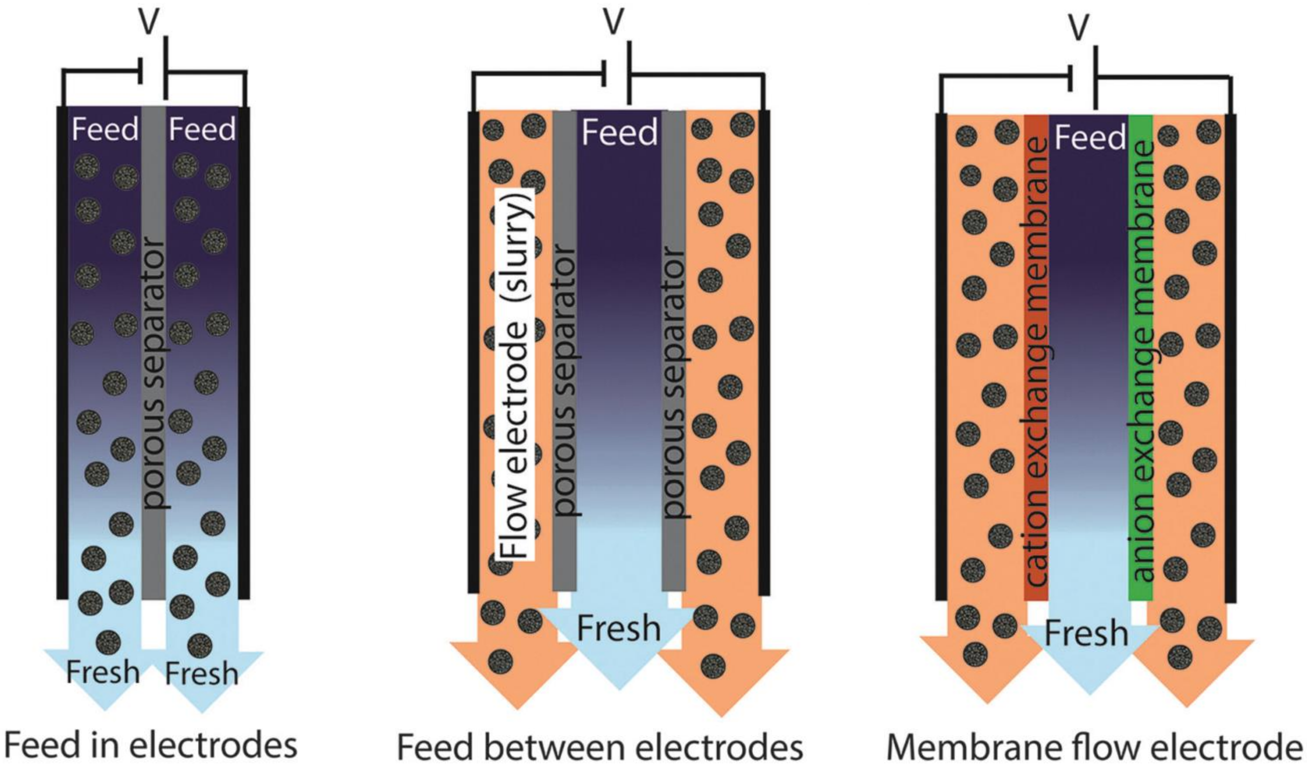
Flow-electrode CDI

* redox functionalities, intercalation, insertion materials

Static electrode architectures

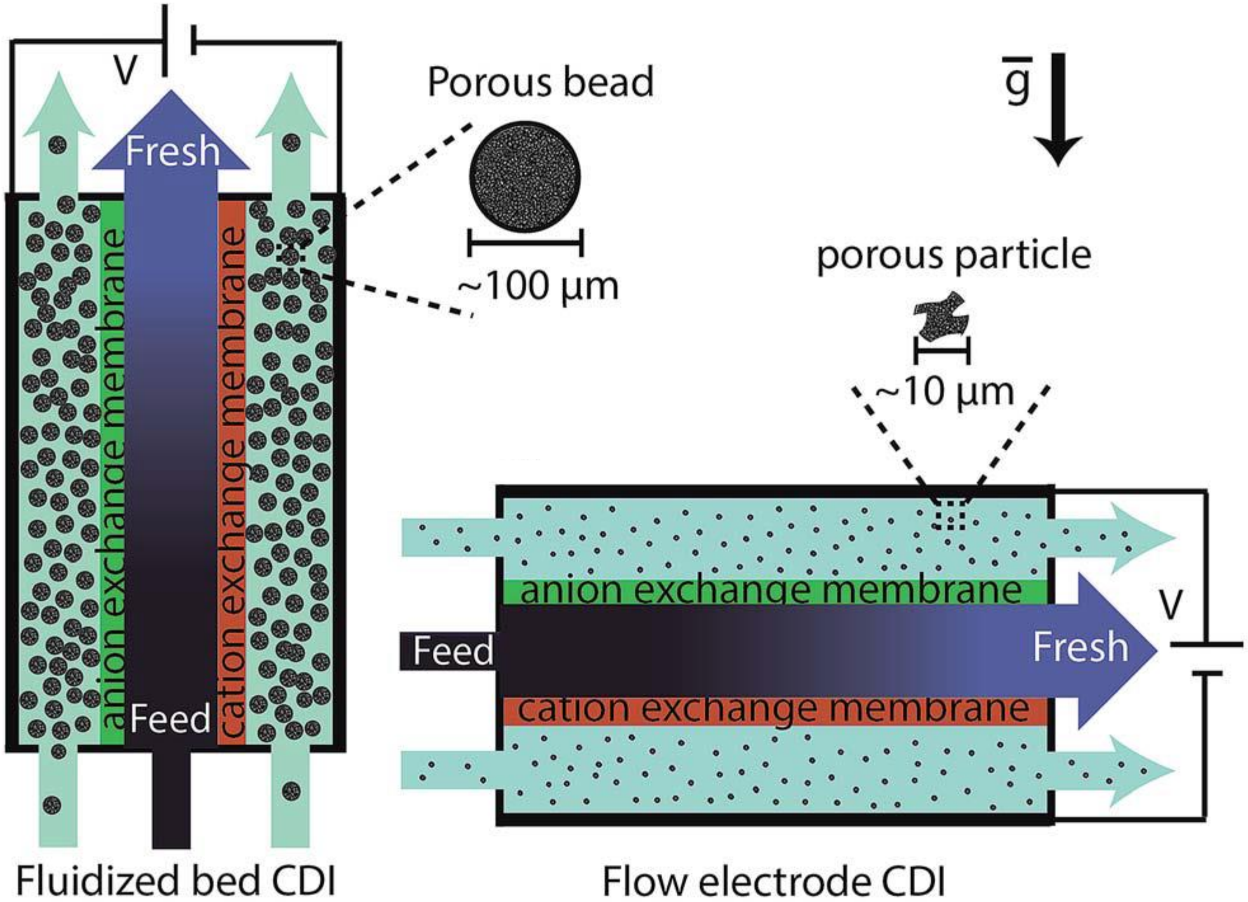


Flow electrode architectures

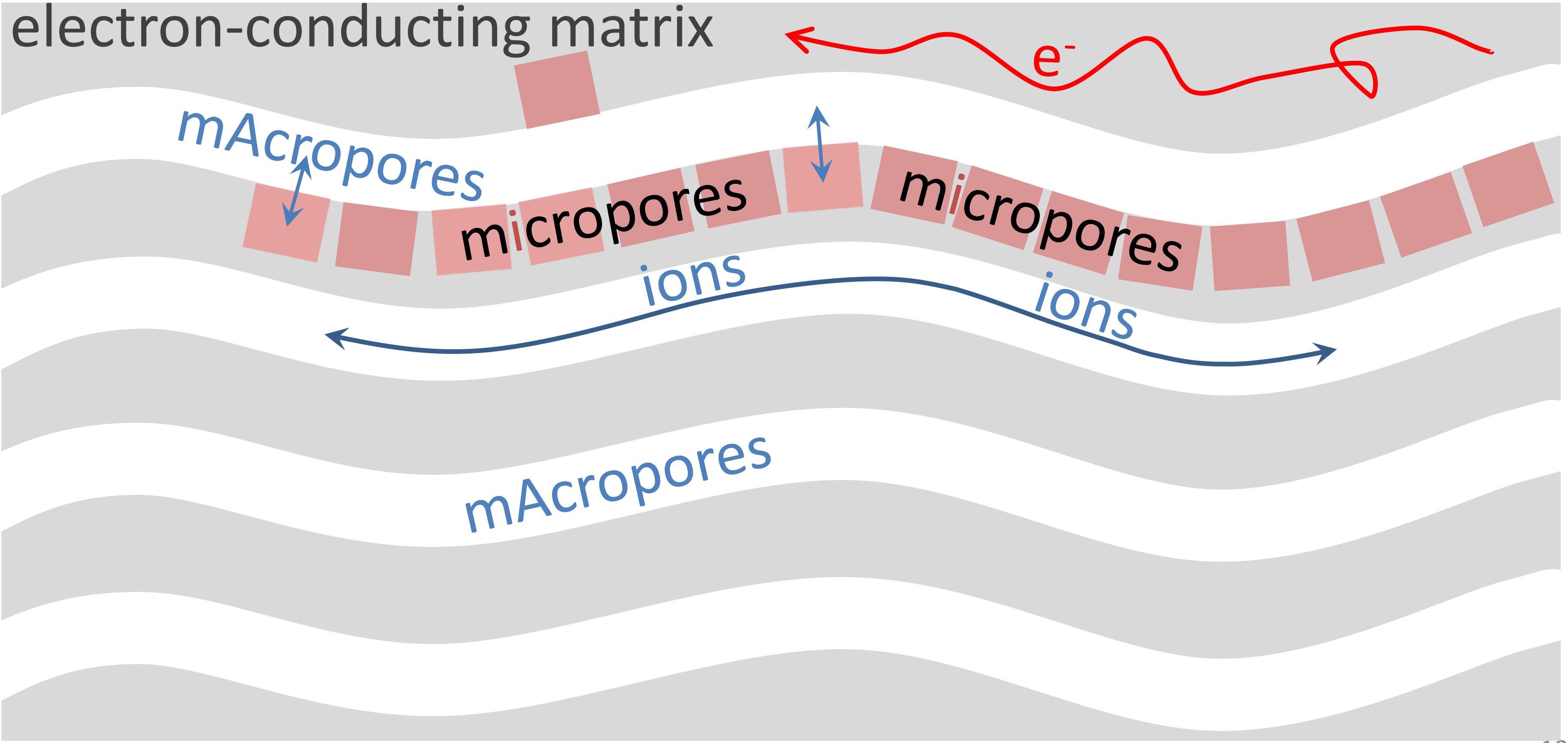


How does a carbon slurry conduct electrons ?

Flow electrode architectures



Transport in porous electrodes



Generalized porous electrode theory

Transport equation in mAcropores & EDL-model in carbon micropores

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot J_{NP,i} - j_{i,mA\rightarrow mi}$$

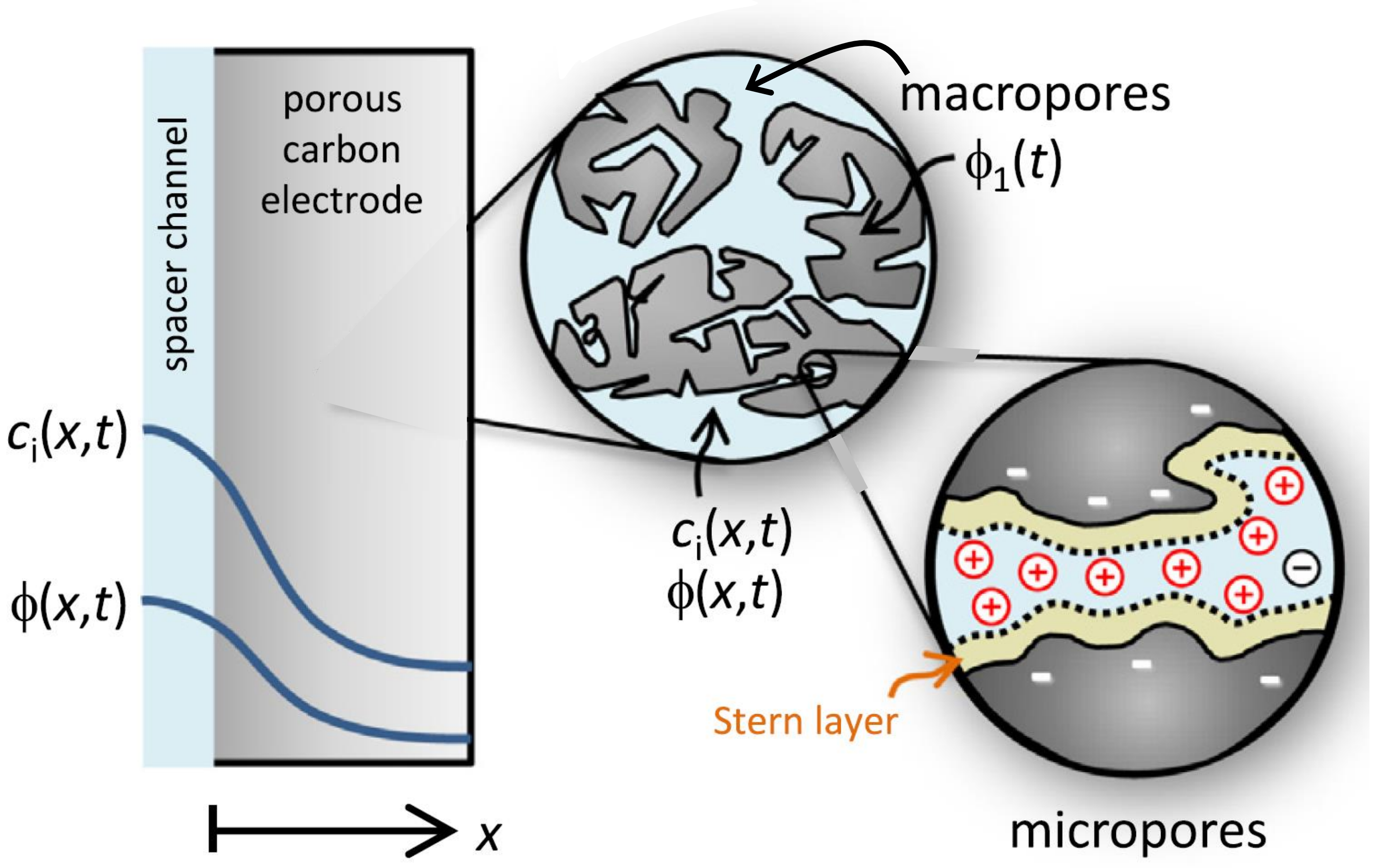
$$J_{NP,i} = -D_i \left(\nabla c_i + z_i c_i \nabla \phi \right)$$

$$\Delta V_{EDL}, c_{i,mA} \Leftrightarrow \sigma, c_{i,mi}$$

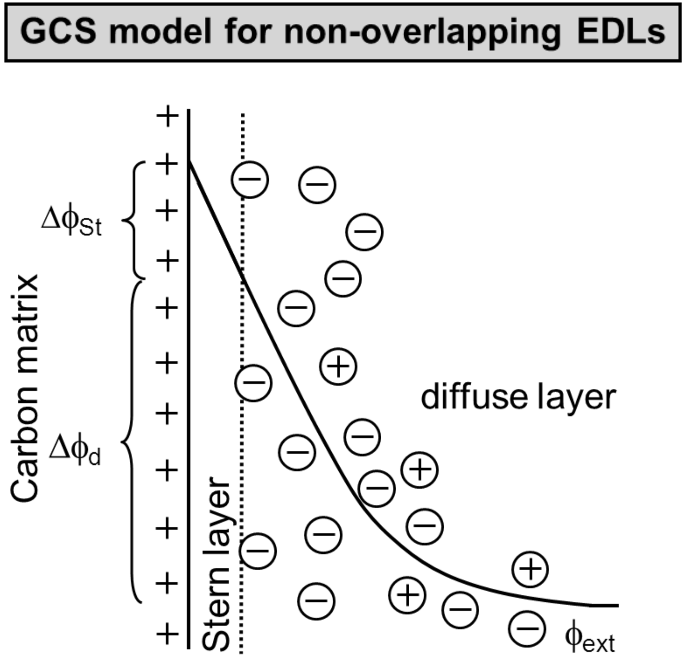
Prof. Martin Bazant
MIT, USA

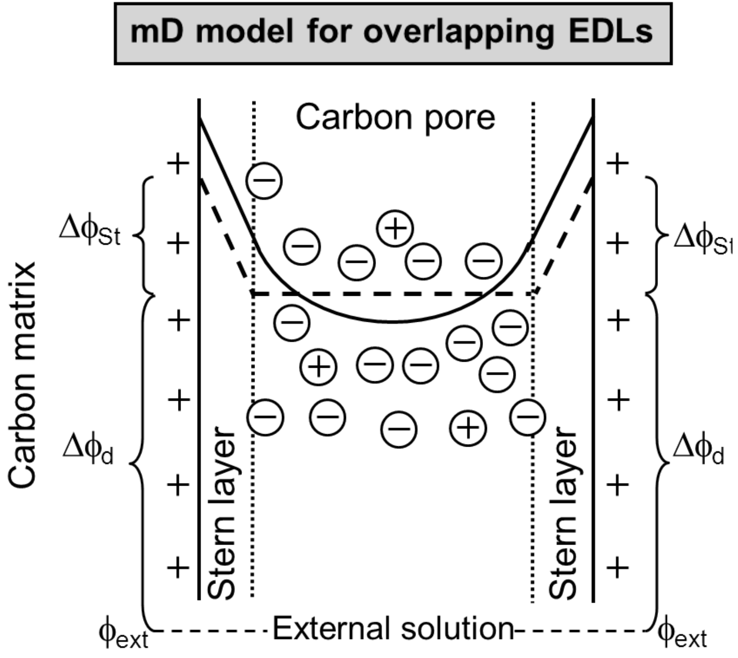
J. Colloid Interface Sci. **384** (2012) 38-44; **446** (2015) 317-326.

Transport in porous carbon electrodes



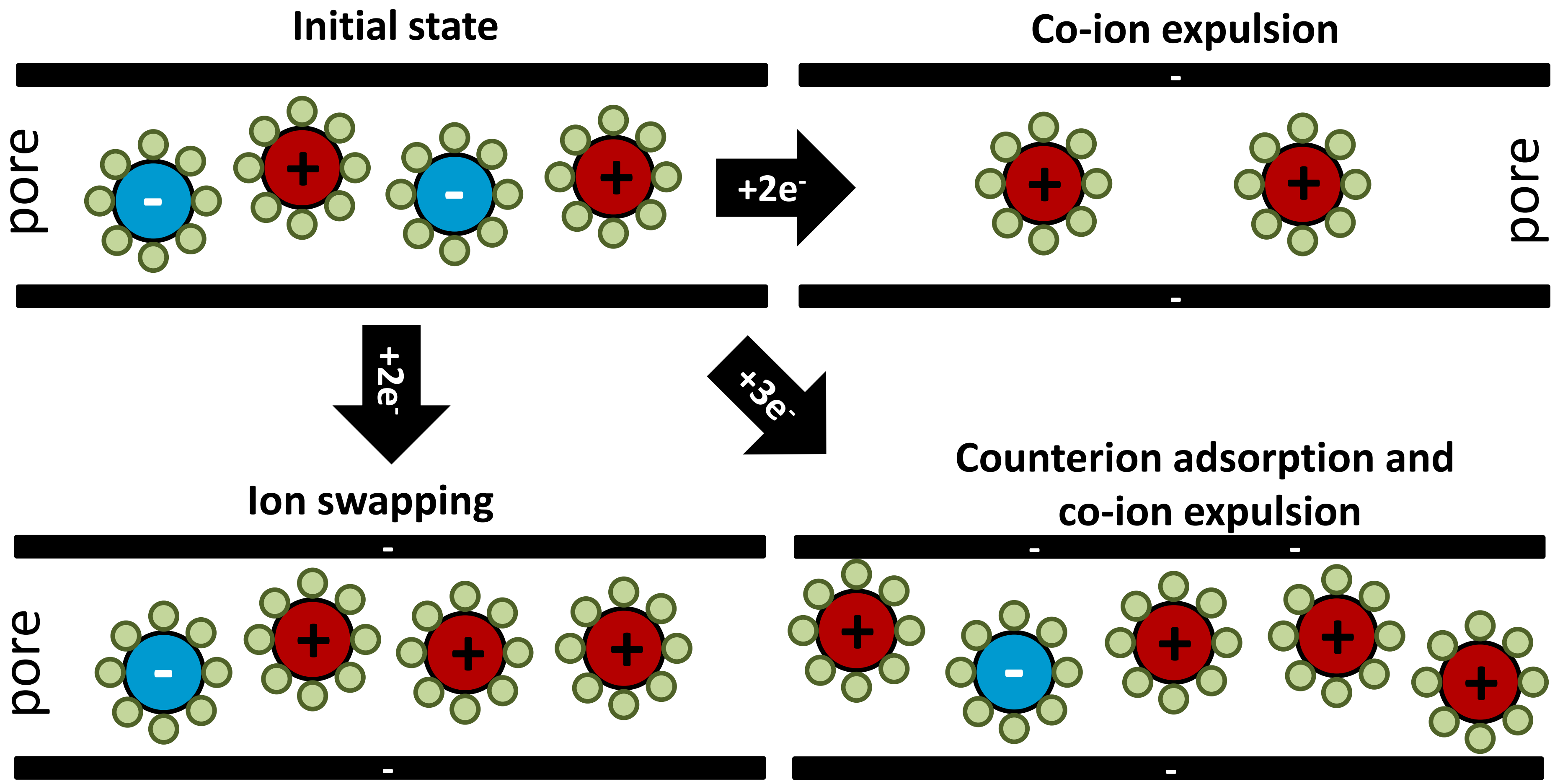
Electrical Double Layer (EDL) models in CDI



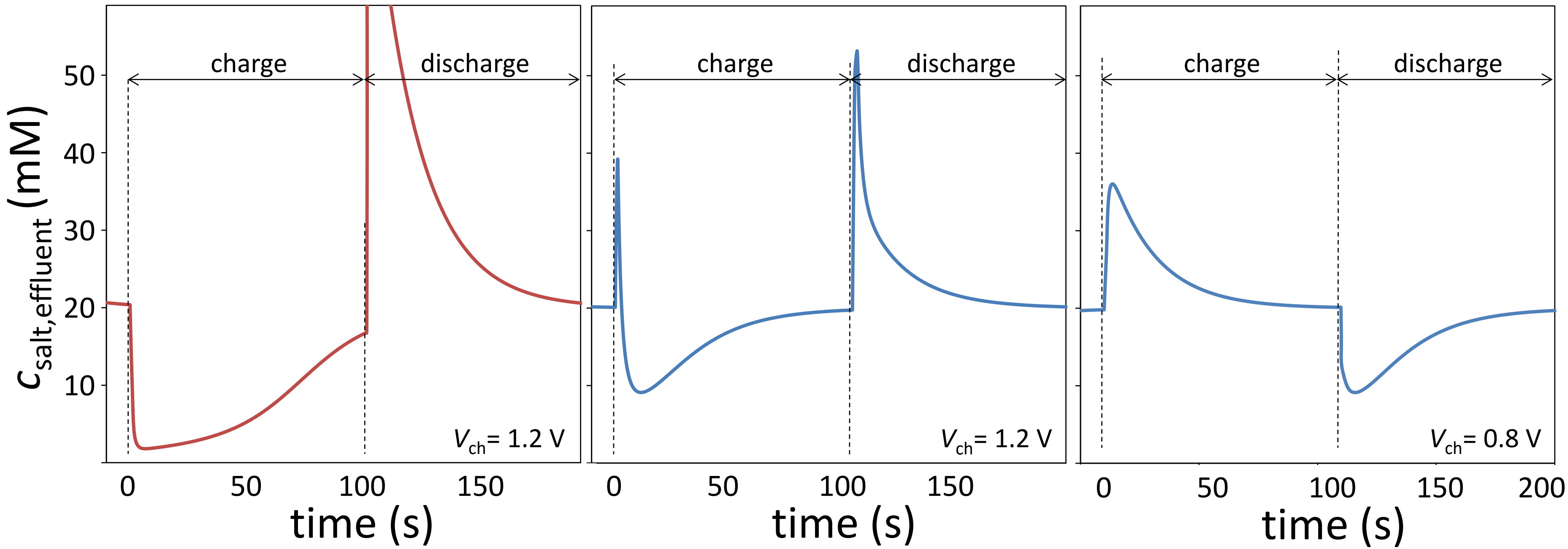


dependent on **pore area**

dependent on **pore volume**


Initial state
Co-ion expulsion
pore
pore
+2e-
+2e-
+3e-
Ion swapping
Counterion adsorption and co-ion expulsion
pore

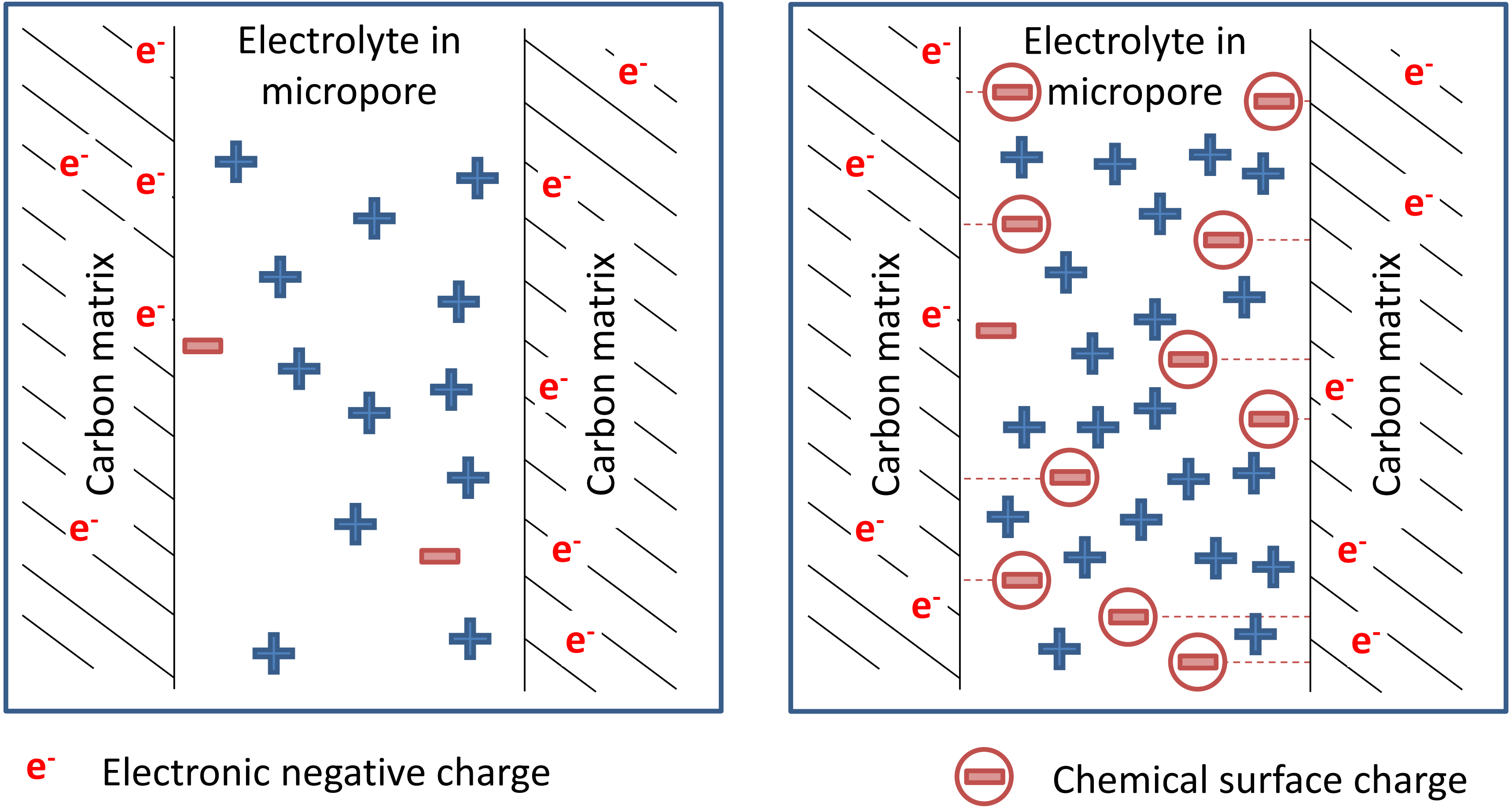
The puzzle of Inverted CDI



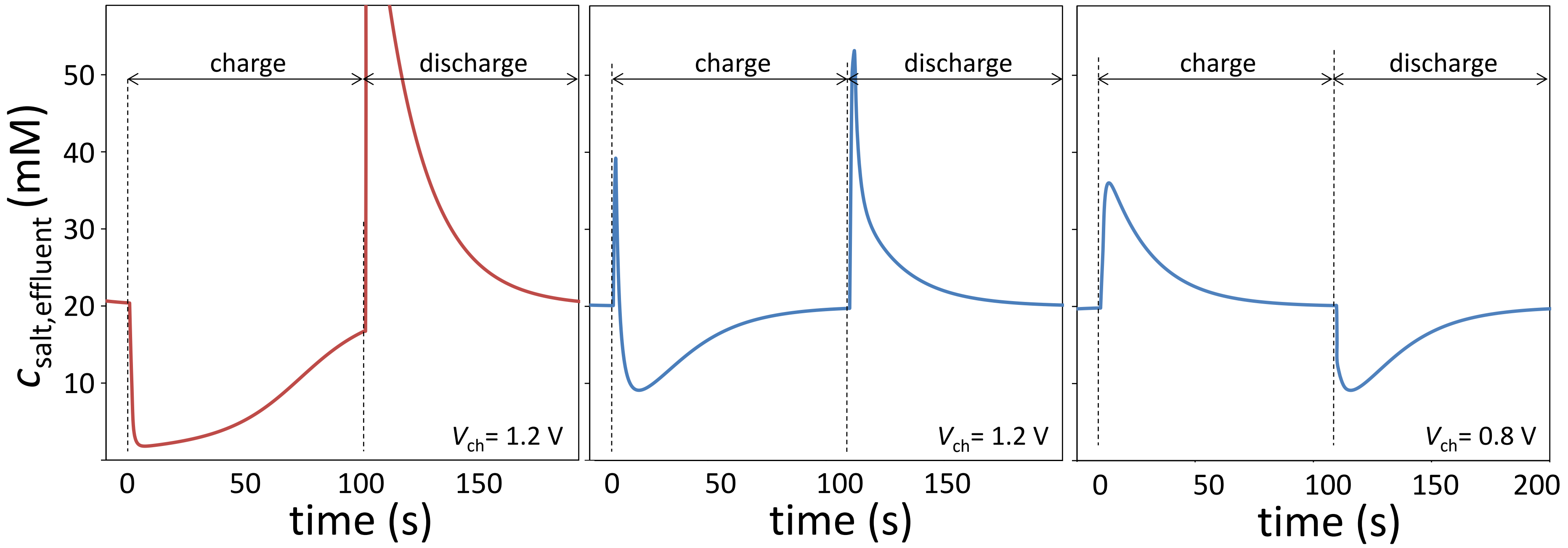
Normal operation

Inversion Peaks

Inverted CDI

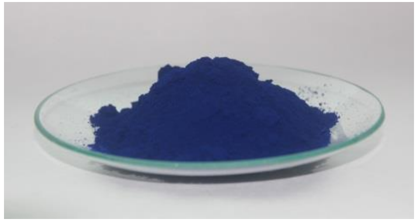

Electrolyte in micropore
Carbon matrix
Carbon matrix
e-
Electronic negative charge
Electrolyte in micropore
Carbon matrix
Carbon matrix
Chemical surface charge

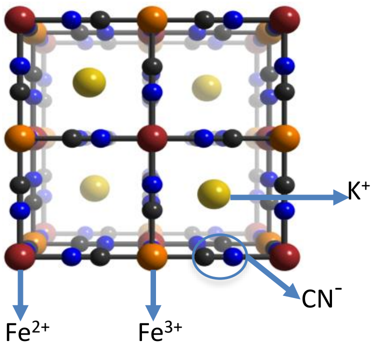
Theoretical predictions with modified EDL model

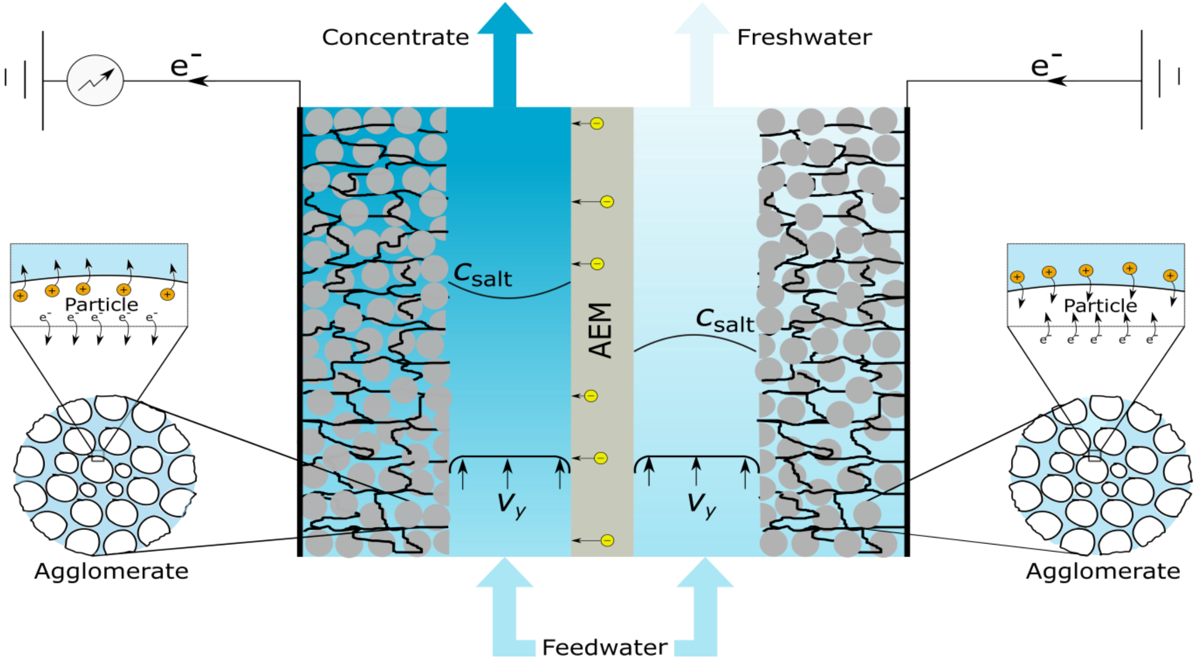


Biesheuvel, Hamelers, Suss, *COLCOM* **9** (2015) 1

CDI with intercalation materials
(Prussian Blue -- nickel hexacyanoferrate)

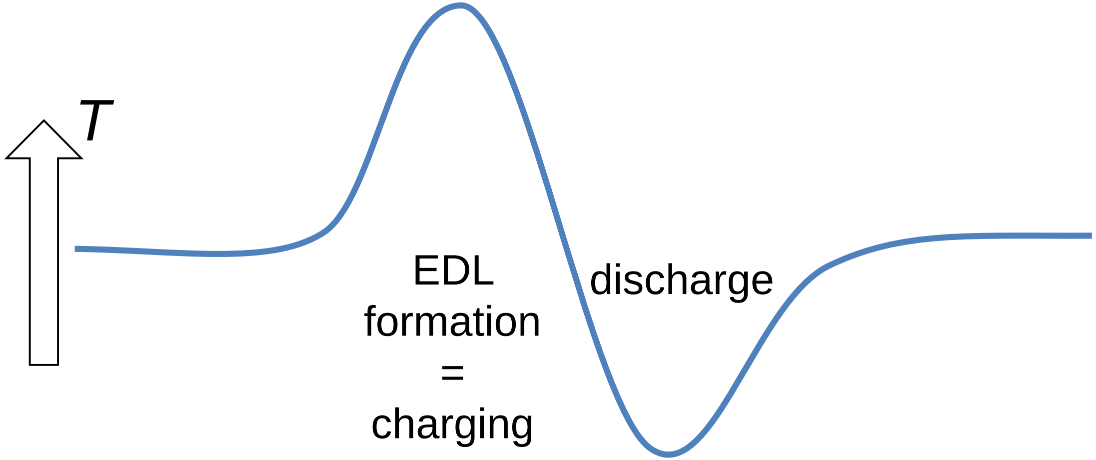






K Singh, PM Biesheuvel, LCPM de Smet, *Phys Rev Applied* (2018).

Heat effects in carbon micropores



M. Janssen, PM Biesheuvel, R. van Roij, B. Erne, *Phys. Rev. Lett.* (2017)

De Groot, 1951

may carry electrical charges. This means that in the external force $\mathbf{F}_k$ we have a term

$$-e_k \operatorname{grad} \varphi, \qquad (179)$$

where e_k is the charge of component k per unit of mass and φ the electrical potential. In literature the cases including electrical phenomena are almost invariably treated by means of the combination $\mu_k + e_k\varphi$ as "chemical potential". In the formalism developed so far and especially in §§ 43, 44 and 45 it is clear, however, that if we insert (179), we do not obtain equations, which contain μ_k and $e_k\varphi$ exclusively in the combination $\mu_k + e_k\varphi$, when we consider the general case of non-uniform temperature. Yet we will prove in this section that the procedure of using this combination can be justified by the thermodynamical theory of irreversible processes. In fact we shall see that by a particular linear transformation of fluxes and forces we can obtain expressions for the flow and production of entropy and therefore also for phenomenological equations which contain μ_k and $e_k\varphi$ only in the combination $\mu_k + e_k\varphi$. All these expressions and equations contain the transformed fluxes and forces, but have otherwise completely the same form as the original expressions and equations. This is also true for the fundamental equations: the force equation, the energy equation and the second law (v. § 43), when we neglect the total charge of the system. In the following we give the derivation of these statements. Thus it is possible to settle the question of the use of $\mu_k + e_k\varphi$, i.e., to indicate the circumstances under which the application of this function can be justified.

We introduce first the partial specific energy of component k, including the electrical energy

$$\tilde{u}_k = u_k + e_k\varphi. \qquad (180)$$

As a consequence of this we can write

$$\tilde{u} = u + \varphi \sum_k e_k c_k = u + e\varphi \qquad (181)$$

for the specific energy, including electric energy. We used the

abbreviations $c_k = \varrho_k/\varrho$ for the concentration and $e = \sum_k e_k c_k$ for the total charge per mass unit. We also have now from (180)

$$\tilde{\mu}_k = \mu_k + e_k\varphi \qquad (182)$$

for the chemical potential, including the electrical energy. We write the external force

$$\mathbf{F}_k = \tilde{\mathbf{F}}_k - e_k \operatorname{grad} \varphi \qquad (183)$$

separating it into a non-electrical part $\tilde{\mathbf{F}}_k$ and an electrical force $- e_k \operatorname{grad} \varphi$.

We introduce at this point the new thermodynamical flux

$$\tilde{\mathbf{J}}_q = \mathbf{J}_q + \sum_k e_k \mathbf{J}_k\varphi = \mathbf{J}_q + \mathbf{I}\varphi, \qquad (184)$$

which is the heat flow including the flow of electrical energy. The total electrical current density is written as

$$\mathbf{I} = \sum_k e_k \mathbf{J}_k. \qquad (185)$$

We continue using the material flows $\mathbf{J}_k$ as thermodynamical fluxes. We might proceed as in the preceding section to find immediately the corresponding thermodynamical forces. It is preferable to repeat the derivation of §§ 43 and 44 in order to show the physical consequences of the introduction of quantities which include electrical terms. We get from the force equation (12) and the relation (183)

$$\varrho d\mathbf{v}/dt = -\operatorname{grad} P + \sum_k \tilde{\mathbf{F}}_k \varrho_k - \varrho e \operatorname{grad} \varphi, \qquad (186)$$

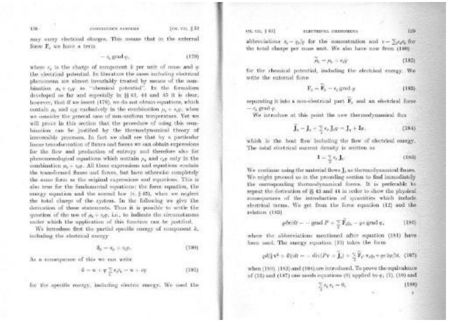
where the abbreviations mentioned after equation (181) have been used. The energy equation (13) takes the form

$$\varrho d(\tfrac{1}{2}\mathbf{v}^2 + \tilde{u})/dt = -\operatorname{div}(P\mathbf{v} + \tilde{\mathbf{J}}_q) + \sum_k \tilde{\mathbf{F}}_k \cdot \mathbf{v}_k \varrho_k + \varrho e\, \partial\varphi/\partial t, \qquad (187)$$

when (180), (183) and (184) are introduced. To prove the equivalence of (13) and (187) one needs equations (6) applied to φ, (7), (10) and

$$\sum_k e_k \nu_k = 0, \qquad (188)$$

De Groot, 1951



128 CONTINUOUS SYSTEMS [CH. VII, § 51]

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CH. VII, § 51] ELECTRICAL PHENOMENA 129

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$$\rho\, d\mathbf{v}/dt = -\operatorname{grad} P + \sum_k \tilde{\mathbf{F}}_k \rho_k - \rho e \operatorname{grad} \varphi, \quad (186)$$

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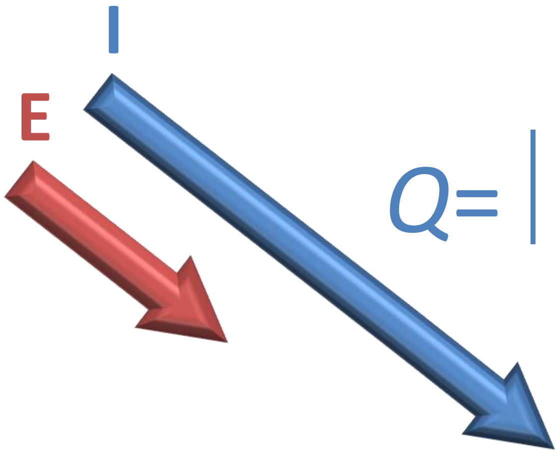
$$\sum_k e_k \sigma_k = 0, \quad (188)$$

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{v} \cdot \nabla T \right) = \lambda \nabla^2 T + \mathbf{I} \cdot \mathbf{E} - \mathbf{v} \cdot \nabla P^h$$

Joule Heating

Dot-product of the VECTORS **I** and **E**: $Q = \mathbf{I} \cdot \mathbf{E}$

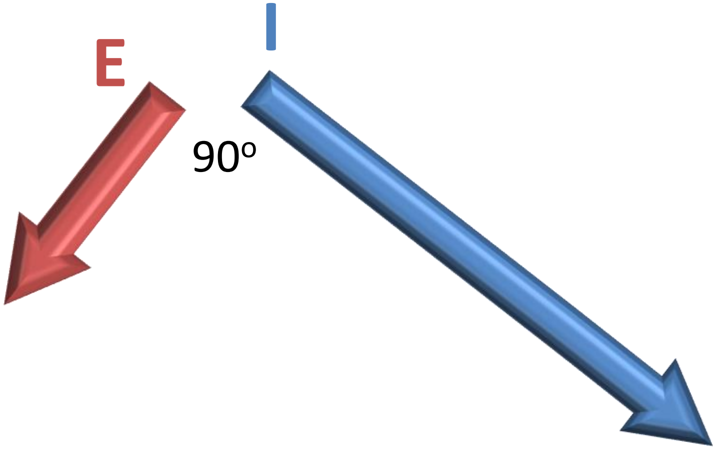


$$Q = |\mathbf{I}| \cdot |\mathbf{E}|$$

$$Q = I^2 \cdot R$$

Joule Heating

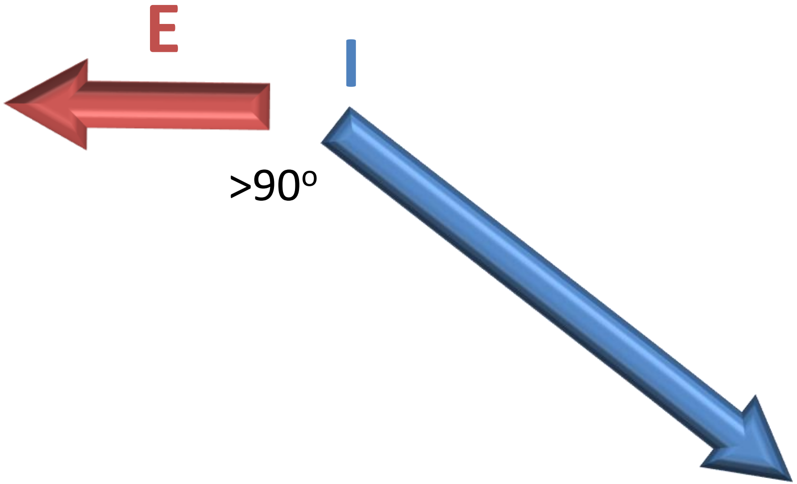
Dot-product of the VECTORS **I** and **E**: $Q = \mathbf{I} \cdot \mathbf{E}$



Q=0 !

Joule Heating

Dot-product of the VECTORS **I** and **E**: $Q=\mathbf{I}\cdot\mathbf{E}$



$Q < 0$!

Joule Cooling, or Negative Joule Heating

Conclusions

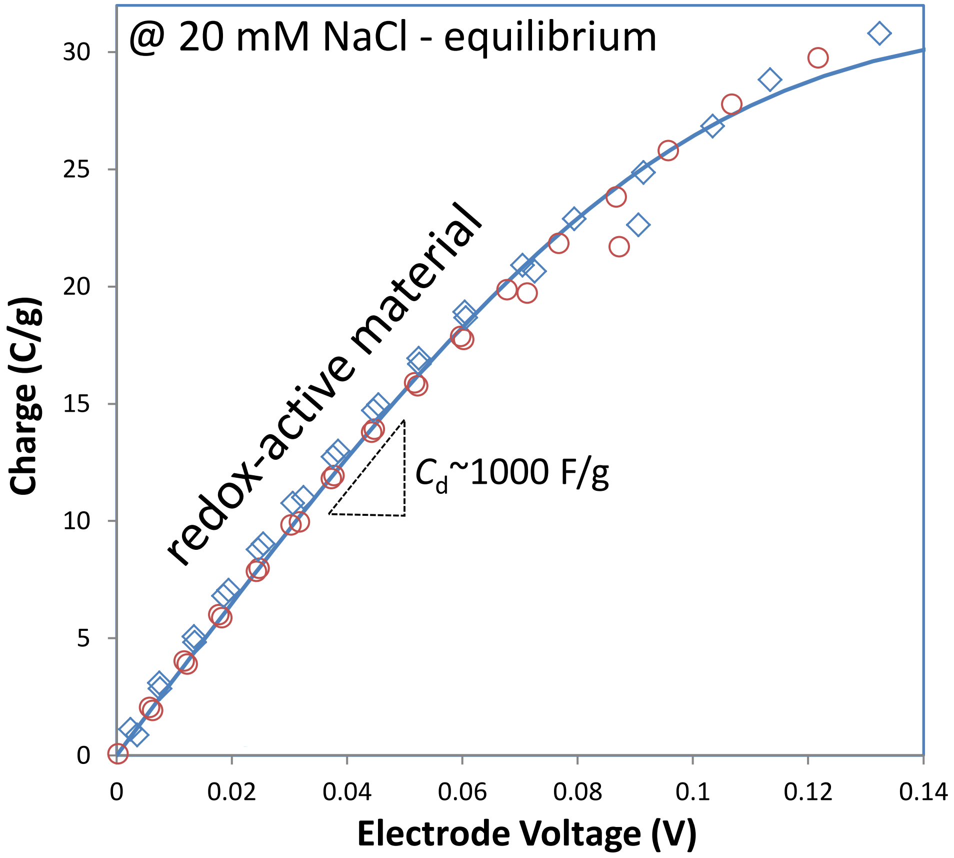
- Porous capacitive electrodes have applications for energy harvesting, energy storage and water desalination
- It uses ideally polarizable electrodes, and is thus a non-Faradaic process
- Correct EDL models for carbon consider three types of charge
- Heat effects correctly captured by considering dot-product of **I** and **E**.

Thank you for your attention !

CDI, what type of process?

Colloid Science	Electrochemistry	Exp.?
Polarizable electrode	Non-Faradaic process	V-Charge curve
Non-polarizable electrode	Faradaic process	V-Current curve

Different chemistries, but all CDI



Materials:

- Activated carbons
- Intercalation materials = redox-active material

- Charge-voltage curve applies
- Polarizable electrode
- Non-Faradaic process

Capacitive Deionization

What is CDI ?

- A **process** where water is desalinated using electrodes
- **Operation** is by cyclically adsorbing ions in the electrodes, and release
- Driven by transfer of electronic charge (back and forth)
- Different architectures and chemistries are possible

Faradaic vs non-Faradaic ?

- Because in time the electrode changes composition and potential, it is a non-Faradaic process, whatever the chemistry on the electrode