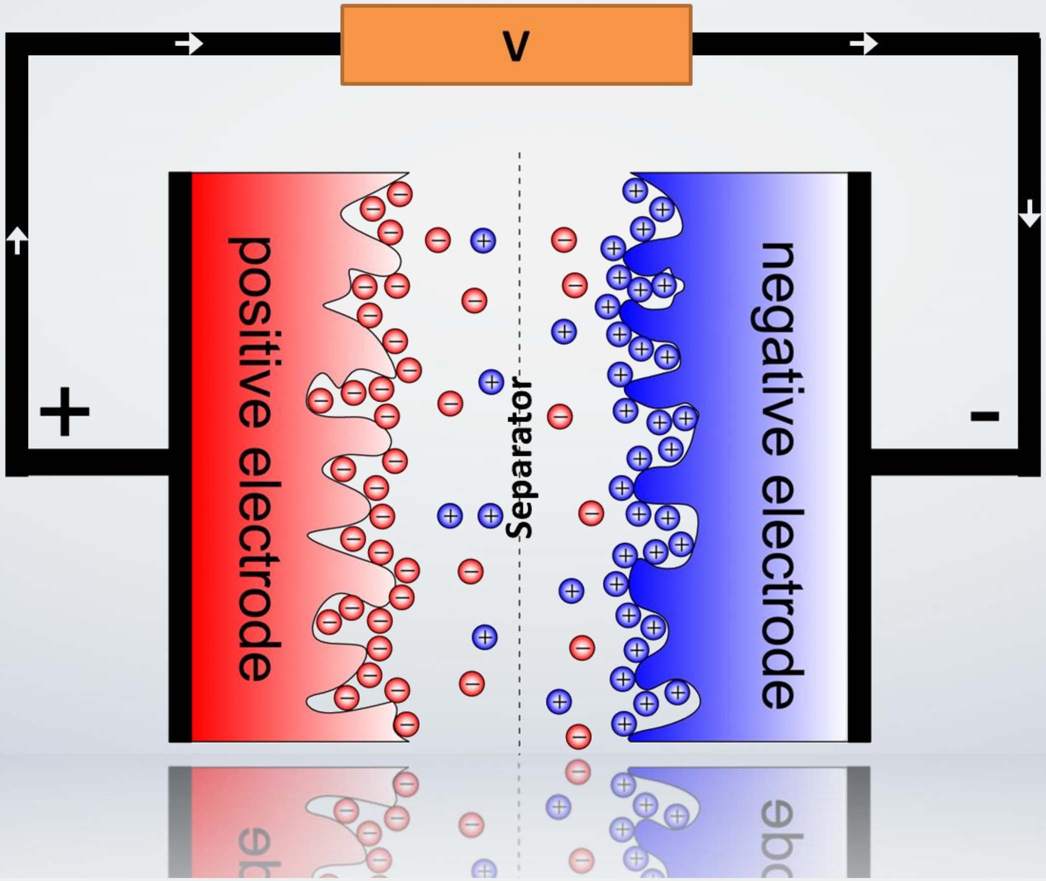


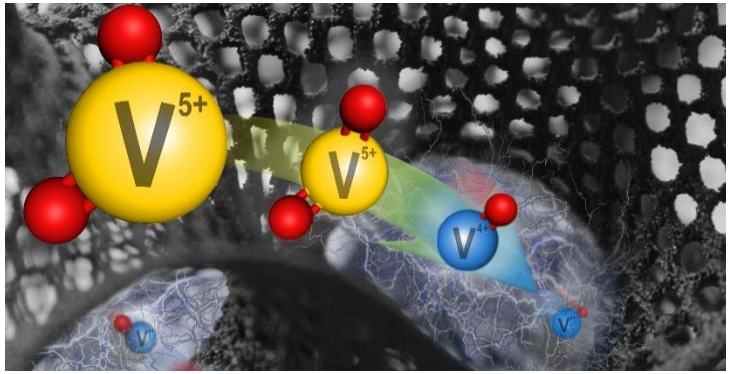
NanoBioMaterials:
ELECTRICAL DOUBLE LAYER CAPACITORS (EDLCs)

Prof. Dr. Volker Presser

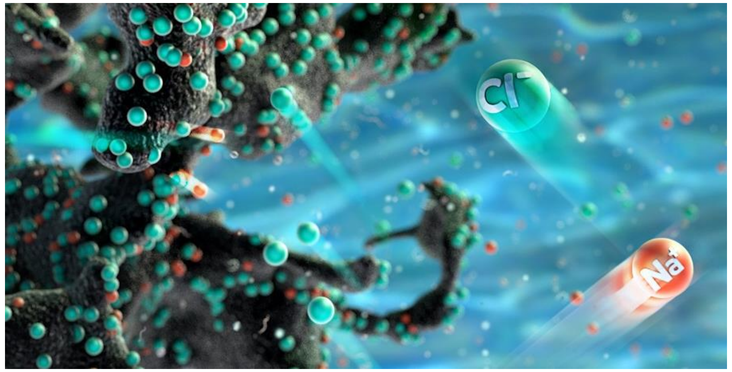
CHAIR OF ENERGY MATERIALS

RESEARCH PORTFOLIO

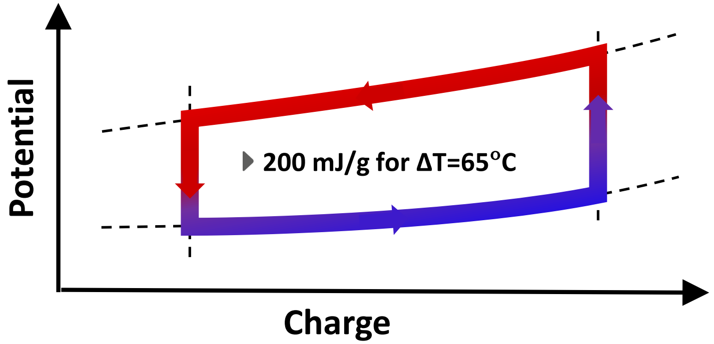
Electrochemical energy storage



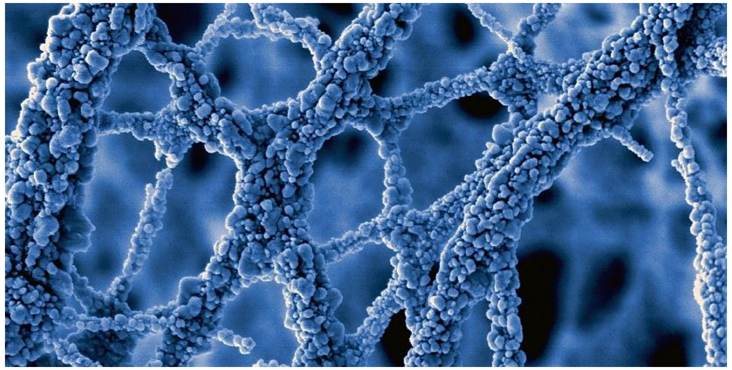
Electrochemical water treatment



Electrochemical energy harvesting

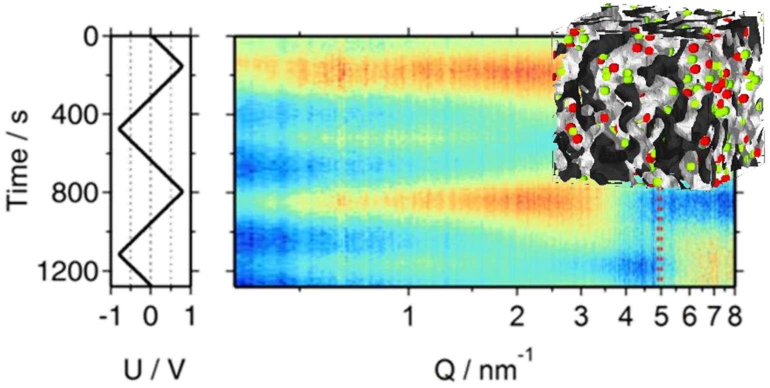


Nanomaterials design



Electrochemical benchmarking

in situ techniques & modelling

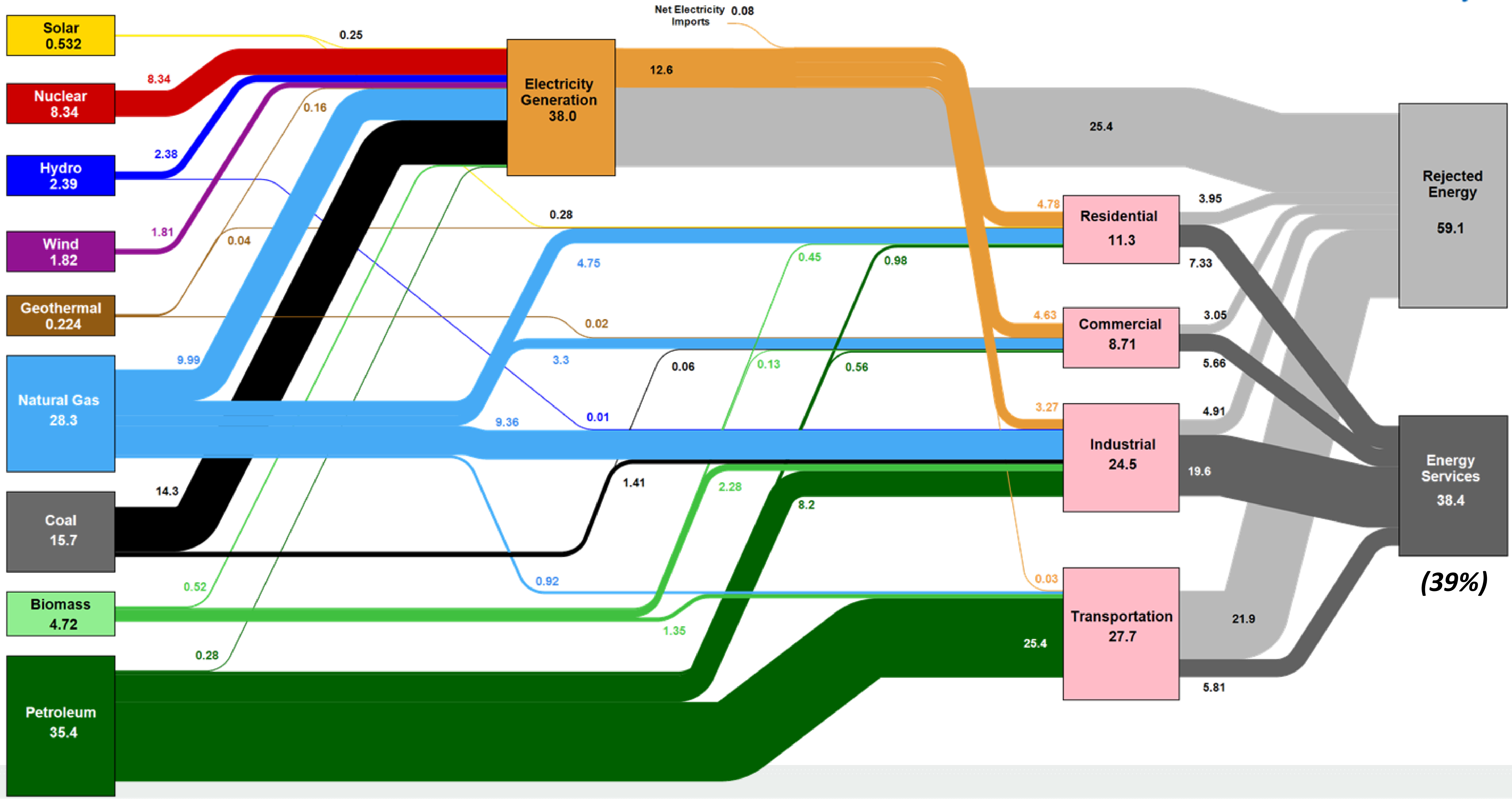


Introduction


INTRODUCTION
10 kcal
179 kcal
(39%)
450 kcal

INTRODUCTION

Estimated U.S. Energy Consumption in 2015: 97.5 Quads

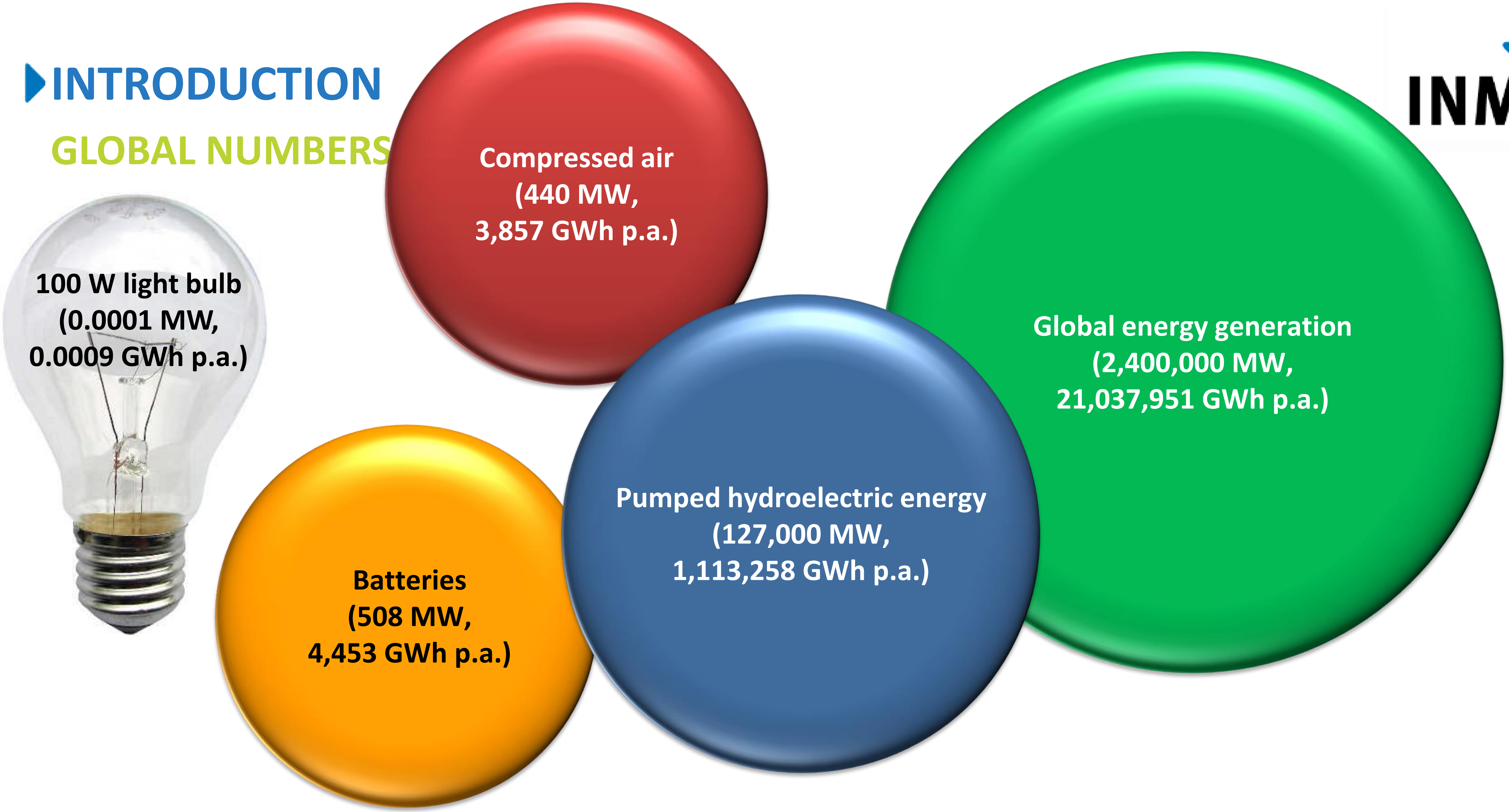


INTRODUCTION

ENERGY STORAGE

INTRODUCTION

GLOBAL NUMBERS



INTRODUCTION

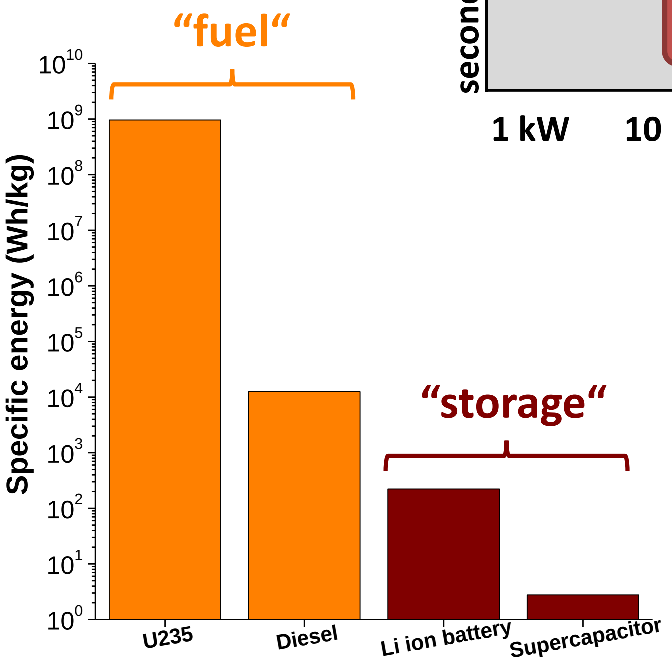
ENERGY STORAGE – A PROBLEM ON ALL SCALES

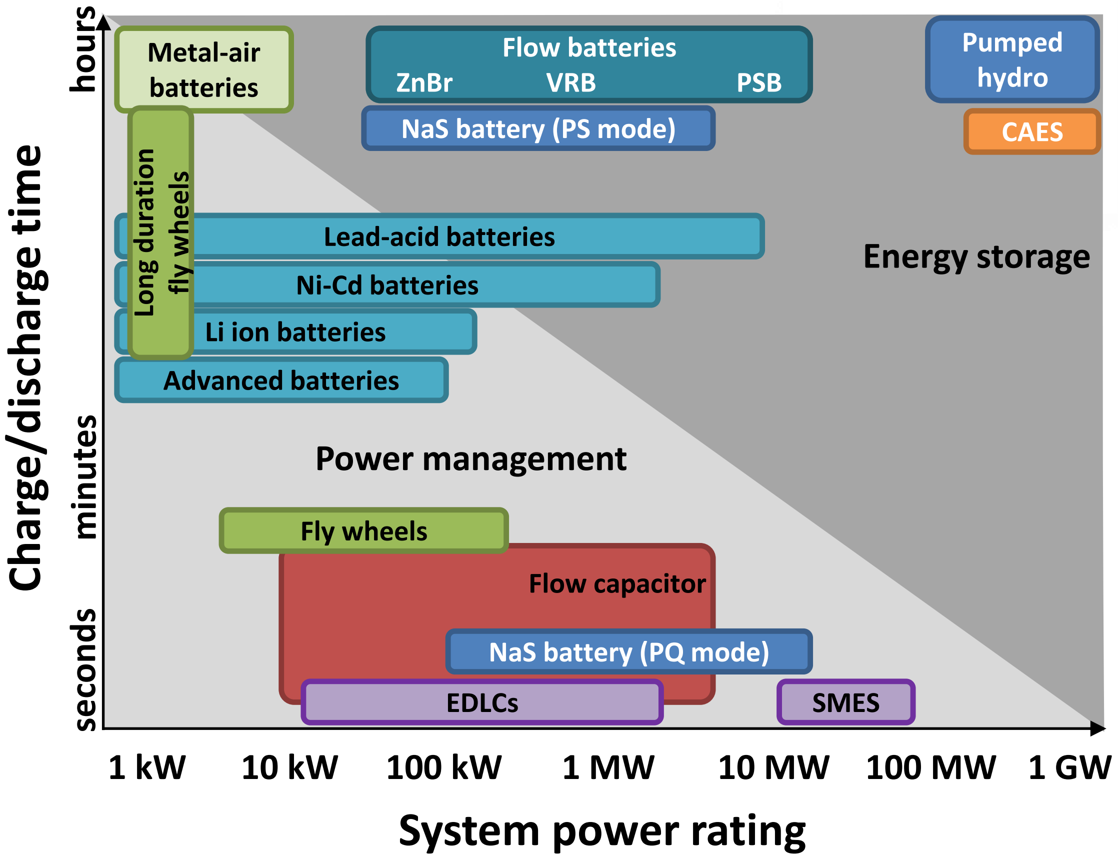
INTRODUCTION

ENERGY STORAGE PORTFOLIO

70 kJ of energy

- = 2 t car travelling at 30 km/h
- = 1 mL of diesel fuel (1 g)
- = 1 tea spoon of sugar (4 g)
- = 1 D-cell battery (140 g)
- = 22 kF supercapacitor (4.6 kg)





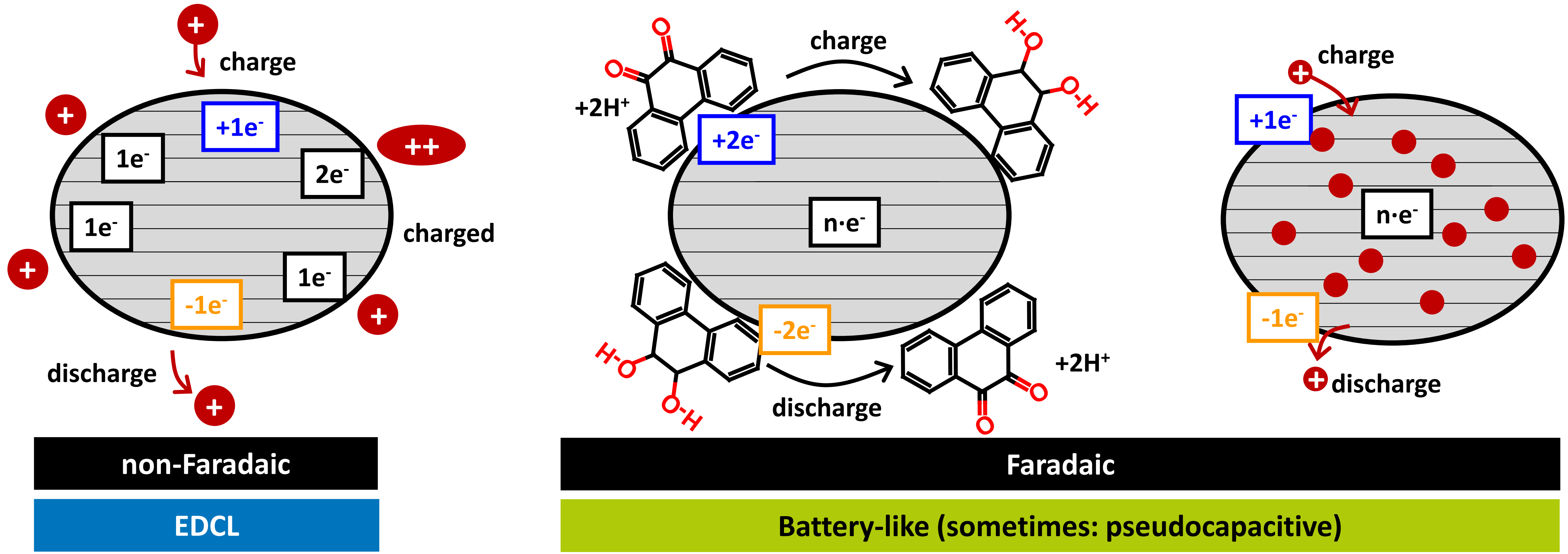
INTRODUCTION

COMPETITION OF TECHNOLOGIES

INTRODUCTION

INTERFACIAL ELECTROCHEMISTRY

- Double-layer capacitance
- Surface redox capacity
- Intercalation capacity

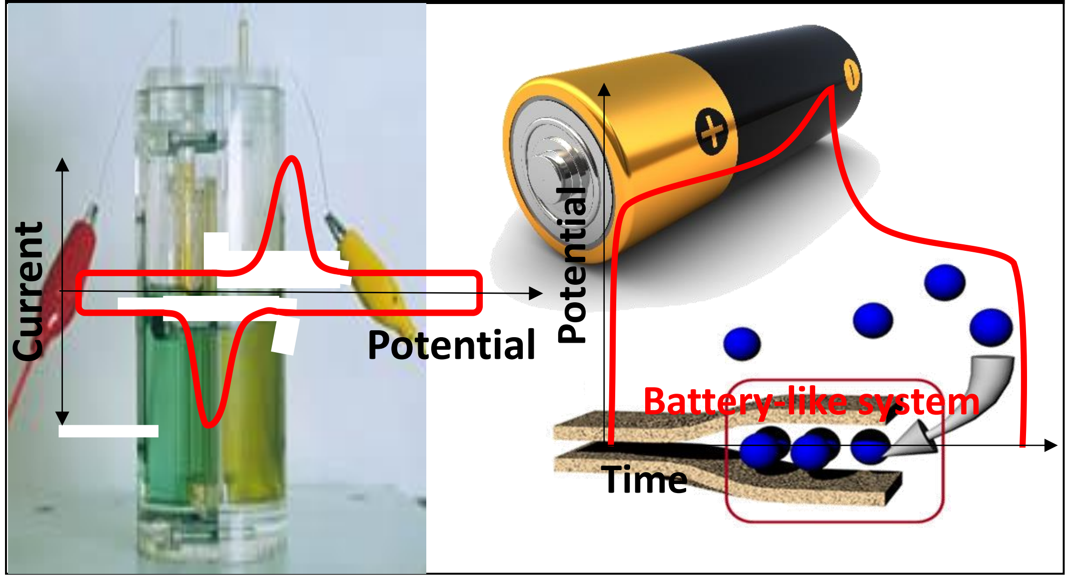


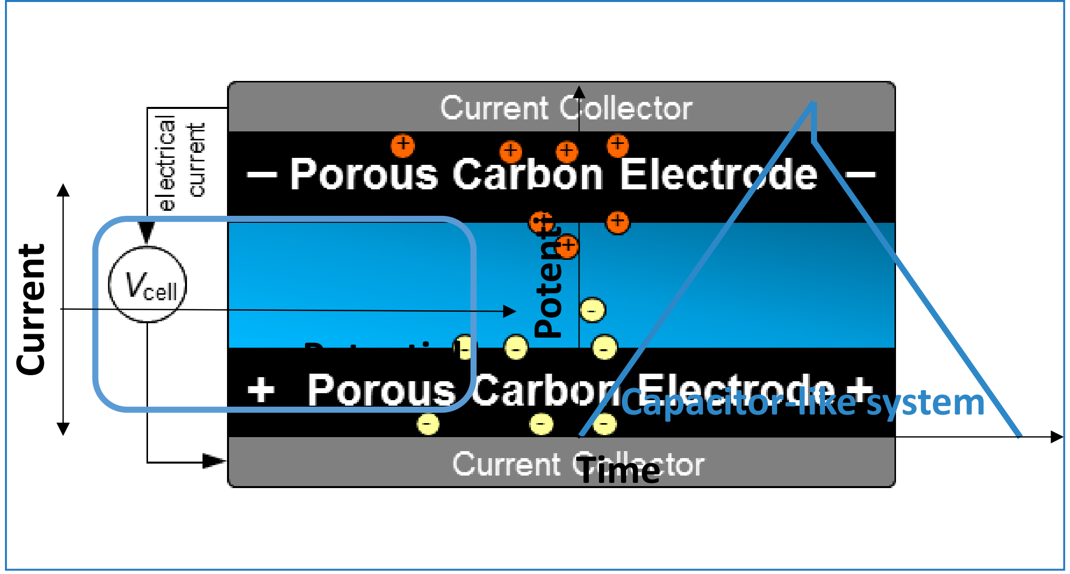
 Praxis der Naturwissenschaften. Chemie in der Schule. 63(7) (2014) 16-21.

INTRODUCTION

BATTERIES VERSUS SUPERCAPACITORS

Batteries	Supercapacitors



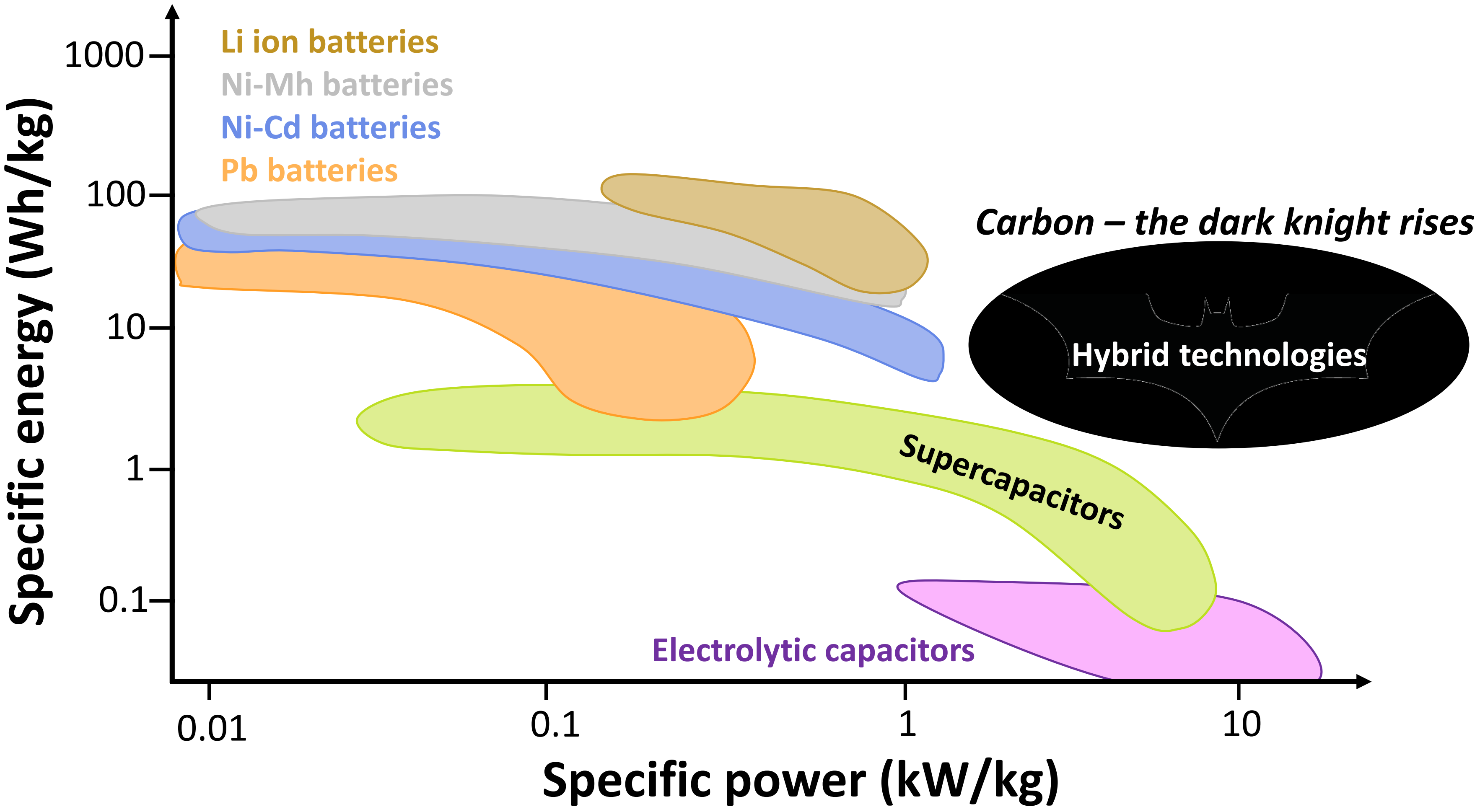


- Chemical reactions / ion insertion
- High energy density (100 Wh/kg)
- Low power density (1 kW/kg)
- Limited cycle lifetime (below 10,000)

- Electrosorption of ions and / or pseudocapacitance
- Low energy density (5 Wh/kg)
- High power density (10 kW/kg)
- Long lifetime (above 100,000)

INTRODUCTION

WHY ARE SUPERCAPACITORS "SUPER" OR "ULTRA"?

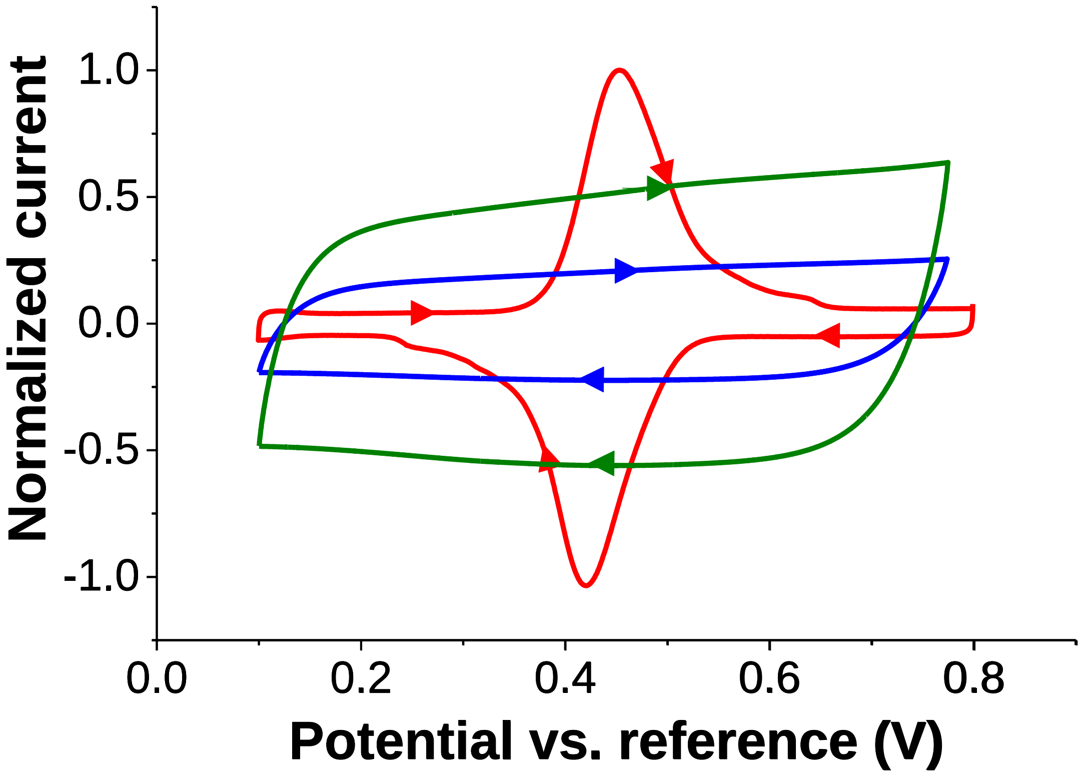


David V. Ragone
Pronunciation: ru-GO-nee

INTRODUCTION

THE CURRENT USE OF "PSEUDO" IN THE SUPERCAPACITOR COMMUNITY

- A capacitor is a system with linear and monotonic correlation between charge and voltage (i.e., the concept of Farad [F] is valid)
- A redox system is characterized by a large amount of charge transfer at a certain redox potential (i.e., the concept of Coulomb [mAh] is preferred)
- A system that behaves like a capacitor but actually accomplished faradaic charge transfer is called pseudocapacitor



Pseudocapacitor: the ultimate capacitor look alike

Brousse T, Bélanger D, Long JW. To be or not to be pseudocapacitive? Journal of the Electrochemical Society. 2015;162(5):A5185-A9.

INTRODUCTION

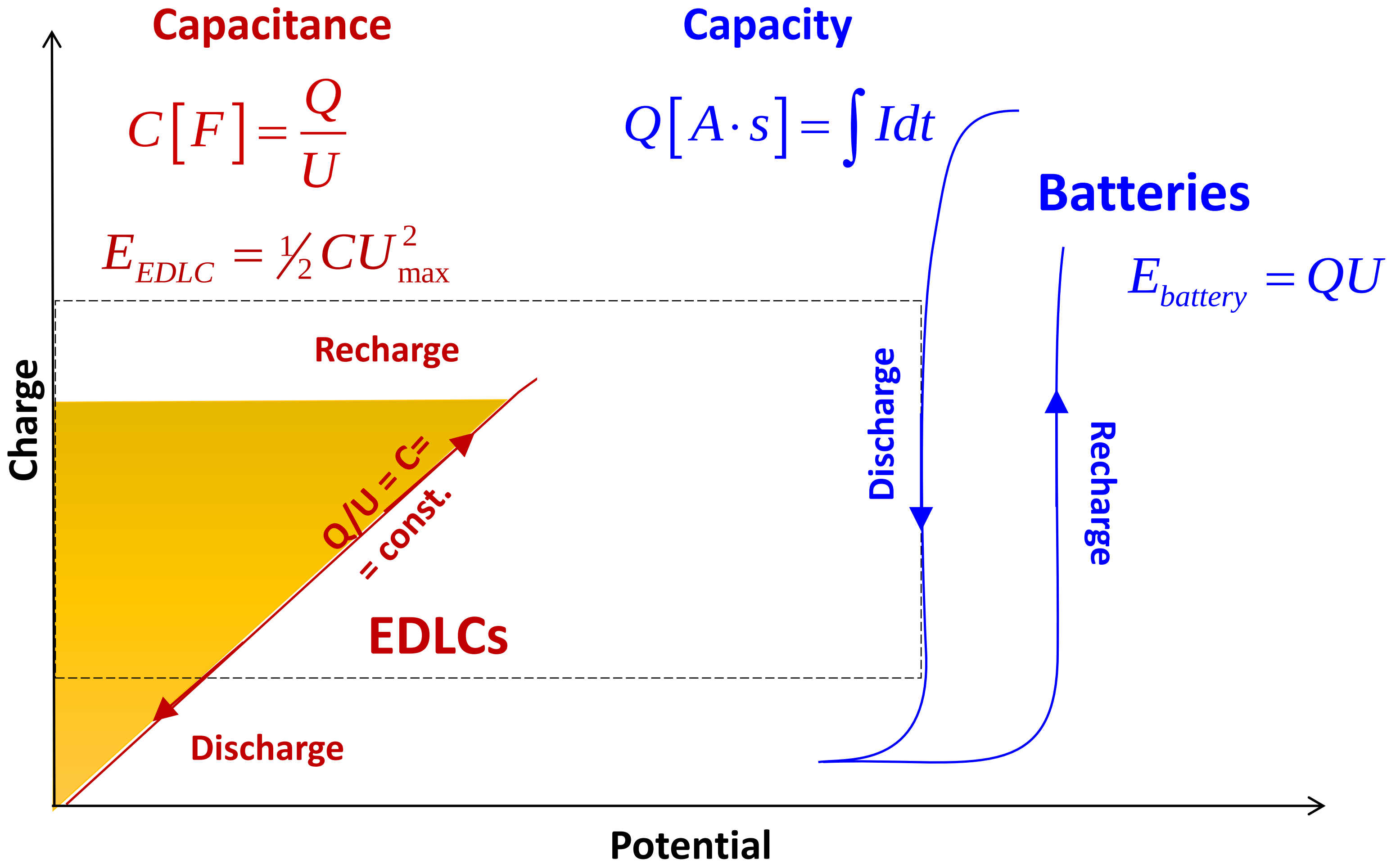
TAKE HOME MESSAGES

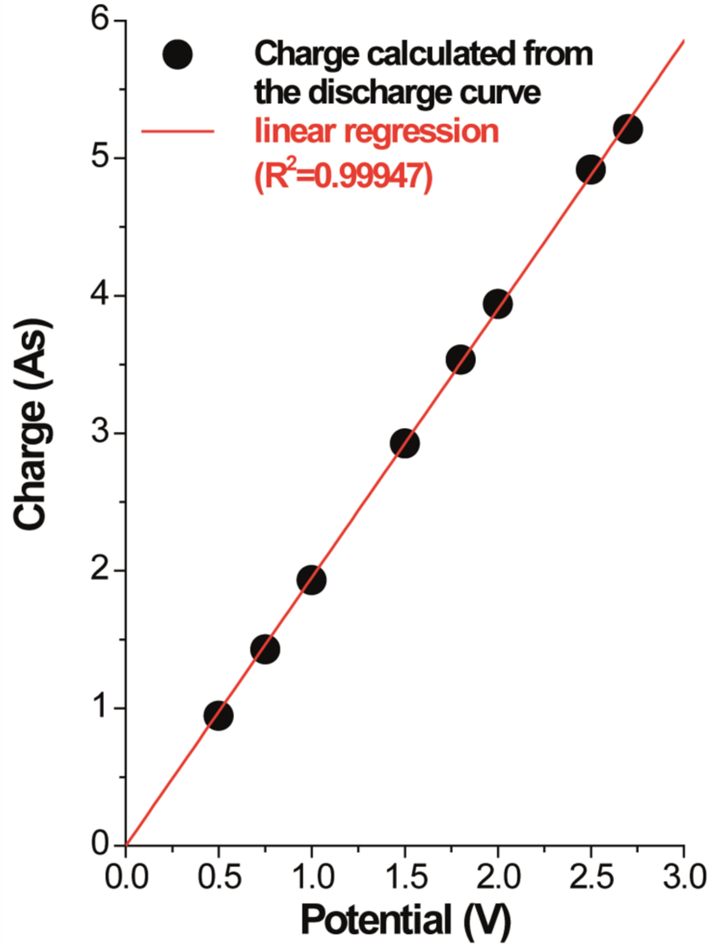
- **Batteries show redox peaks, supercapacitors do not**
- **Batteries are ideal for high energy storage density, but low power density**
- **Supercapacitors are ideal for high power density, but low energy storage density**

The electrical double layer

ELECTRICAL DOUBLE LAYER

CAPACITANCE VERSUS CAPACITY

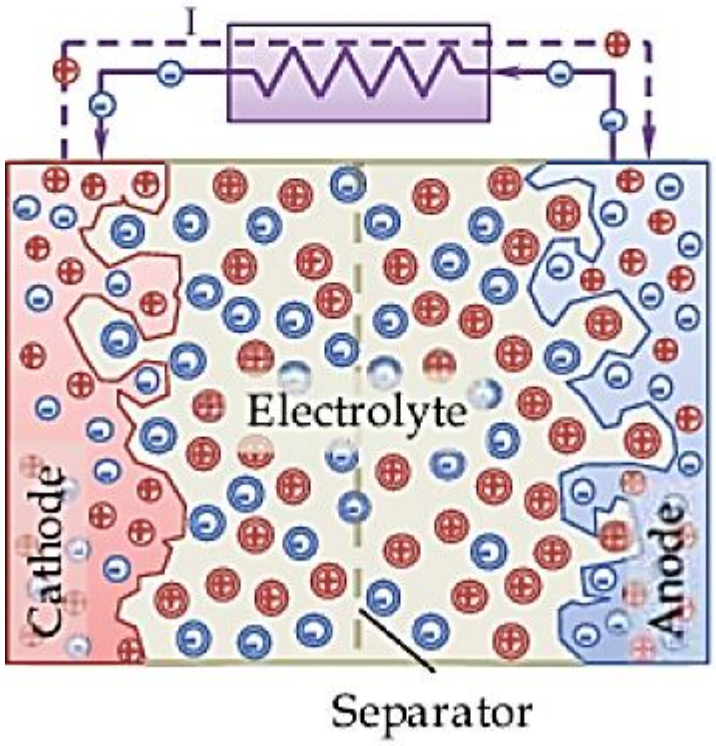




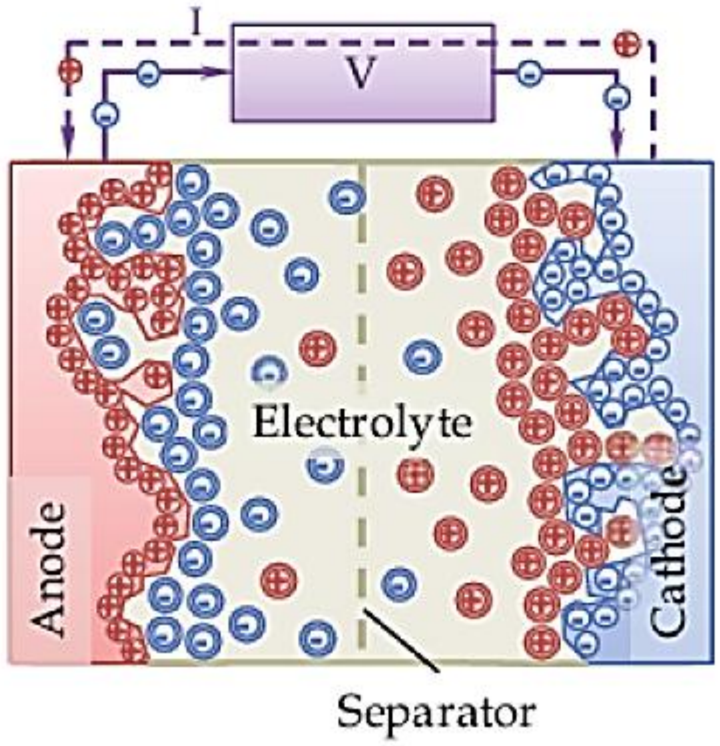
Presser, V., et al., The Electrochemical Flow Capacitor: A New Concept for Rapid Energy Storage and Recovery. Advanced Energy Materials, 2012. 2(7): p. 895 - 902.

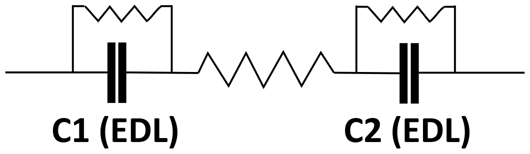
ELECTRICAL DOUBLE LAYER

CHARGE STORAGE MECHANISM



charging



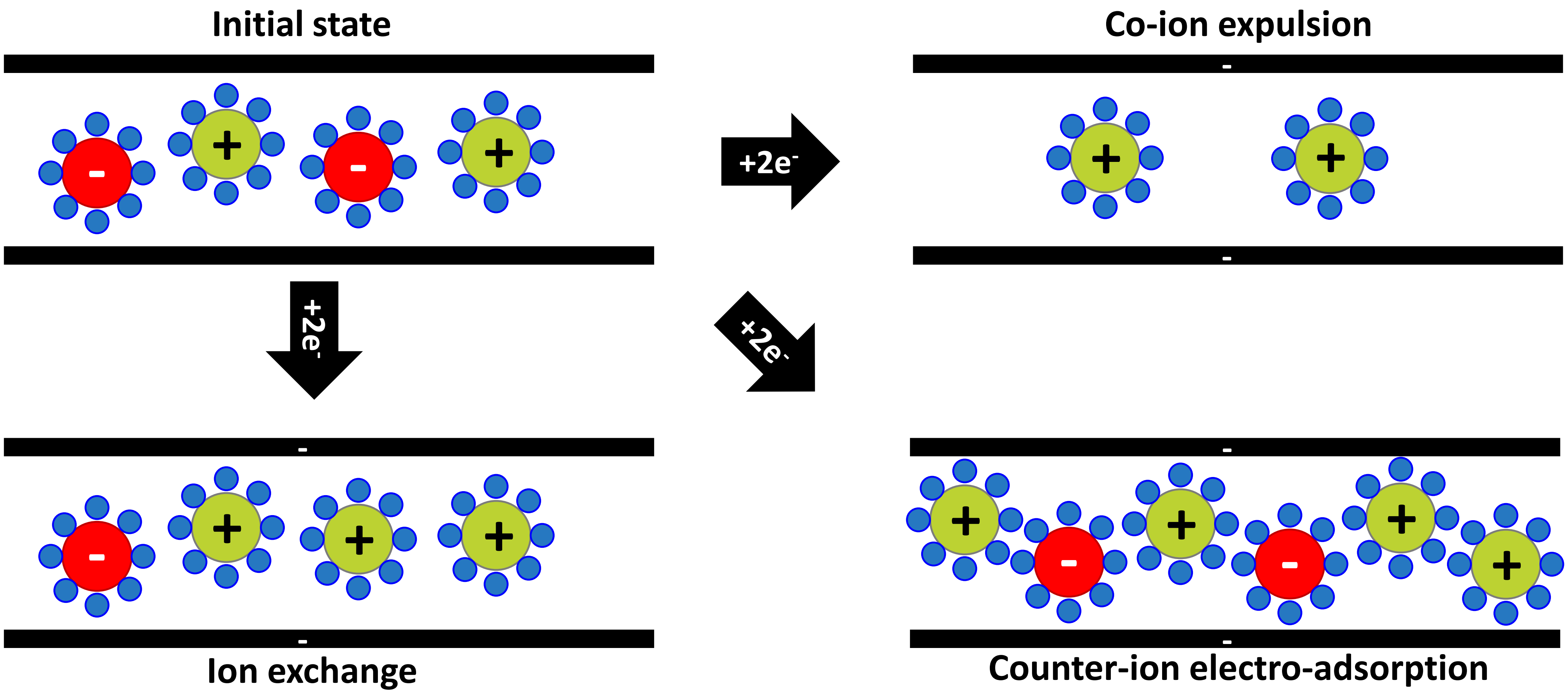


$$P = \frac{U^2}{4 \cdot R} \qquad E = \frac{1}{2} \cdot C \cdot U^2$$

Scherson, D. A.; Palencsár, A., The Electrochemical Society Interface 2006, Spring, 17 - 22.

ELECTRICAL DOUBLE LAYER

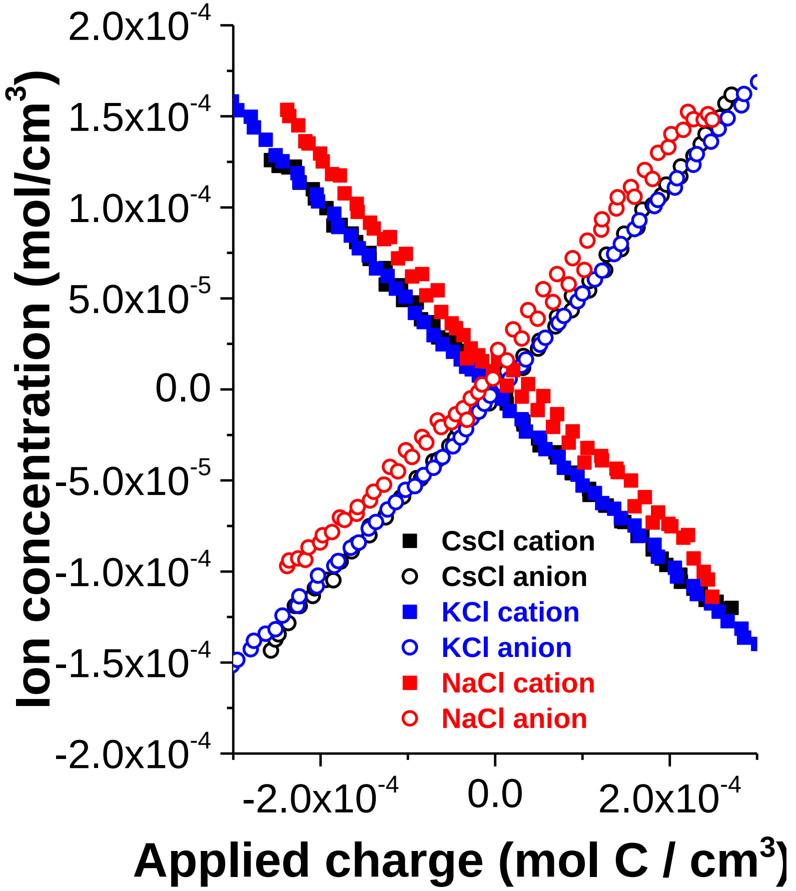
CHARGE STORAGE MECHANISM

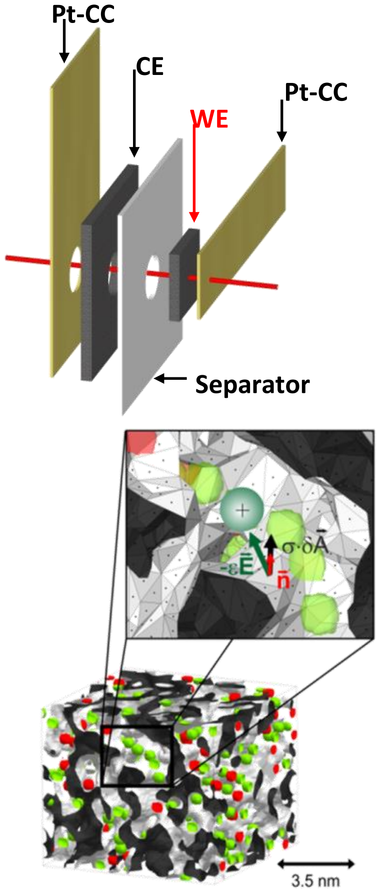


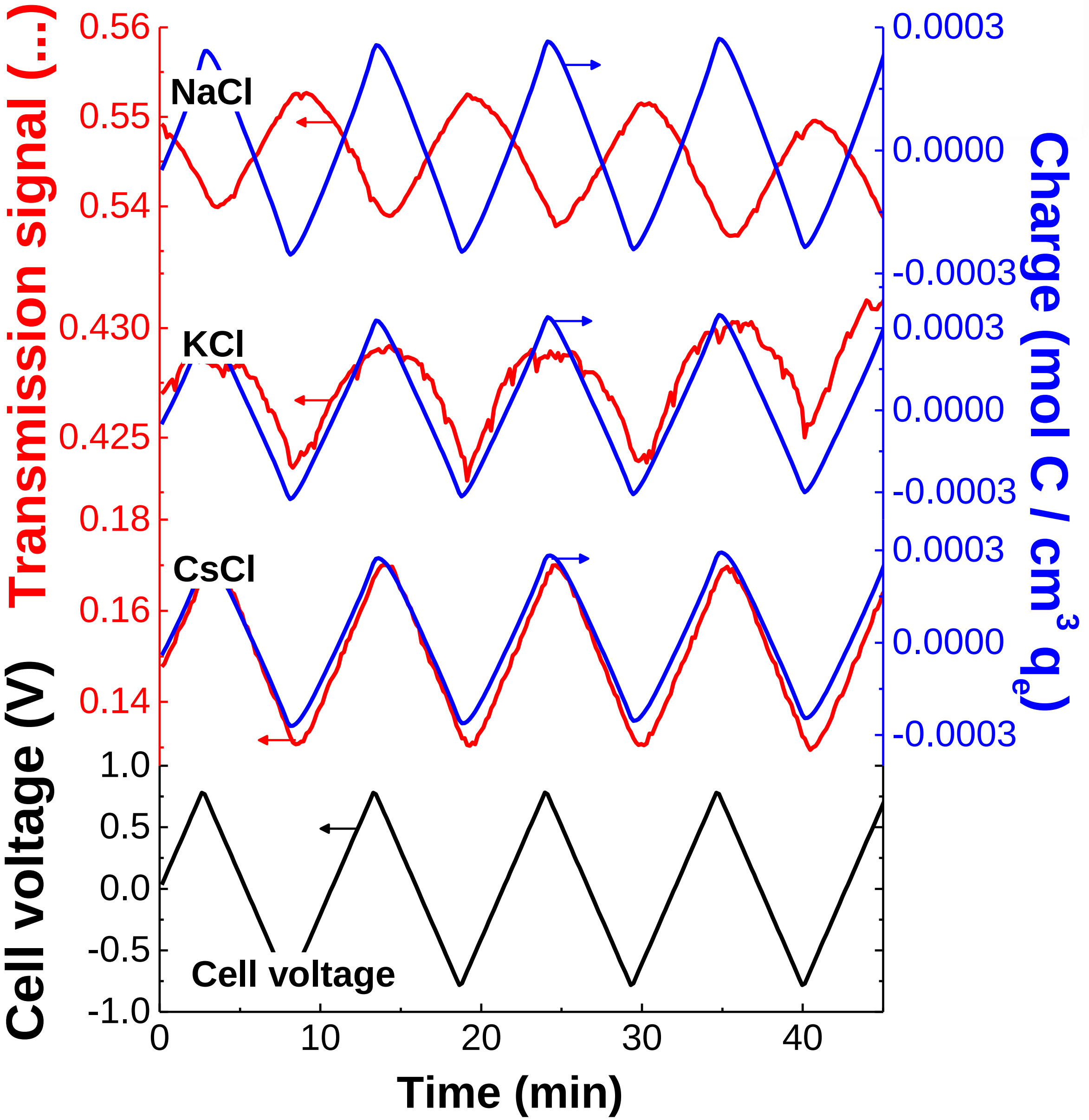
IN SITU RESEARCH PORTFOLIO

IN SITU SMALL ANGLE X-RAY SCATTERING

- **Quantification of ion electrosorption in carbon nanopores**







Energy & Environmental Science, 2015, 8, 1725-1735 / Nature Energy, 2017 (in press).

ELECTRICAL DOUBLE LAYER

HELMHOLTZ MODEL (1853-1879)

- **Helmholtz first coined the phrase "double layer" (1853): two layers of charge at the interface between two dissimilar metals and later expanded this to metal/aqueous solution interface (1879)**
- **Fluid-Solid-Interface: sharp layer of electrons at the surface of the electrode, and a monolayer of ions in the electrolyte**

$$\frac{Q}{U}\left[\frac{As}{V}\right]=C\left[F\right]=\frac{A\cdot\varepsilon_0\cdot\varepsilon_r}{d}$$

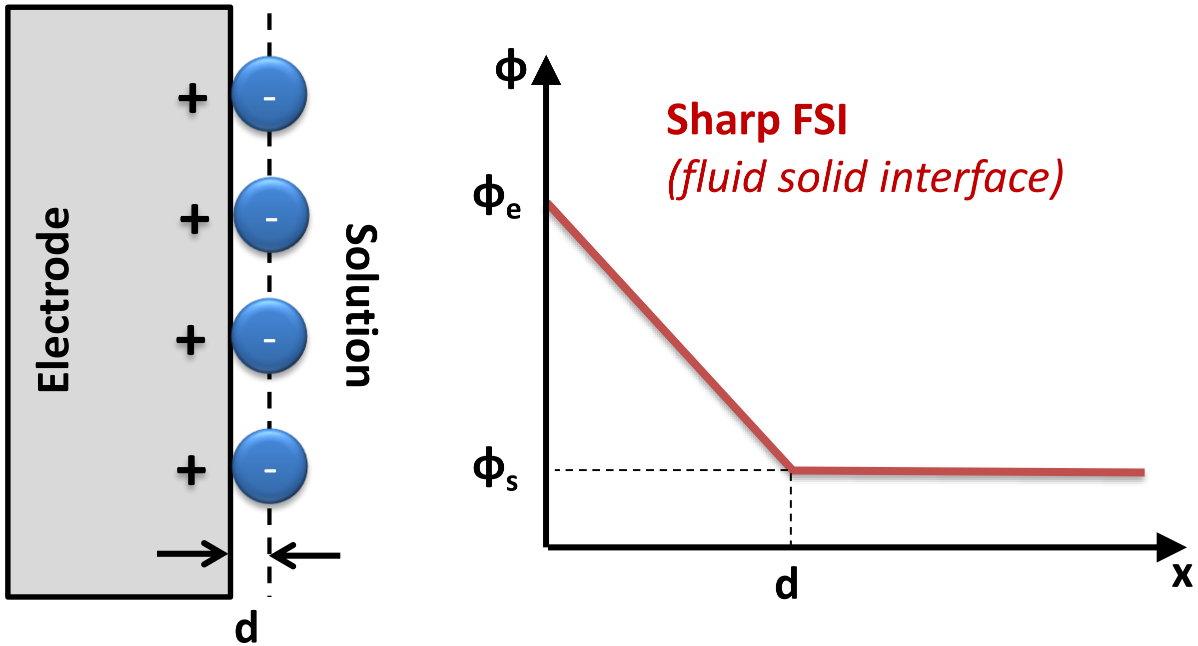
d : distance of closest approach of the charges = ionic radius

ϵ_r : relative permittivity

ϵ_0 : permittivity of vacuum

ϕ_e: potential at the electrode

ϕ_s: potential in the solution (ad infinitum)

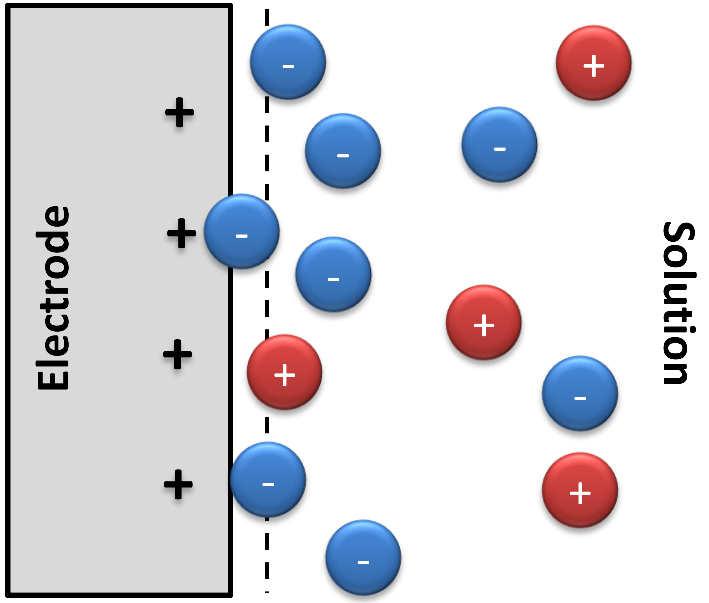


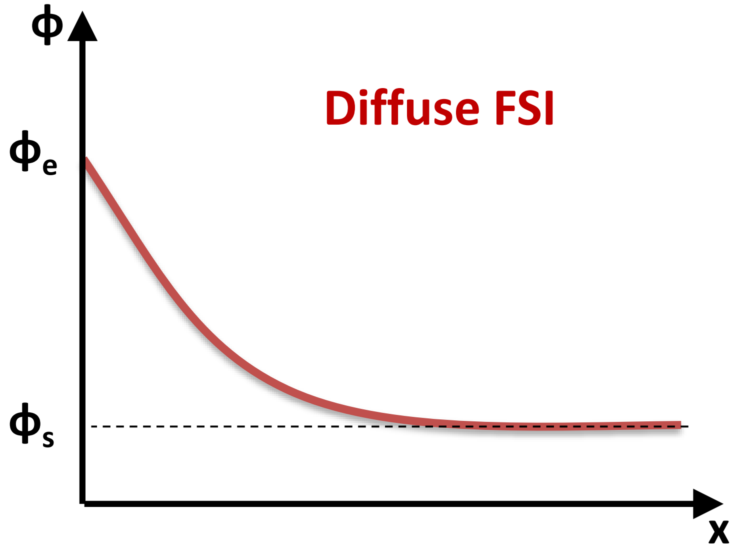
H. L. F. von Helmholtz, *Ann. Physik*, 1853, **89**, 211; 1879, **7**, 337

ELECTRICAL DOUBLE LAYER

GOUY-CHAPMAN MODEL (1910-1913)

- Capacitance depends on the applied potential AND the ionic concentration
- Thermal motion as driving force for diffuse space charge
- Poisson equation: relating potential to charge density
- Boltzmann equation: distribution of ions
- Ions: point charges with no volume



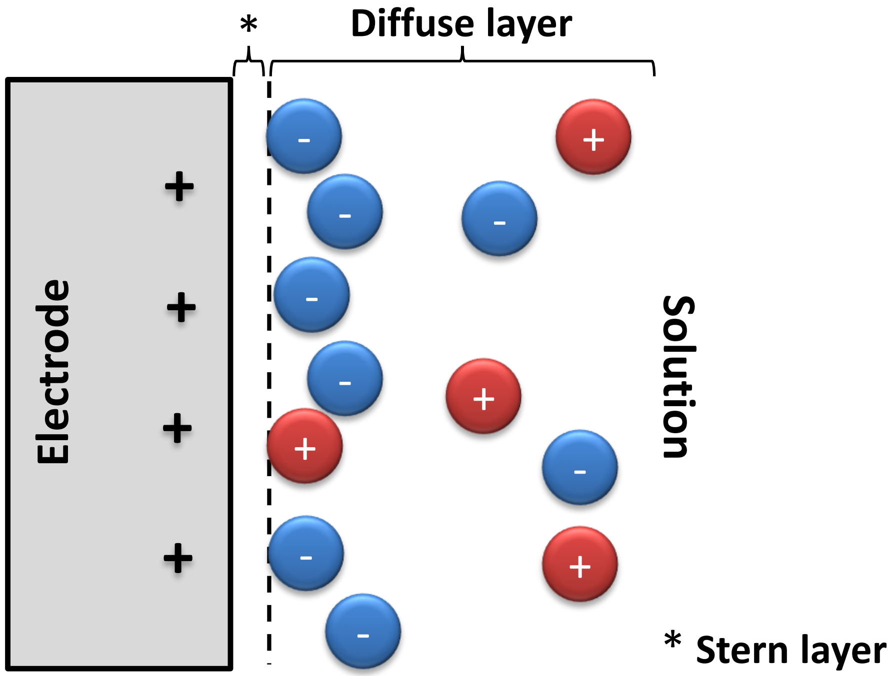


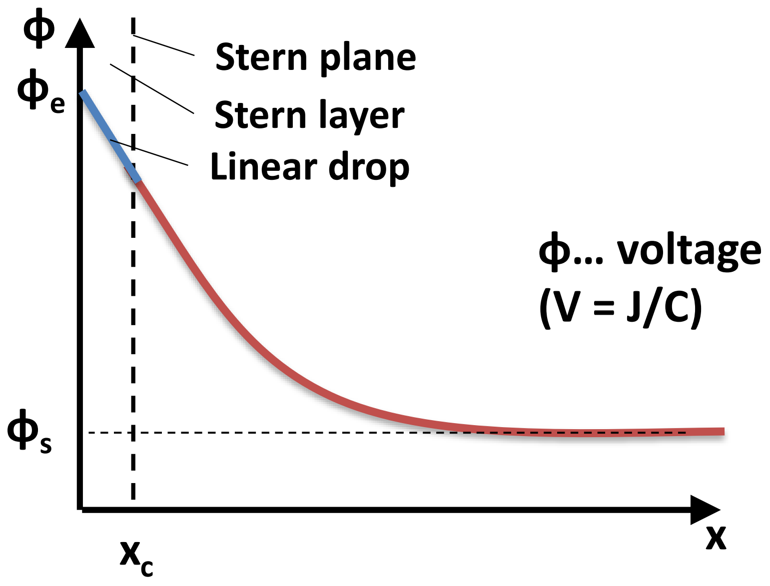
G. Gouy, Compt. Rend., 1910, 149, 654 & D. L. Chapman, Phil. Mag., 1913, 25, 475

ELECTRICAL DOUBLE LAYER

GOUY-CHAPMAN-STERN MODEL (1924)

- Combination: condensed layer = Stern layer and diffuse layer = GC model
- Ions: point charges with no volume in the Diffuse layer
- Point of closest approach (radius of the ion) up to the Stern plane
- No ions or other charge (with their center) exactly in the Stern plane, neither in the Stern layer

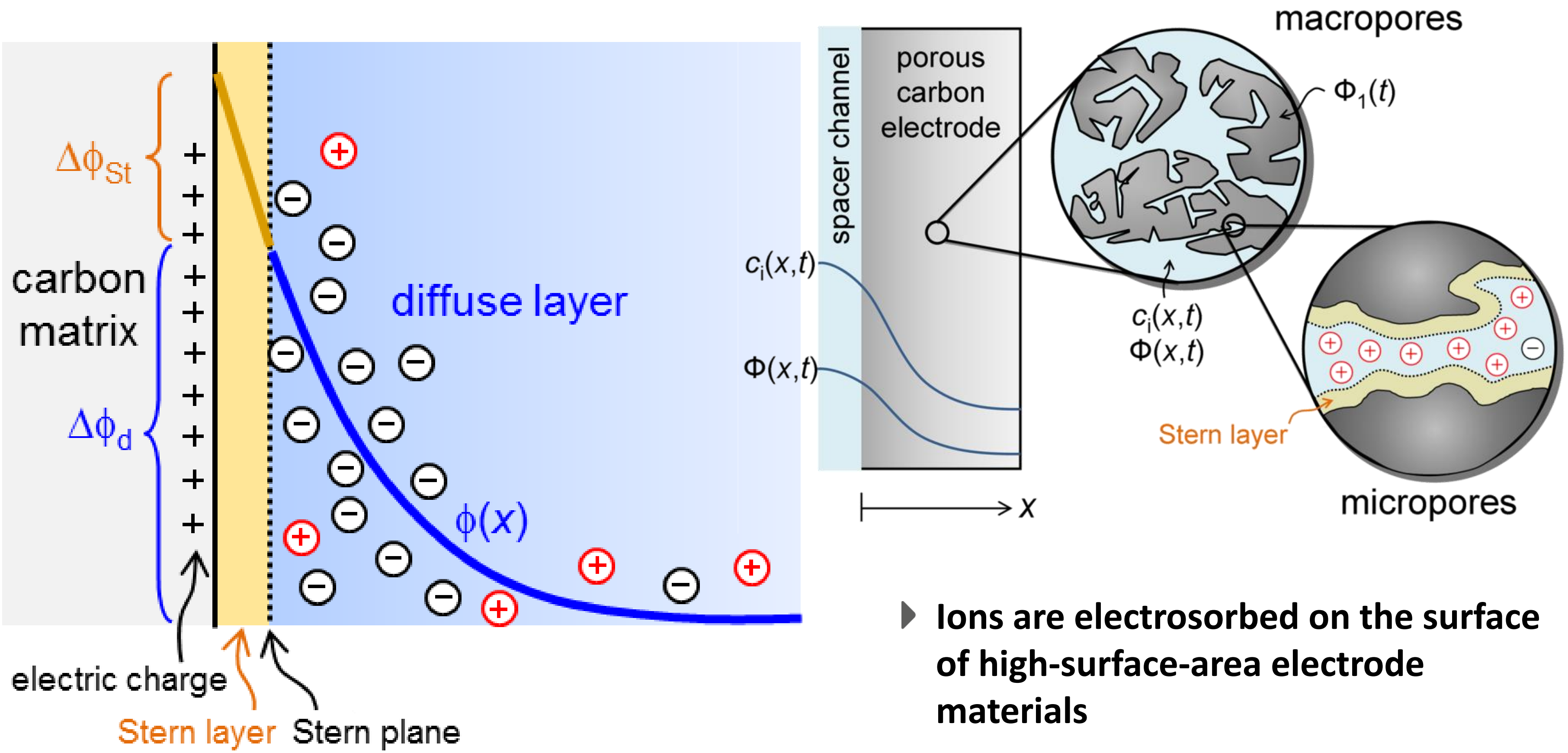




G. Gouy, Compt. Rend., 1910, 149, 654 & D. L. Chapman, Phil. Mag., 1913, 25, 475

ELECTRICAL DOUBLE LAYER

GOUY-CHAPMAN-STERN MODEL (1924)



- **Ions are electrosorbed on the surface of high-surface-area electrode materials**
- **Ion desolvation in micropores**

 G. Gouy, Compt. Rend., 1910, 149, 654 & D. L. Chapman, Phil. Mag., 1913, 25, 475

ELECTRICAL DOUBLE LAYER

GOUY-CHAPMAN-STERN MODEL (1924)

$$\boxed{\sigma\left[\frac{Coulomb}{m^2}\right]} = \boxed{C_{stern}\left[\frac{F}{m^2}\right]} \cdot \Delta\phi_{stern}\,[V]$$

$$\boxed{C_{stern} = \frac{\varepsilon_r \cdot \varepsilon_0}{x_C}}$$

$$\boxed{\sigma = \sqrt{8 \cdot \varepsilon_r \cdot \varepsilon_0 \cdot R \cdot T \cdot c_{\mathrm{inf}}} \cdot \sinh\left(\frac{F \cdot \Delta\phi_{\text{diffuse layer}}}{R \cdot T \cdot 2}\right)}$$

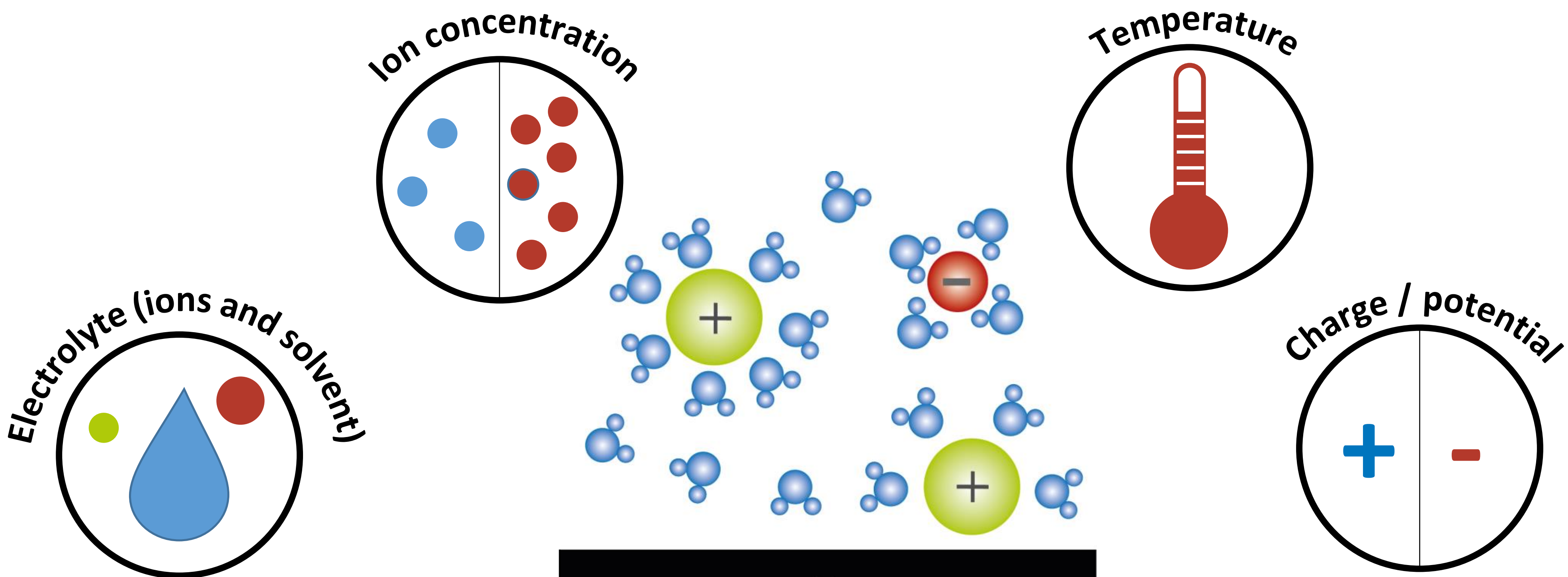
$$\phi_x = \frac{2 \cdot F}{R \cdot T} \cdot \operatorname{arcsinh}\left(\frac{\sigma}{\sqrt{8 \cdot \varepsilon_r \cdot \varepsilon_0 \cdot R \cdot T \cdot c_{\mathrm{inf}}}}\right)$$

σ :	surface charge (C/m²)
R:	gas constant 8.314 J/(mol·K)
T:	temperature (K)
F:	Faraday constant 96485 C/mol (NOT the unit Farad!)
c_{inf} :	bulk solution concentration ad infinitum
ε_0:	$8.854 \cdot 10^{-12}$ C/Vm
ε_r:	water = 78

G. Gouy, Compt. Rend., 1910, 149, 654 & D. L. Chapman, Phil. Mag., 1913, 25, 475

ELECTRICAL DOUBLE LAYER

THE NATURE OF THE ELECTRICAL DOUBLE-LAYER



Storing charge

Ion electrosorption

Storing ions

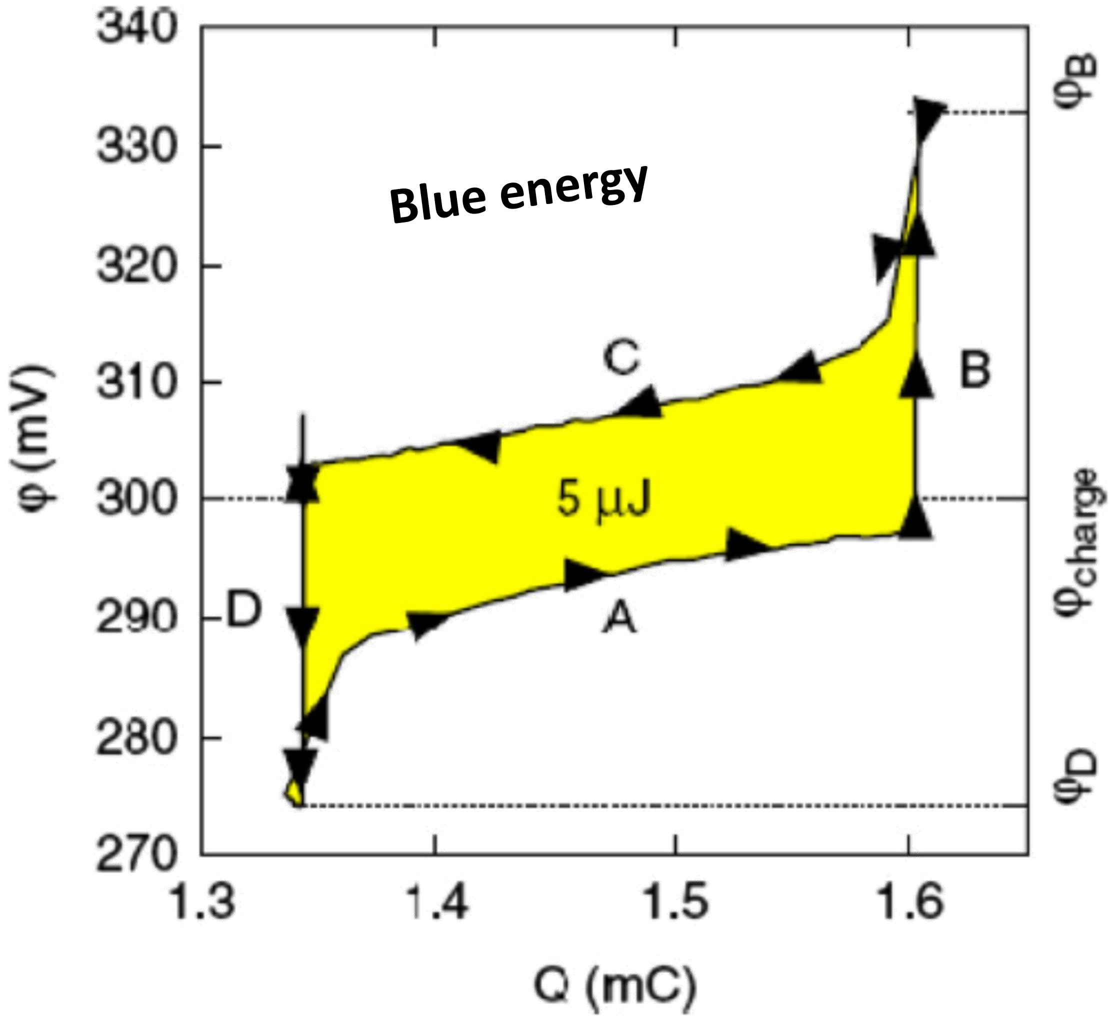
The electric double-layer “communicates” with the environment & vice versa
Unique potential for energy harvesting, sensors, etc.

ELECTRICAL DOUBLE LAYER

ELECTRICAL DOUBLE LAYER EXPANSION

- Double layer capacitance depends on the ionic strength

  - Phase A: The cell is filled with high salinity water. The electrodes are charged from 274 mV to 300mV
  - Phase B: The circuit is open. The cell is flushed with low salinity water. The voltage increases to 333 mV
  - Phase C: The capacitor is discharged, towards 300 mV
  - Phase D: The circuit is open. The cell is flushed with high salinity water and the voltage drops to 274 mV

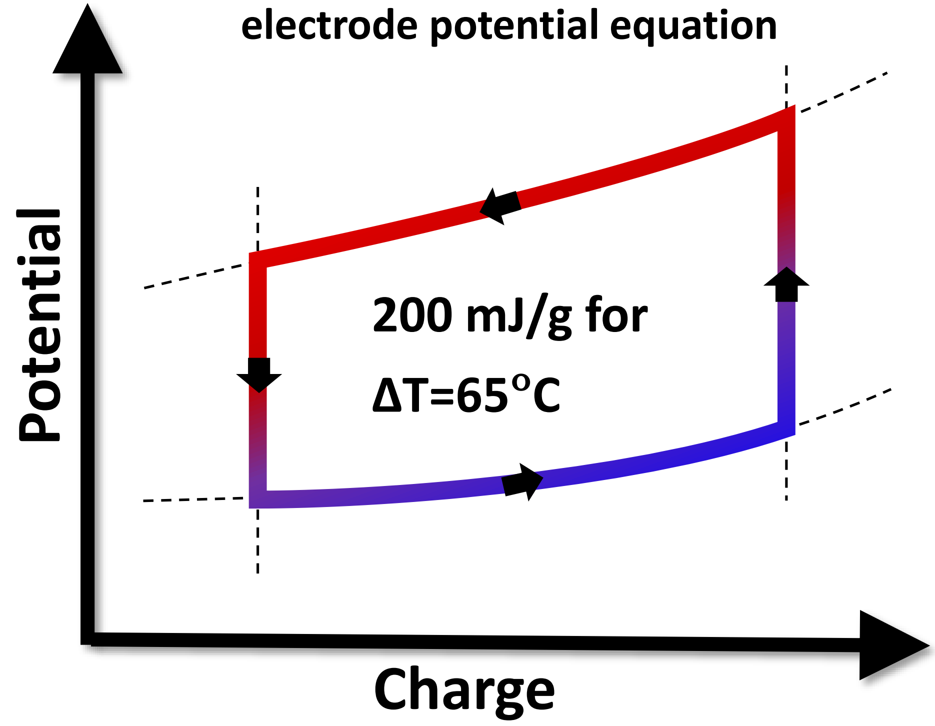


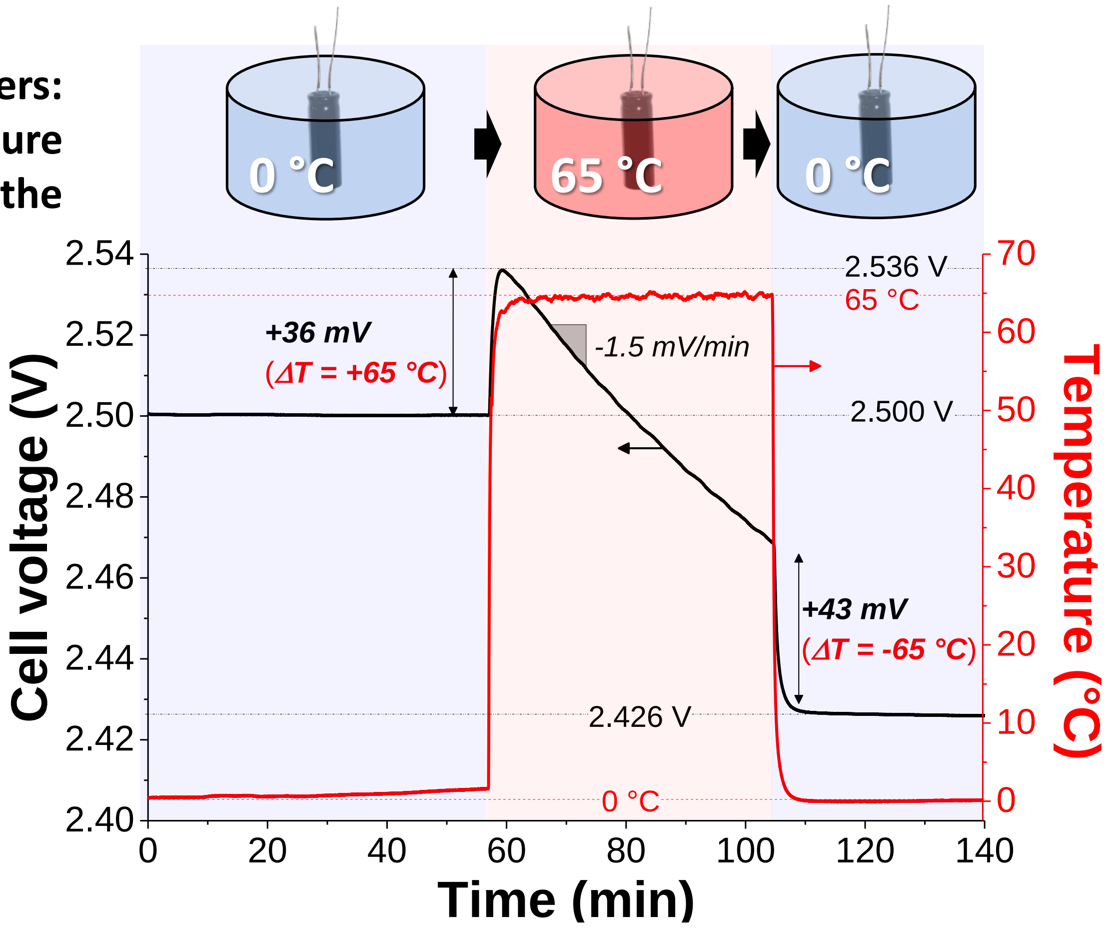
Jia, Z., et al., Blue energy: Current technologies for sustainable power generation from water salinity gradient. Renewable and Sustainable Energy Reviews, 2014. 31(0): p. 91-100.

ELECTRICAL DOUBLE LAYER

ELECTRICAL DOUBLE LAYER EXPANSION

- **Double layer capacitance depends on the <u>temperature</u>**
  - **Actually, this is because of two influencing parameters: the dielectric permittivity of water is temperature dependent (decreases with T) and T is a factor in the electrode potential equation**



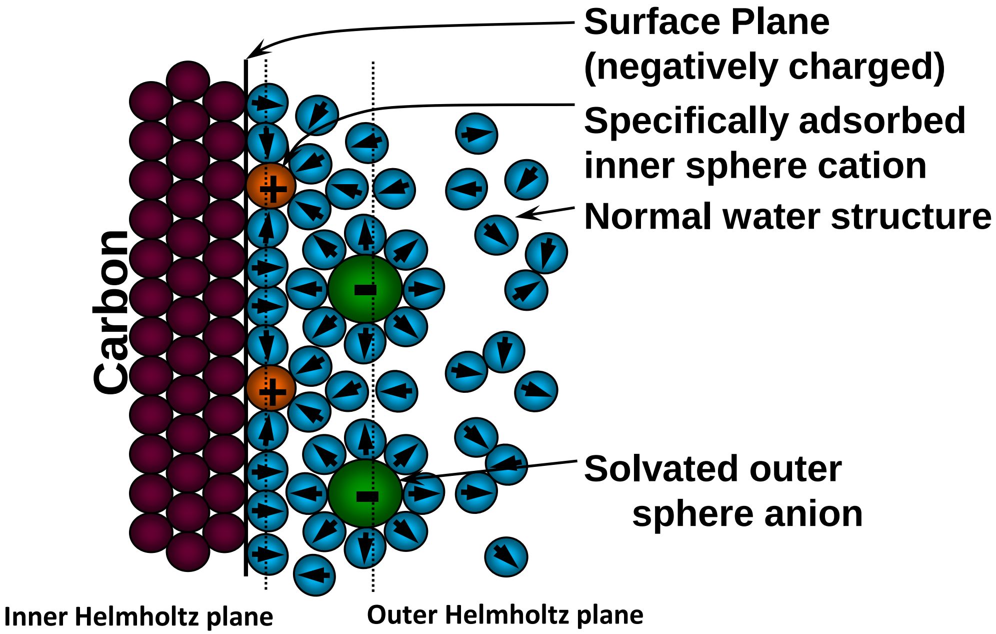


A. Härtel, M. Janssen, D. Weingarth, V. Presser, R. van Roij, Heat-to-current conversion of low-grade heat from a thermocapacitive cycle by supercapacitors, Energ Environ Sci 8(8) (2015) 2396-2401.

ELECTRICAL DOUBLE LAYER

ADVANCED MODELS

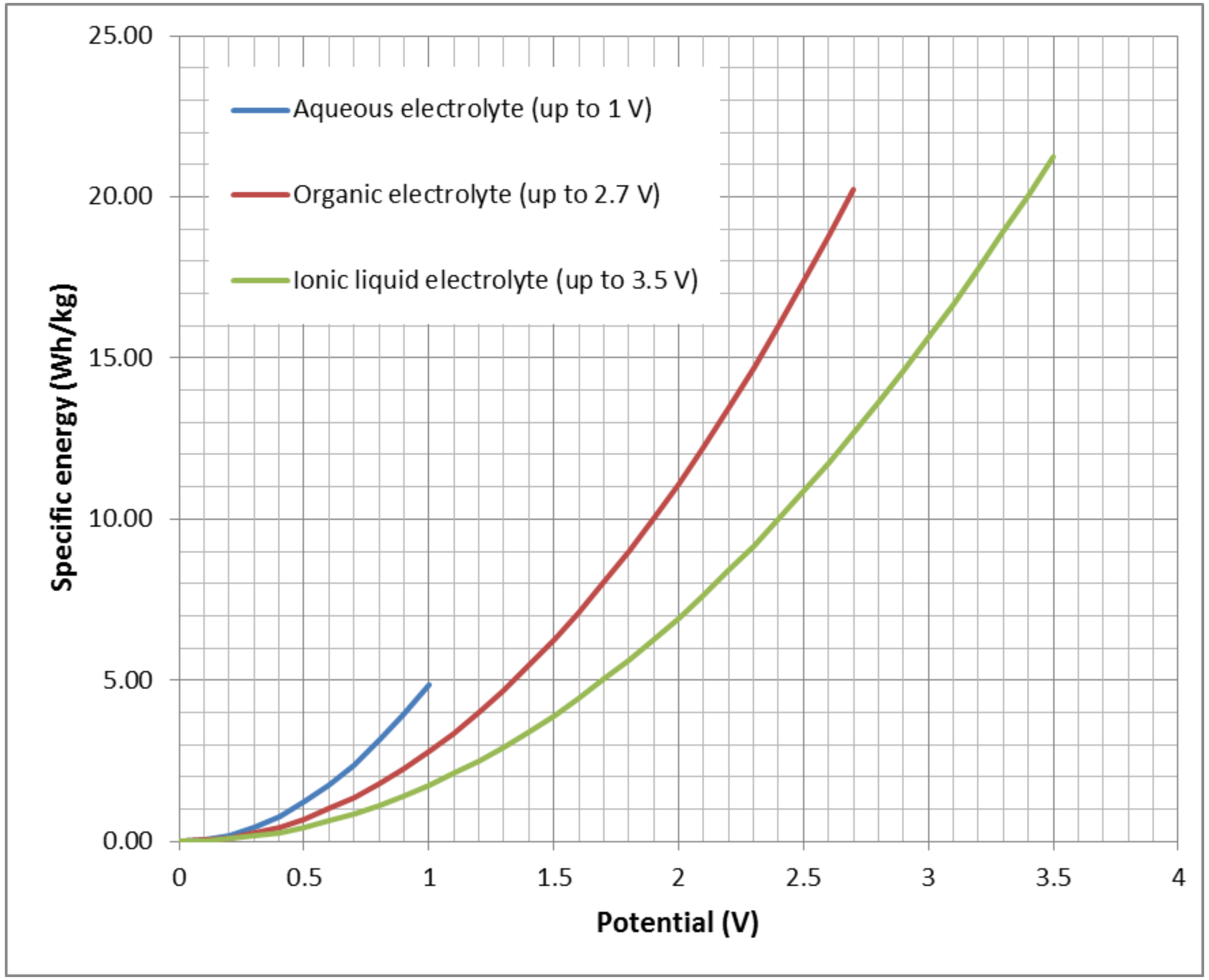
EDL Model
(static)



FSI Models
(dynamic)

ELECTRICAL DOUBLE LAYER

SPECIFIC ENERGY



$C_{aqueous} > C_{organic} > C_{liquid}$

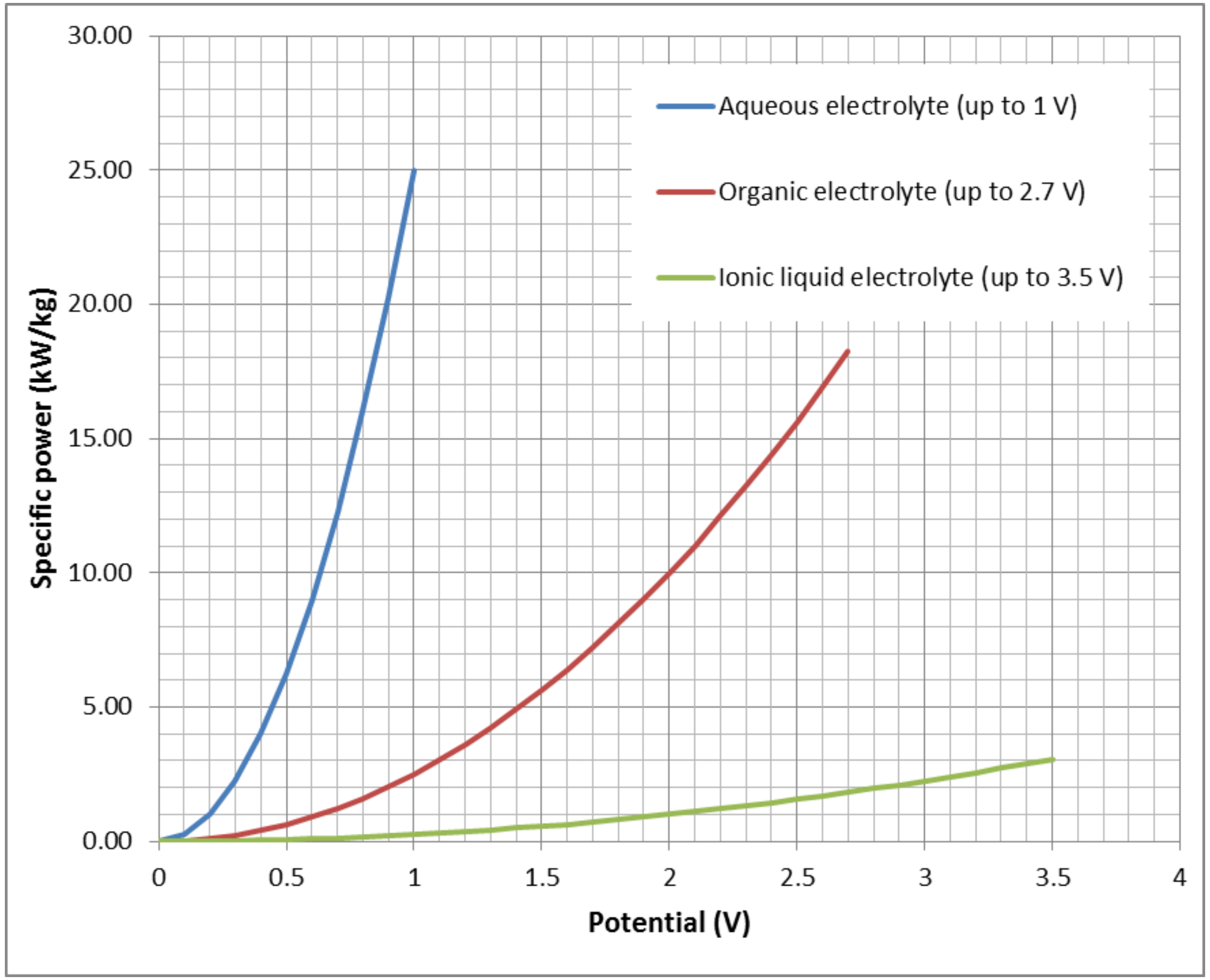
Calculation for $C_{aqueous}$:

- **1.0 V: 4.9 Wh/kg**
- **2.0 V: 19.4 Wh/kg**
- **3.5 V: 59.6 Wh/kg**

$$P = \frac{U^2}{4 \cdot R} \qquad E = \frac{1}{2} \cdot C \cdot U^2$$

ELECTRICAL DOUBLE LAYER

SPECIFIC POWER



$R_{aqueous} < R_{organic} < R_{liquid}$

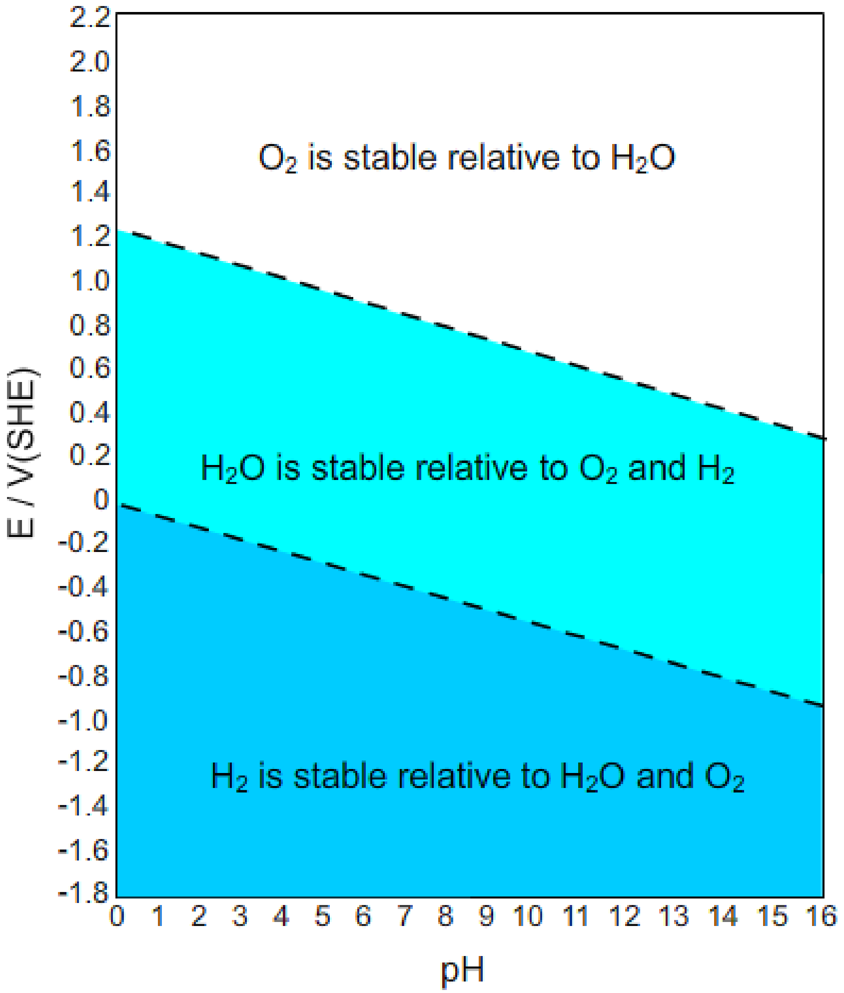
Calculation for $C_{aqueous}$:

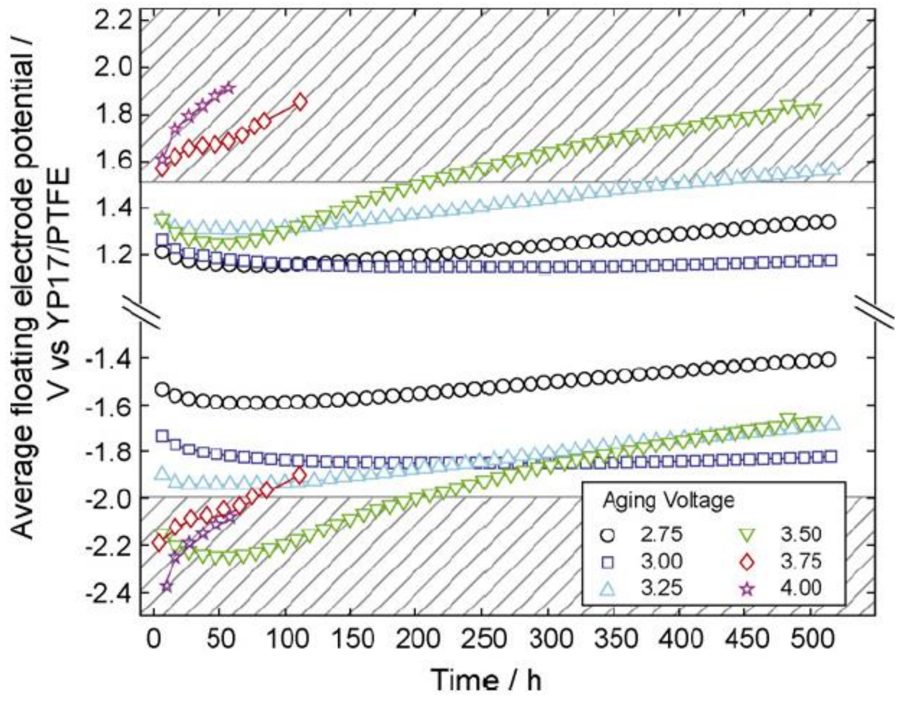
- **1.0 V: 25 kW/kg**
- **2.0 V: 100 kW/kg**
- **3.5 V: 306 kW/kg**

$$P = \frac{U^2}{4 \cdot R} \qquad E = \frac{1}{2} \cdot C \cdot U^2$$

ELECTRICAL DOUBLE LAYER

VOLTAGE WINDOW

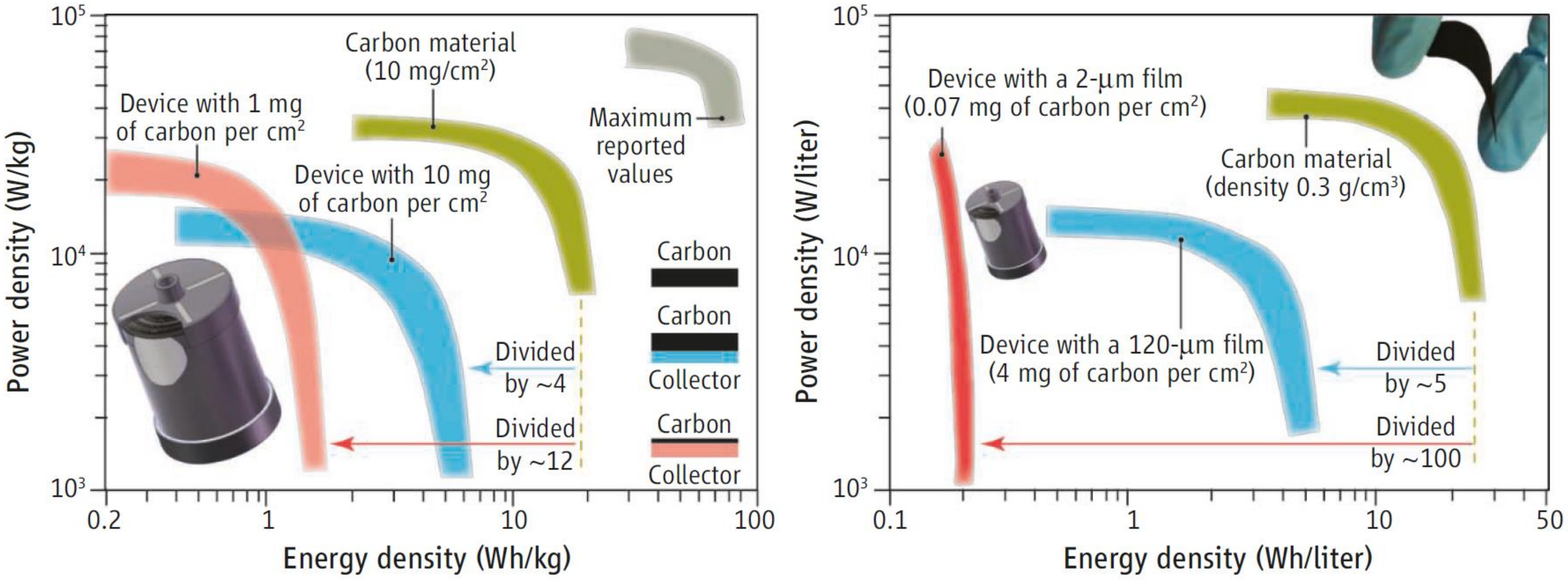




Ruch, P. W.; Cericola, D.; Foelske-Schmitz, A.; Kötz, R.; Wokaun, Electrochimica Acta 2010, 55 (15), 4412-4420

ELECTRICAL DOUBLE LAYER

RAGONE PLOT

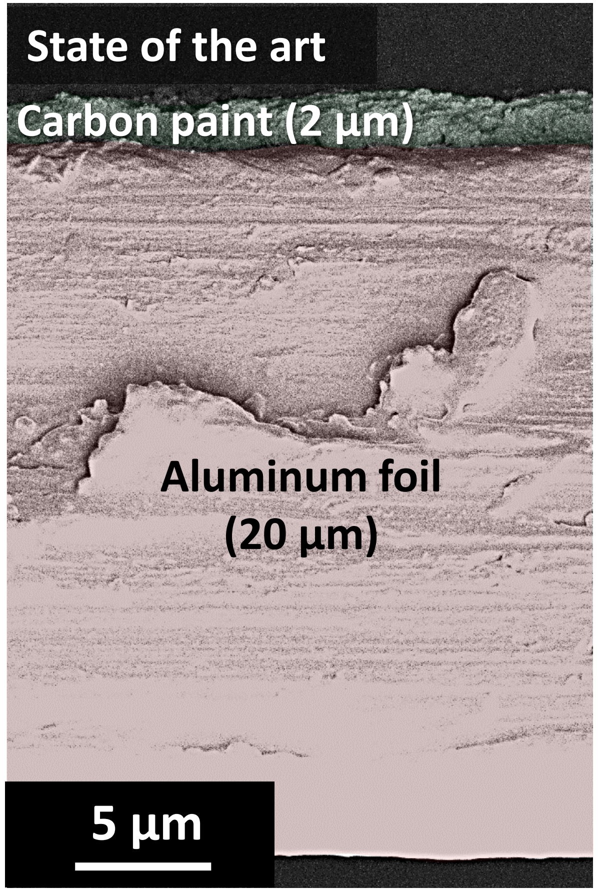


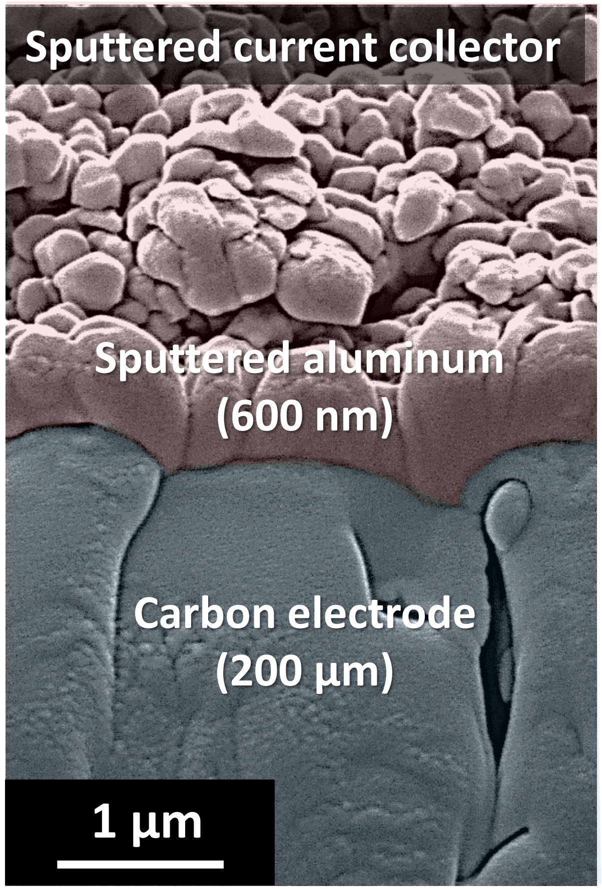
Gogotsi, Y.; Simon, P., True Performance Metrics in Electrochemical Energy Storage. Science 2011, 334 (6058), 917-918.

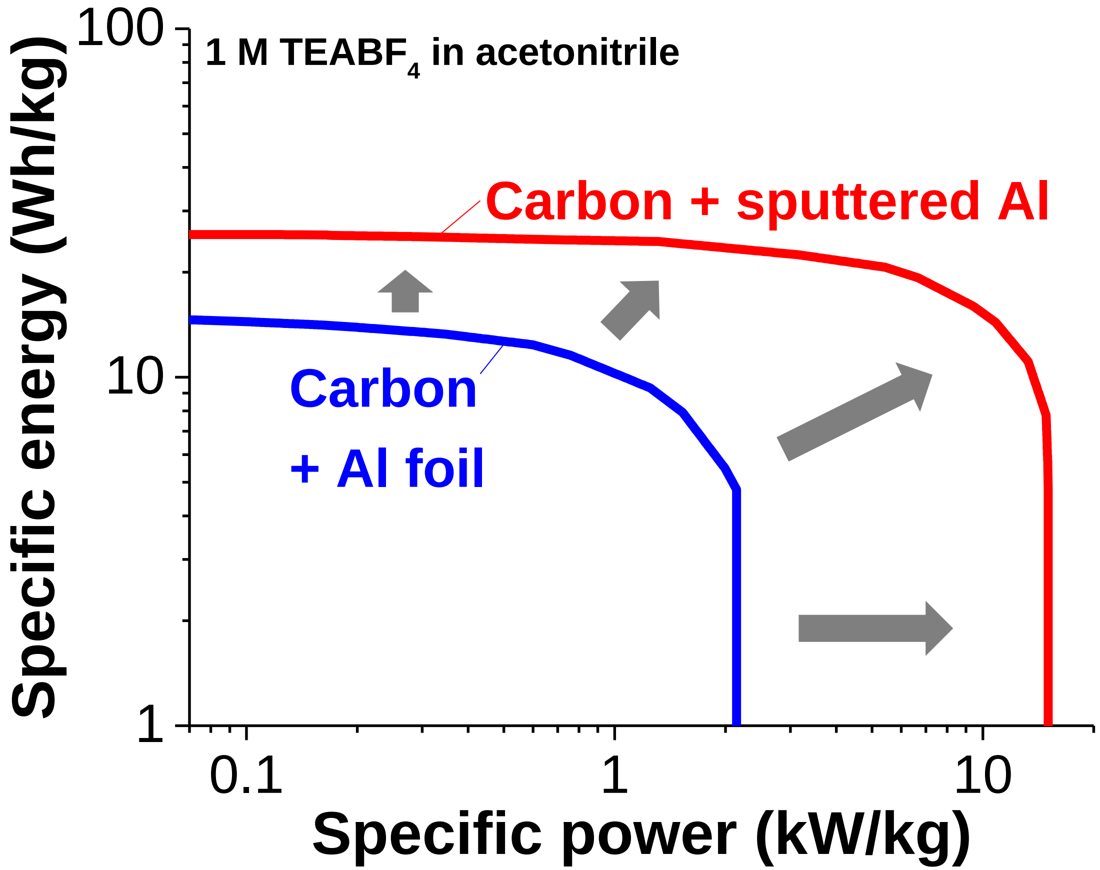
ELECTRICAL DOUBLE LAYER

LIGHTWEIGHT AND COMPACT DESIGN OF THE CURRENT COLLECTOR

- **Magnetron sputtering of thin film Al current collector boosts power and storage capacity of carbon supercapacitors**



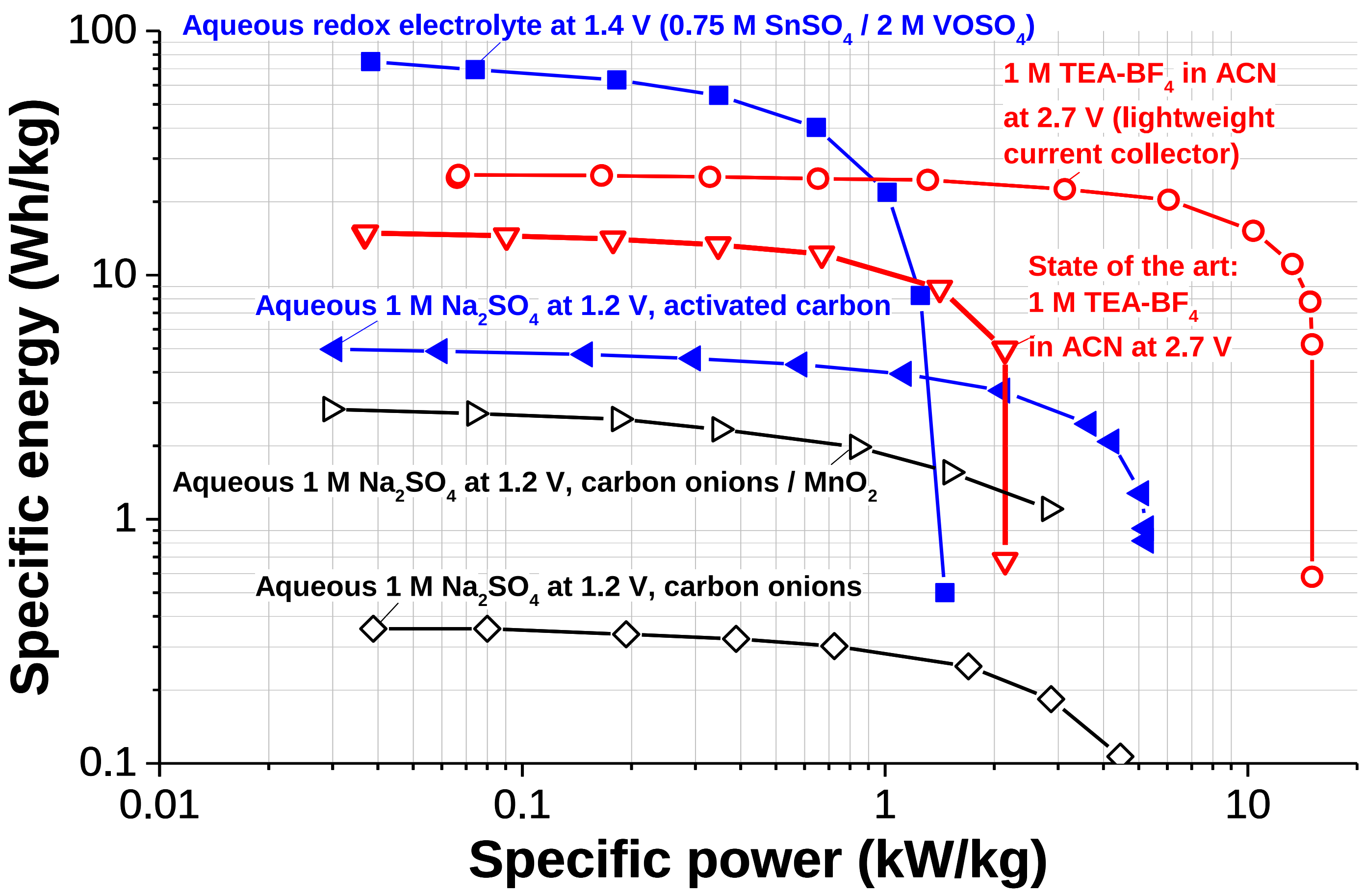




 Journal of Power Sources, 2016, 329, 432-440.

ELECTRICAL DOUBLE LAYER

RAGONE CHART FOR CARBON BASED ENERGY STORAGE TECHNOLOGIES



By engineering: more compact and lightweight results in higher power handling and higher energy ratings

By use of redox-active electrode materials: more energy stored than in supercapacitors, but longevity often limited

By use of redox-active electrolytes: faster than batteries and more energy stored than in supercapacitors

By use of sulfur, chlorine, and fluorine free binders without need for toxic solvents: improved environmental friendliness

ELECTRICAL DOUBLE LAYER

TAKE HOME MESSAGES

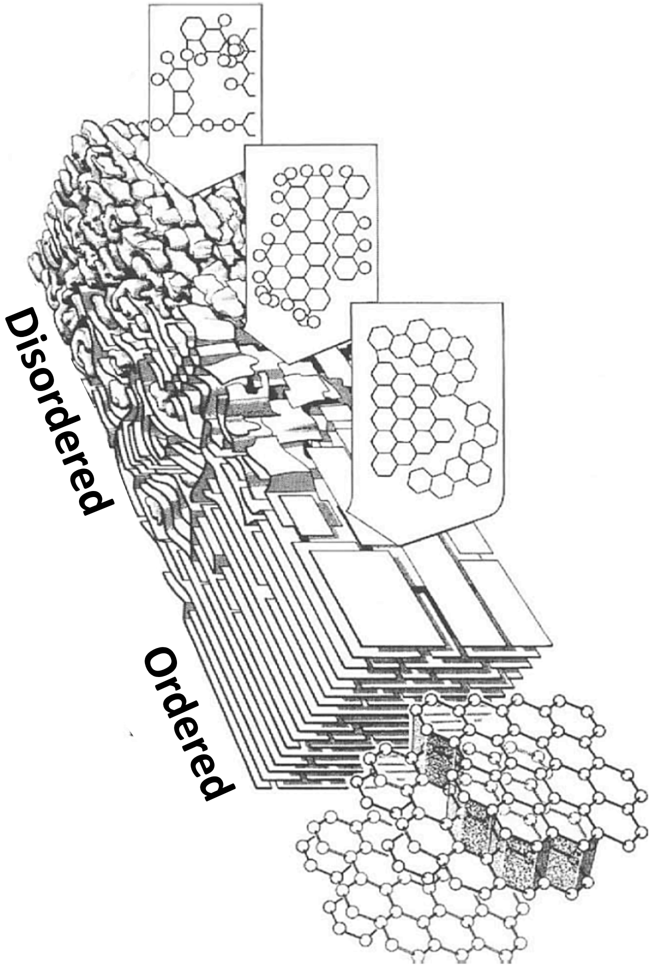
- Ion electrosorption is the energy storage mechanism of double-layer capacitors
- The capacitance depends on electrolyte, surface area, and temperature
- High energy often sacrifices high power

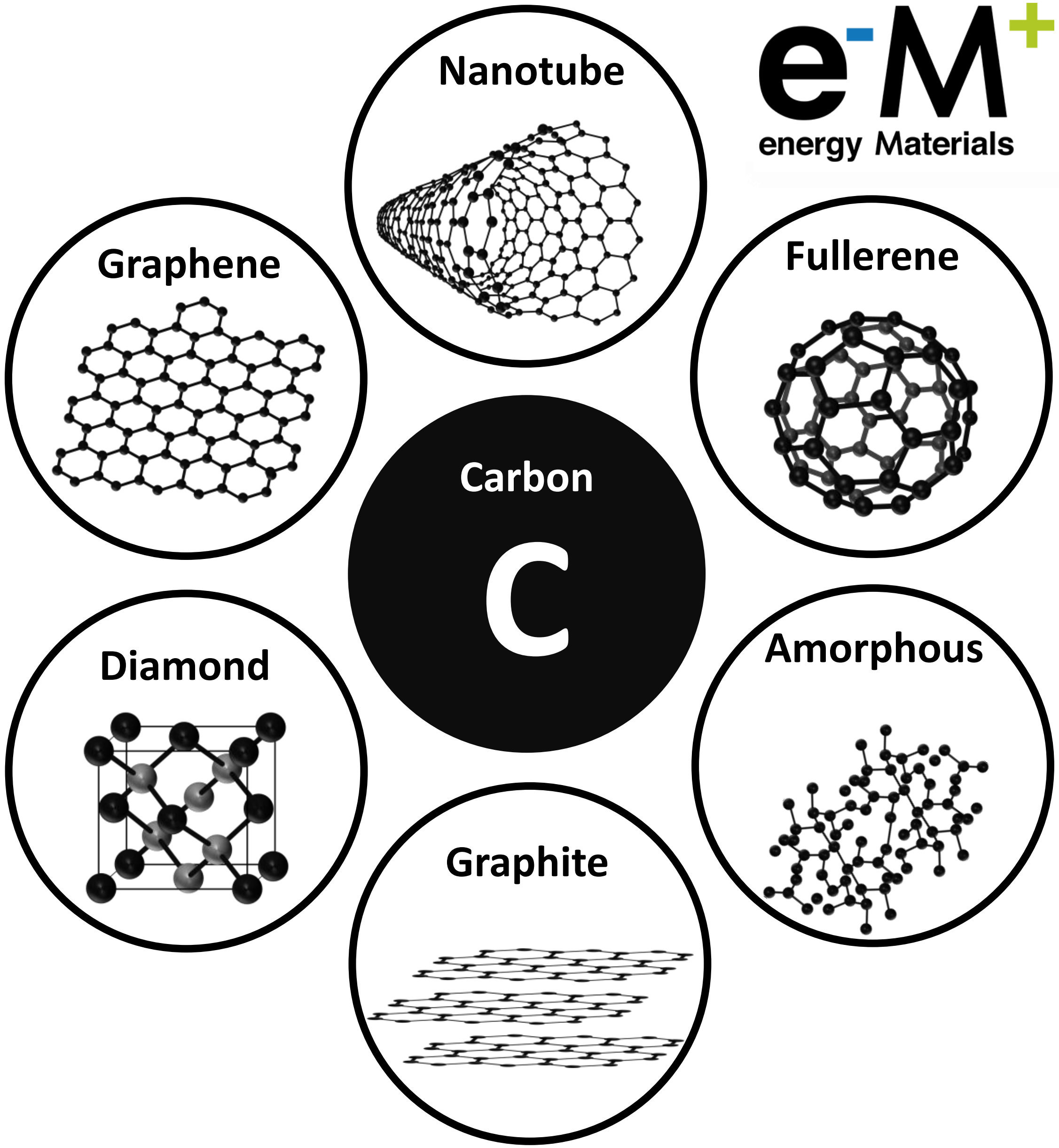
Nanoporous carbon

NANOPOROUS CARBON

CARBON IS VERSATILE

- Tunable
  - sp^2/sp^3
  - porous / dense
  - outer / inner porosity
  - nano / meso / macro
  - conductive / isolative
- Scalable synthesis
- Abundant sources
- Potentially “green”

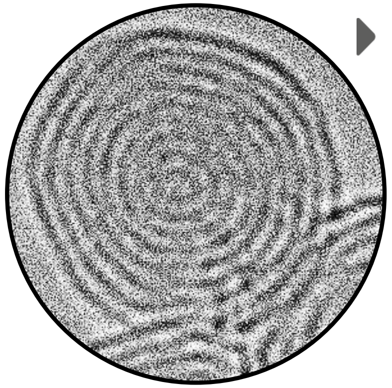




Ban LL, Crawford D, Marsh H. Journal of Applied Crystallography. 1975;8(4):415-20.

NANOPOROUS CARBON

CARBON NANOMATERIALS & NANOCARBONS

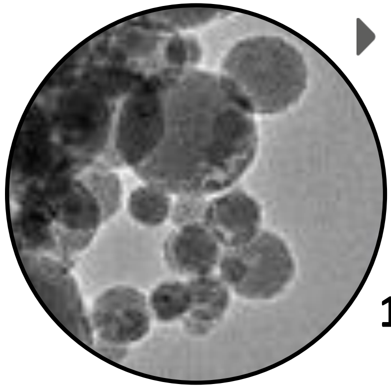


Carbon onions

Ø 5-10 nm

≤ 500 m²/g

2 nm

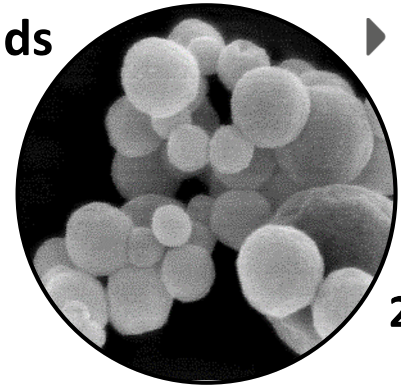


CDC emulsion beads

Ø 20-200 nm

≤ 2300 m²/g

100 nm

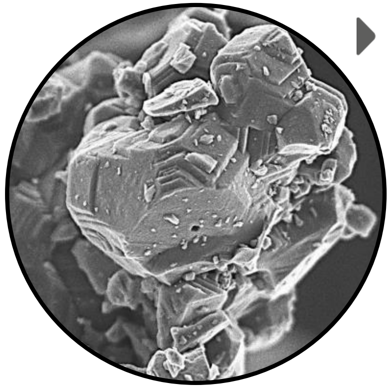


NovoCarb beads

Ø 50-200 nm

≤ 3100 m²/g

200 nm

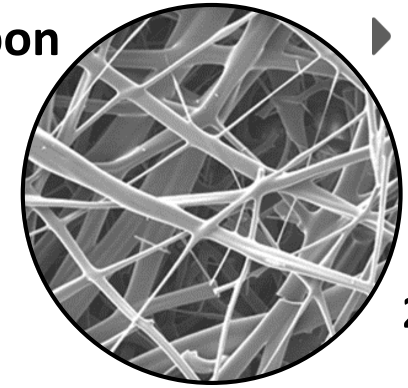


Carbide-derived carbon

Ø µm range

≤ 2600 m²/g

5 µm

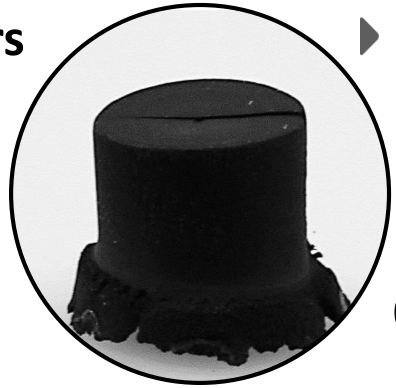


CDC ultrafine fibers

Ø µm range

≤ 3000 m²/g

25 µm



NovoCarb monoliths

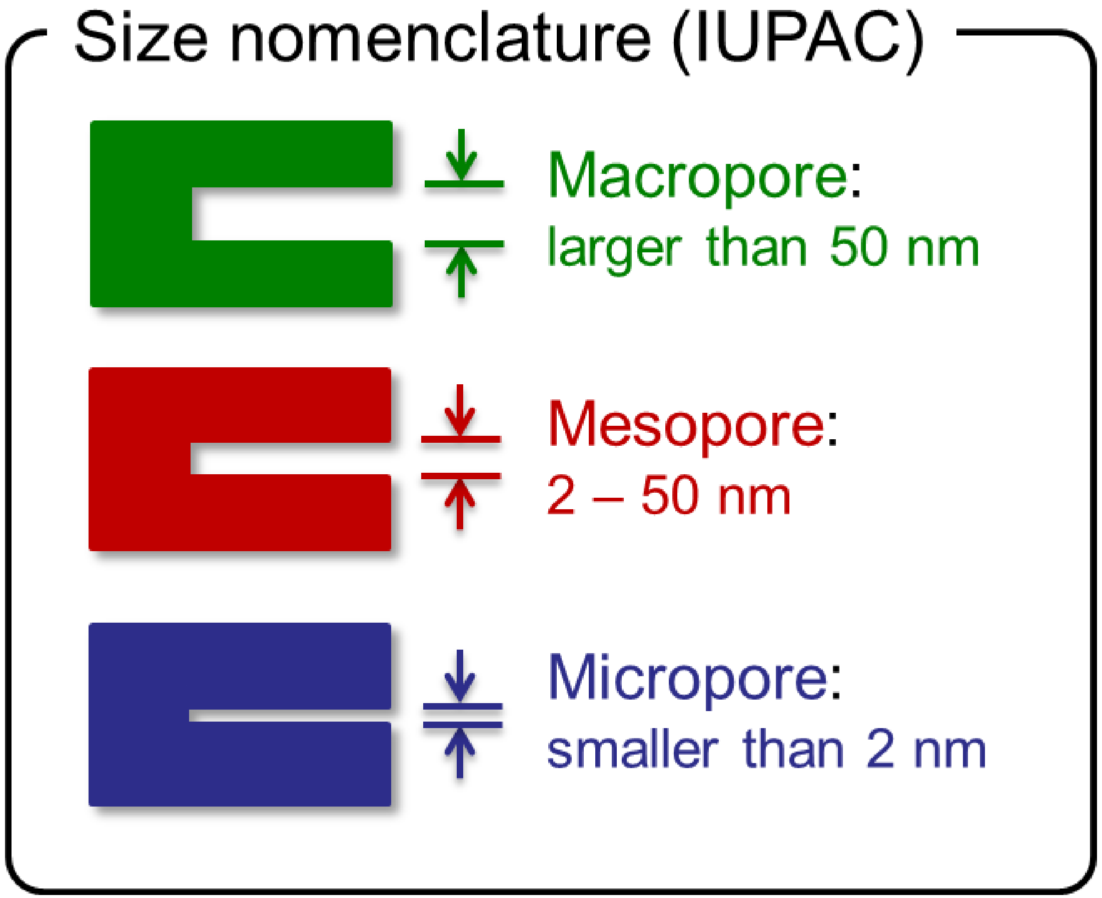
Ø mm-cm range

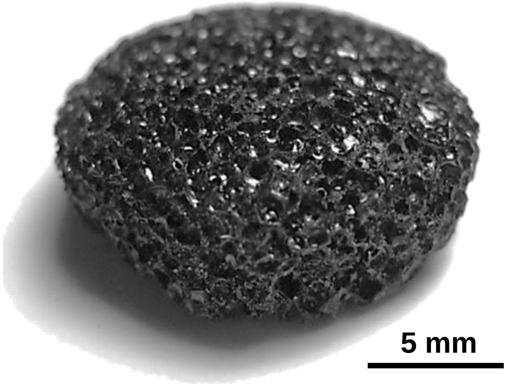
≤ 2800 m²/g

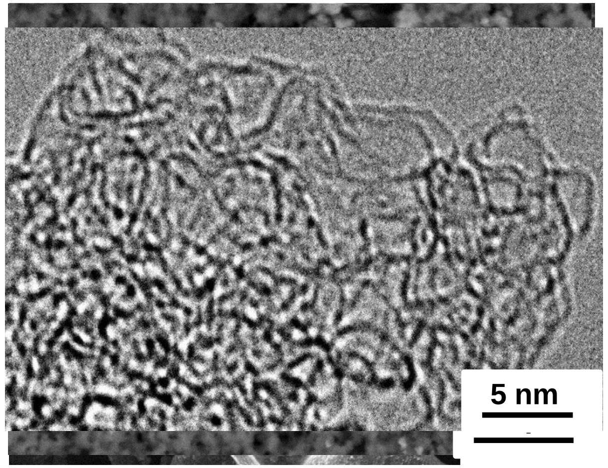
0.5 cm

NANOPOROUS CARBON

CARBON MATERIALS



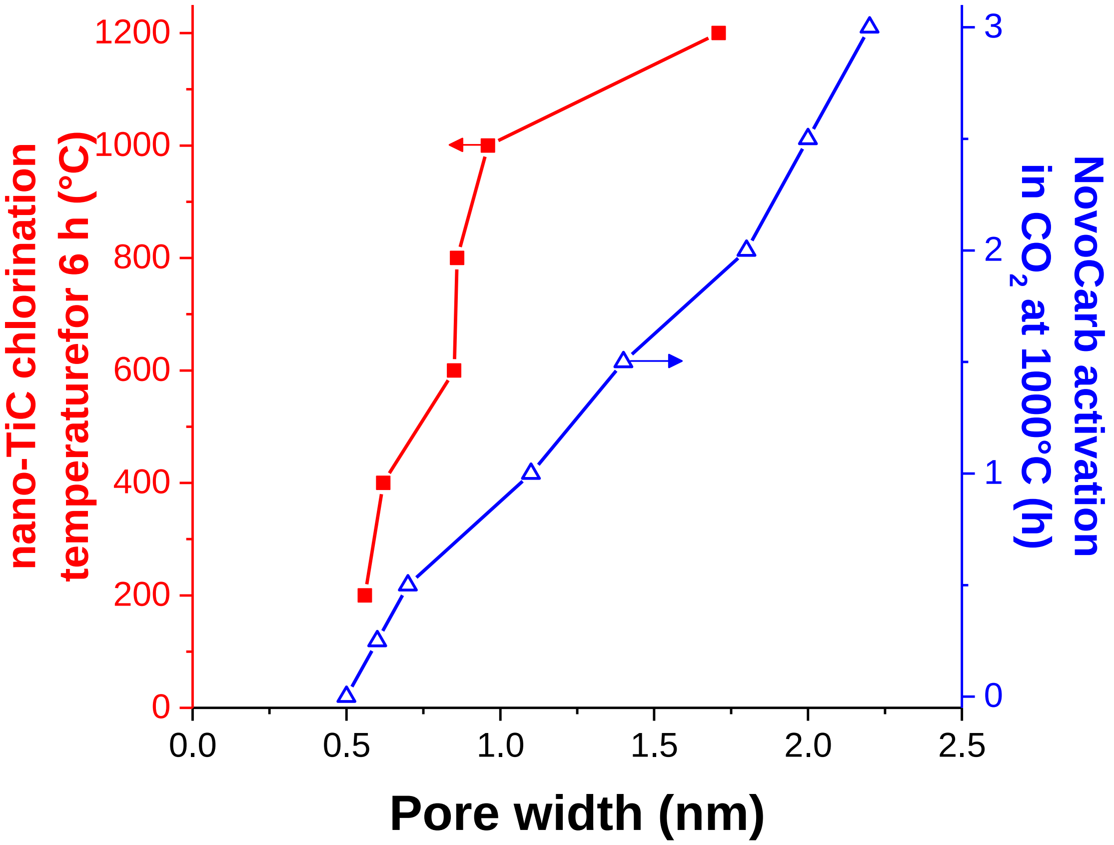


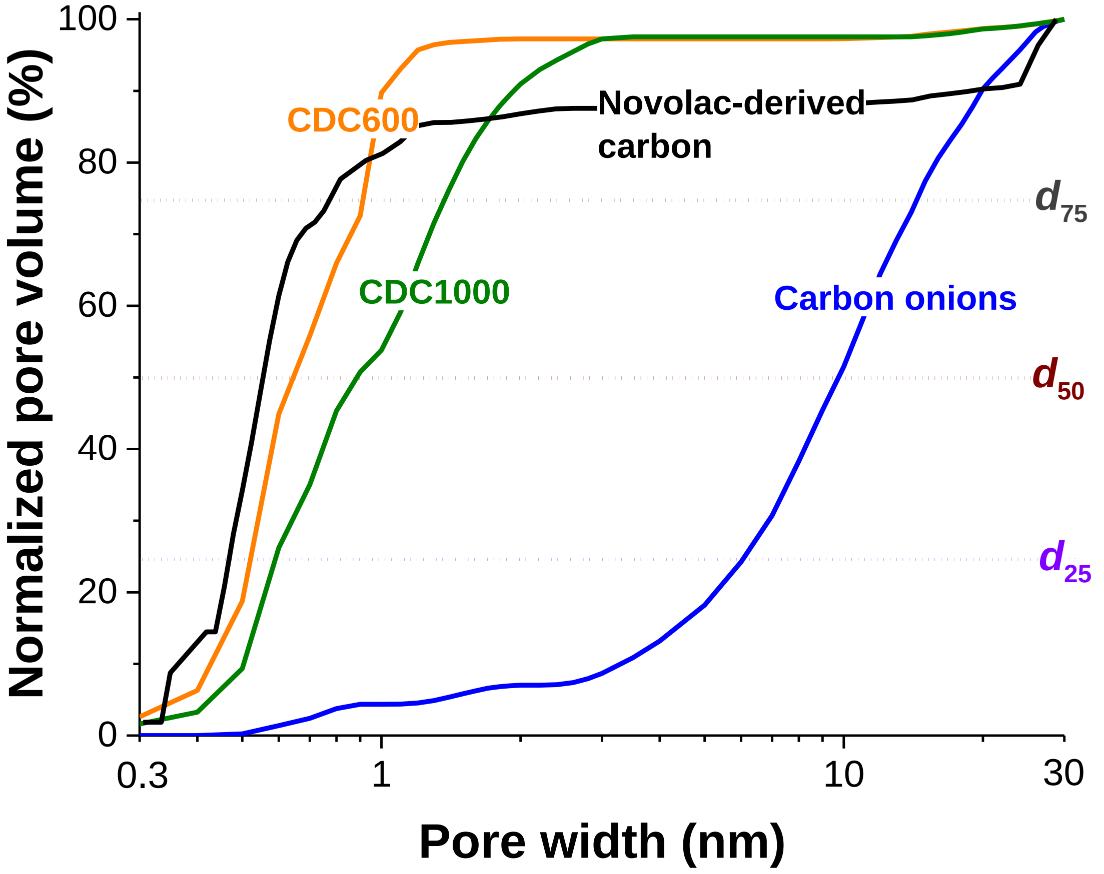


NANOPOROUS CARBON

BESPOKEN CARBON POROSITY

- **Tuning carbon nanopores per activation parameters / synthesis strategy**



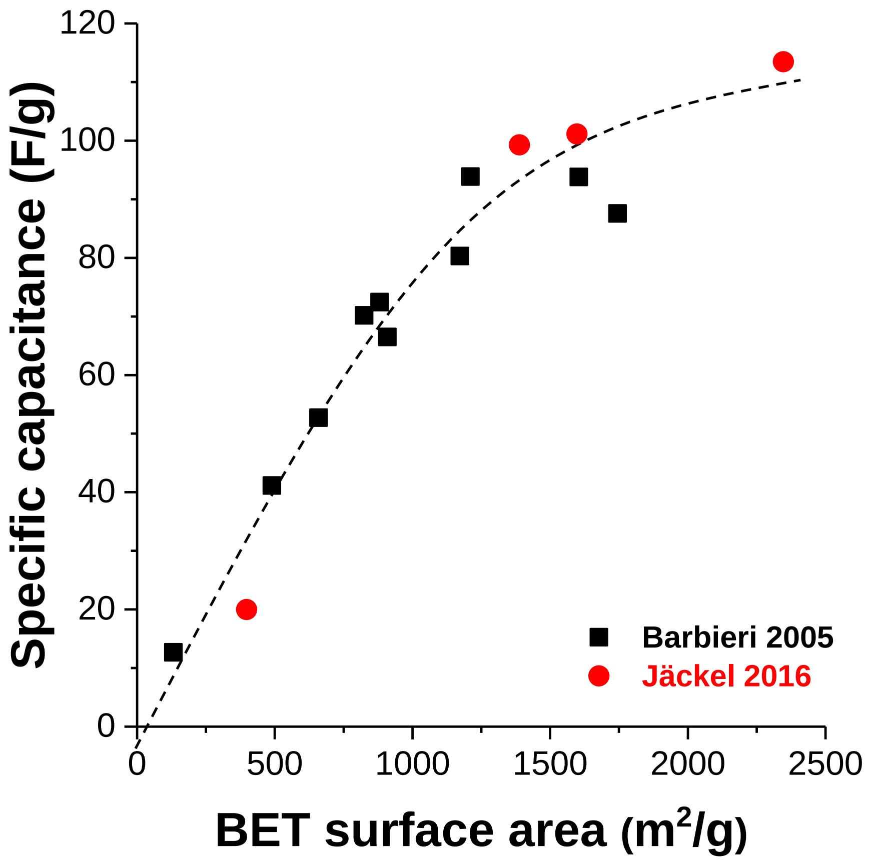


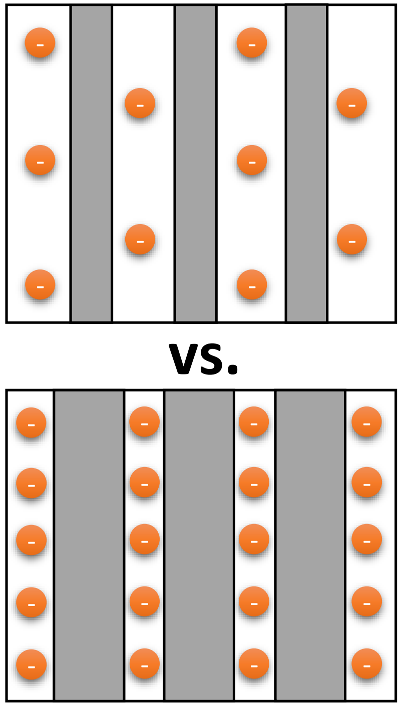
 ACS Applied Materials & Interfaces, 2016, 8, 9104-9115 / Advanced Functional Materials, 2011, 21, 810-833.

NANOPOROUS CARBON

ELECTRICAL DOUBLE-LAYER CAPACITANCE

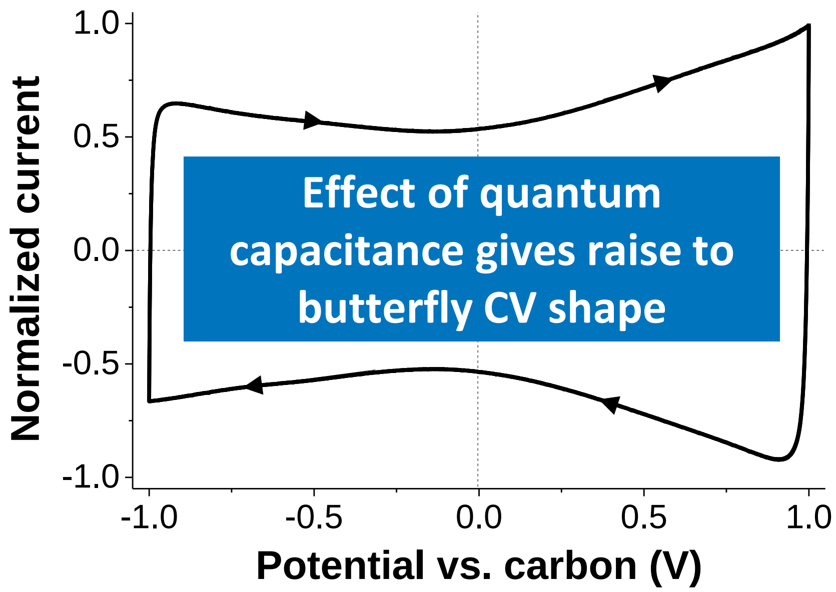
- **Limited charge screening ability of carbon materials**





<u>Some complications</u>:

- **Capacitance dependent on electrolyte**
- **Voltage-dependency of differential capacitance**
- **Equilibrium or kinetic capacitance?**
- **Normalized to (what?) area or (which?) mass**

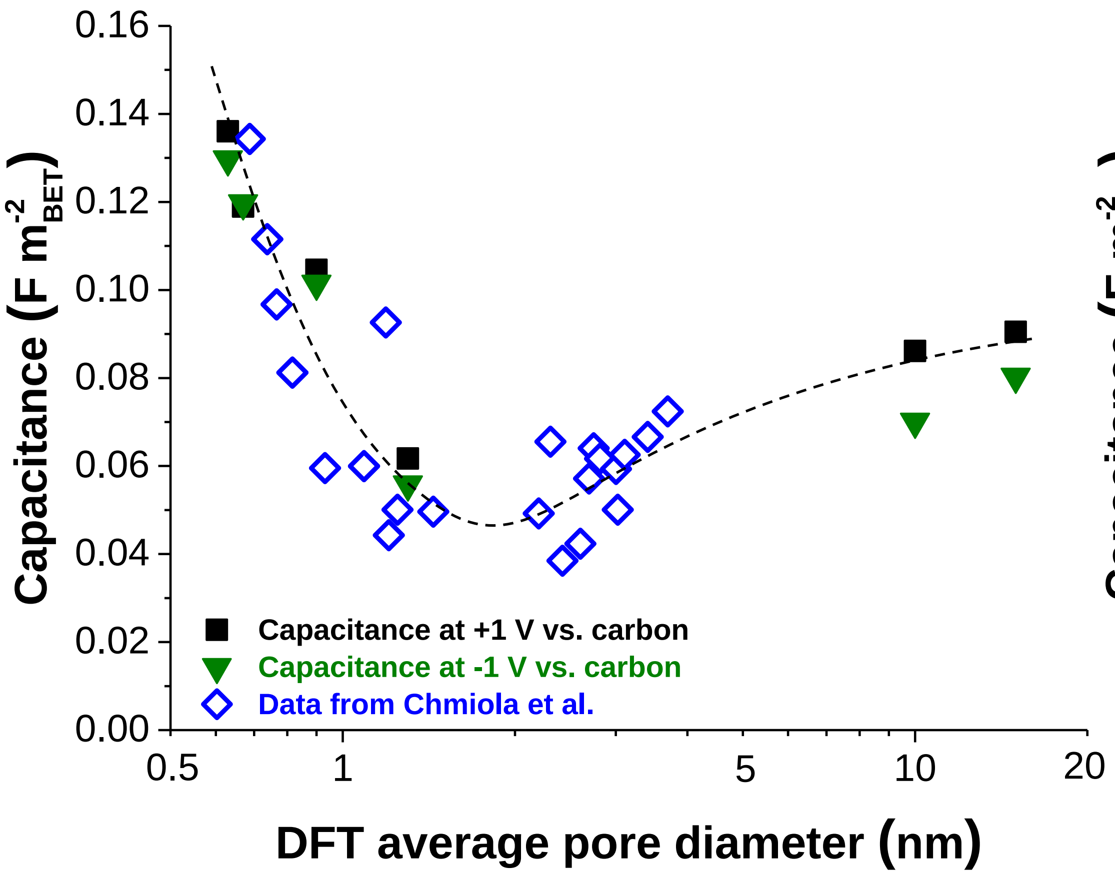


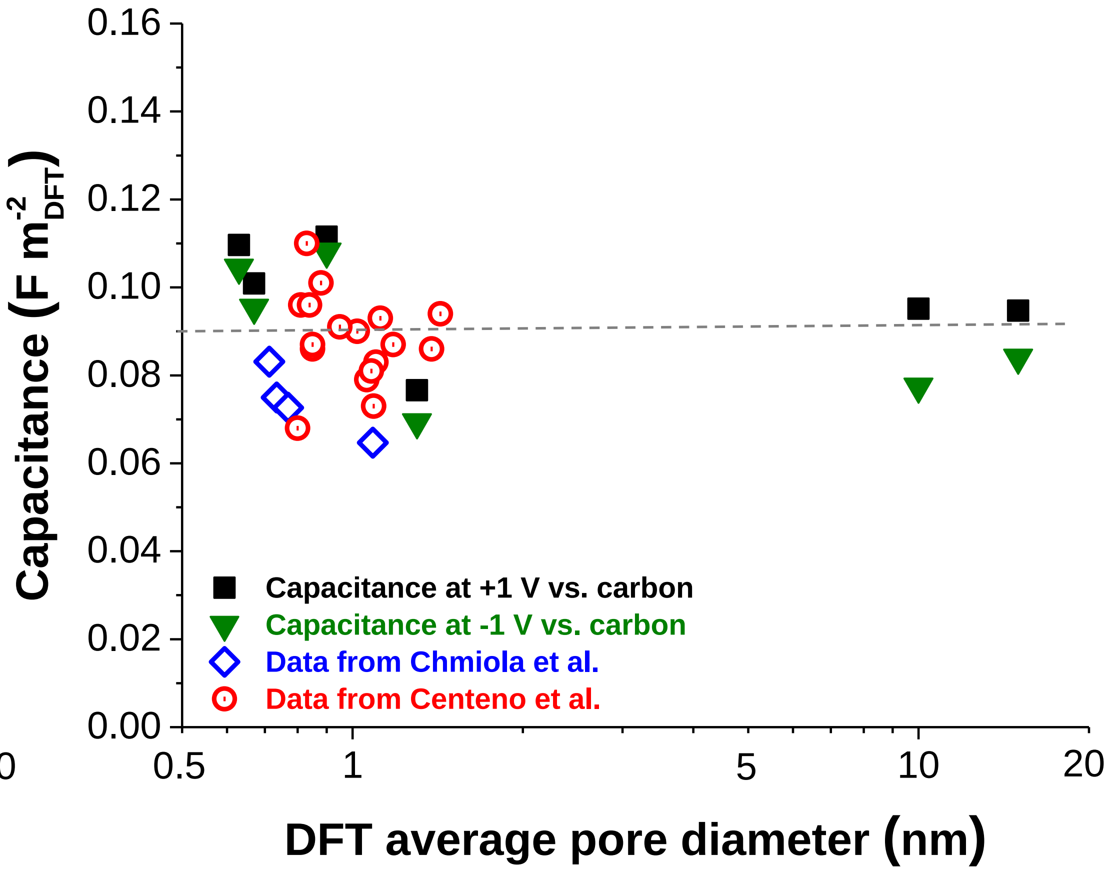
 Journal of Power Sources, 2016, 326, 660-671.

NANOPOROUS CARBON

ROLE OF CARBON POROSITY

- **Two conflicting views in the literature: regular vs. anomalous dependency of capacitance on pore size**



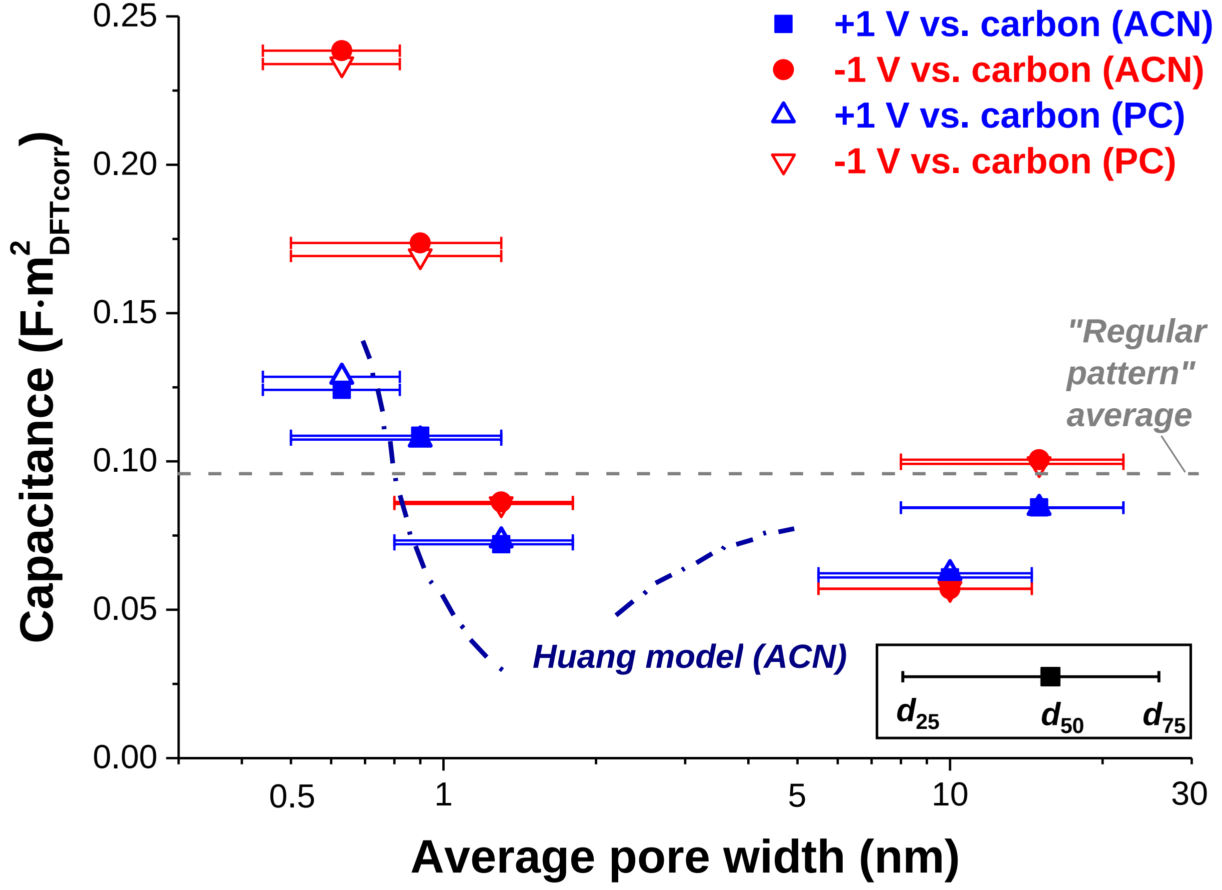


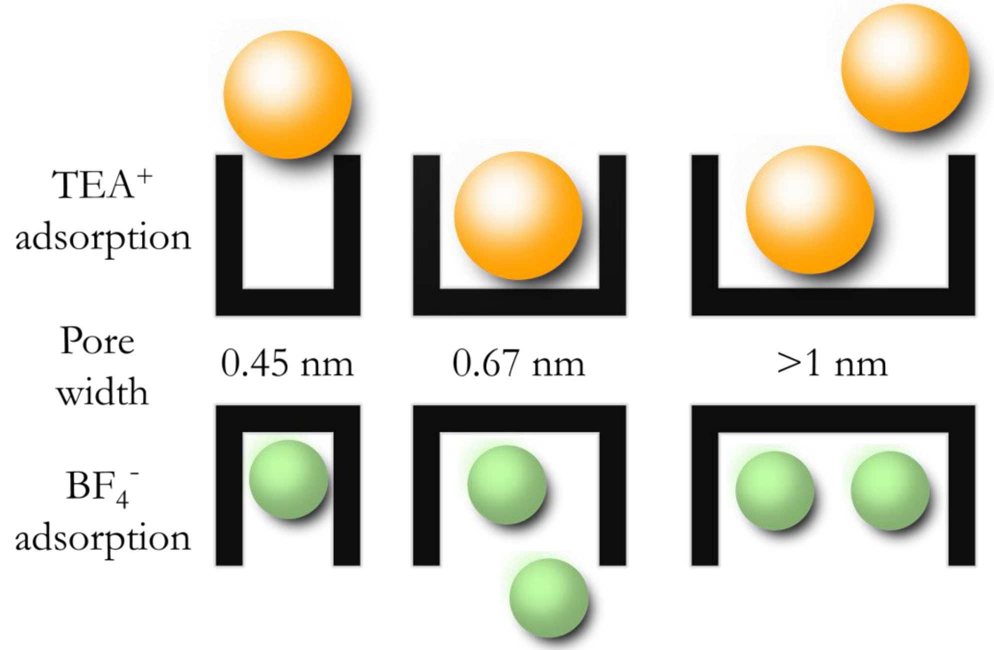
 Journal of Power Sources, 2016, 326, 660-670.

NANOPOROUS CARBON

ROLE OF CARBON POROSITY

- Big picture: “anomalous” pattern is true, but we also have to consider different ion sizes for anode and cathode





 ACS Energy Letters, 2016, 1, 1262-1265.

NANOPOROUS CARBON

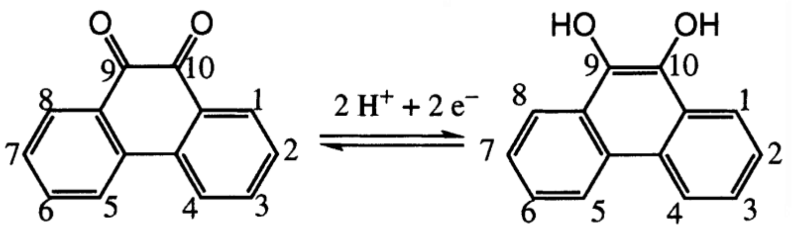
TAKE HOME MESSAGES

- **Capacitance is pore size dependent**
- **Carbon shows a very limited charge screening ability**
- **Optimized performance only when carbon is matched to a certain electrolyte**

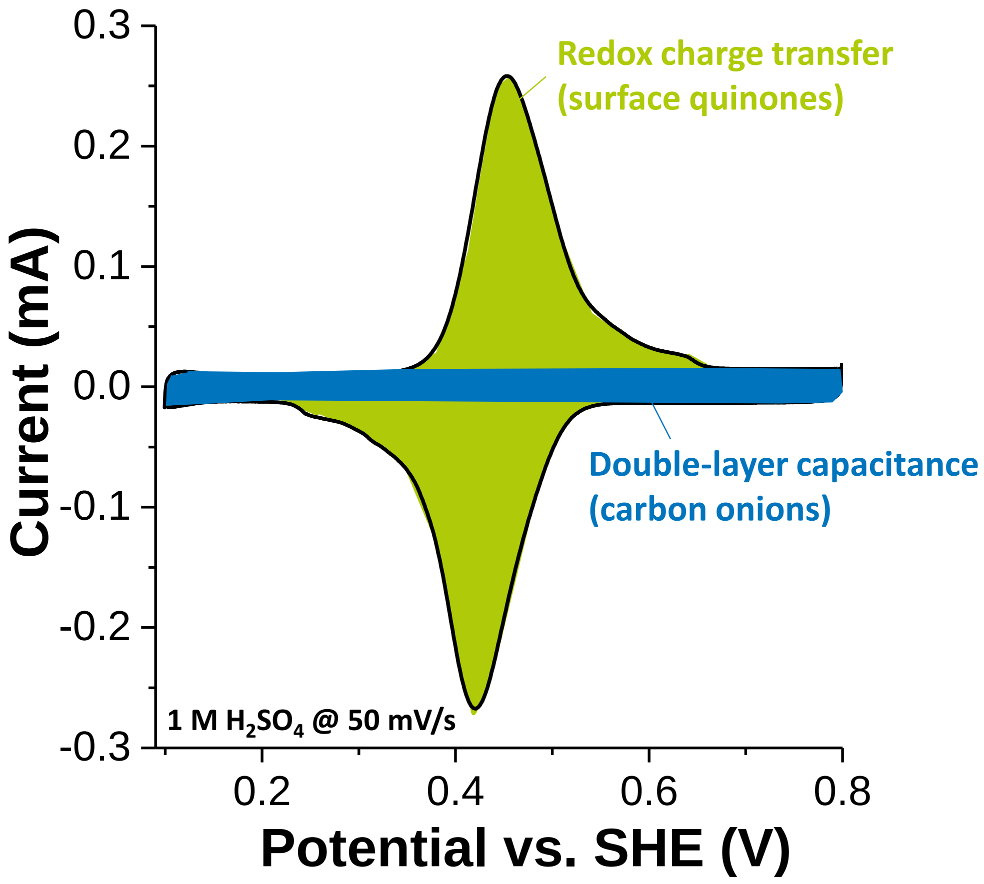
Redox enabling EDLC

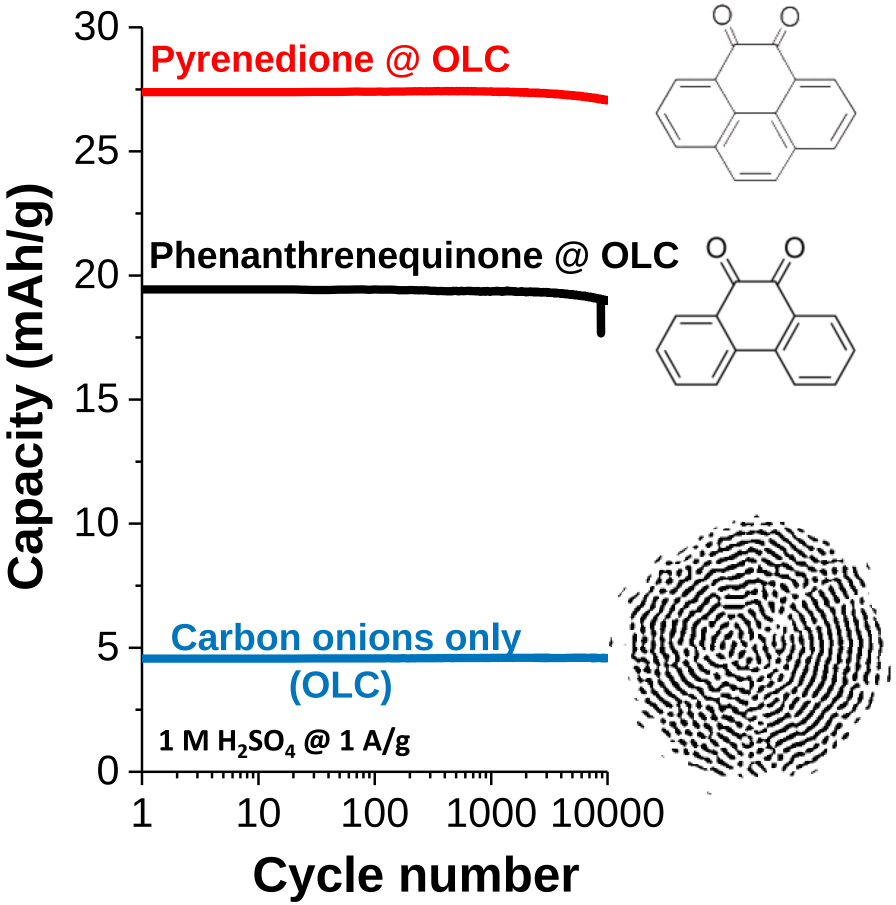
REDOX-ENABLING EDLC

QUINONE-DECORATED CARBON ONIONS



- 9fold increase in capacitance and very stable cycling performance



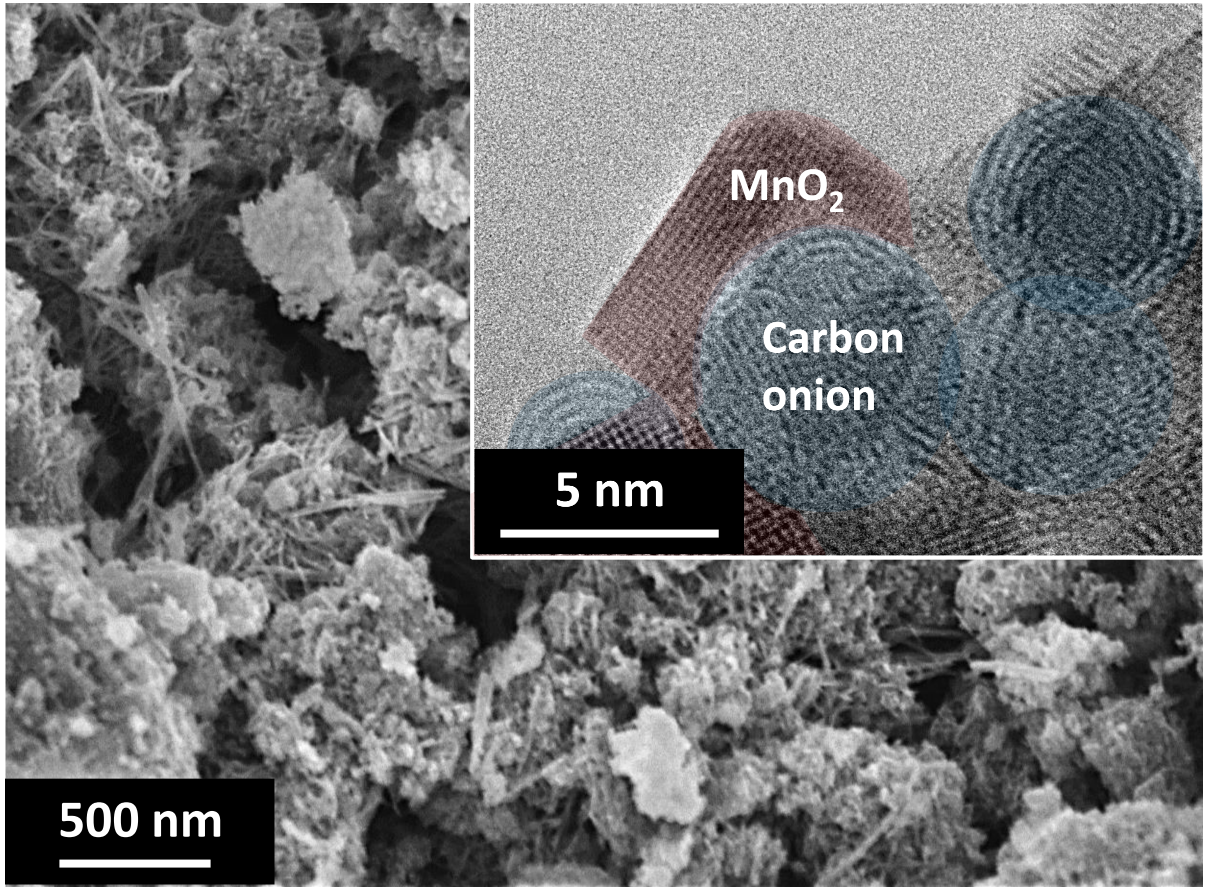


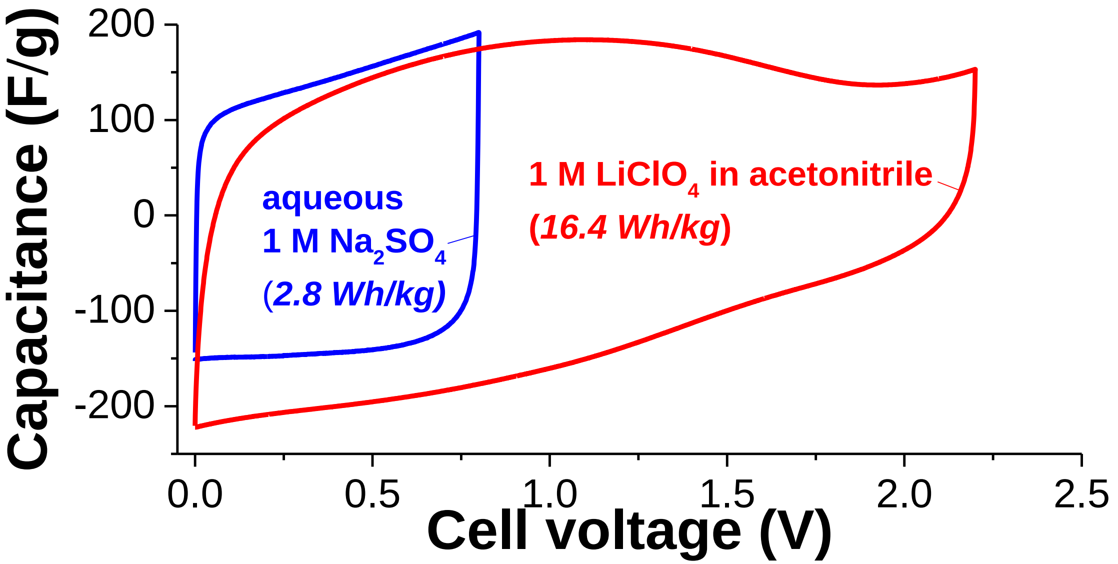
 Nano Energy, 2013, 2, 702-712.

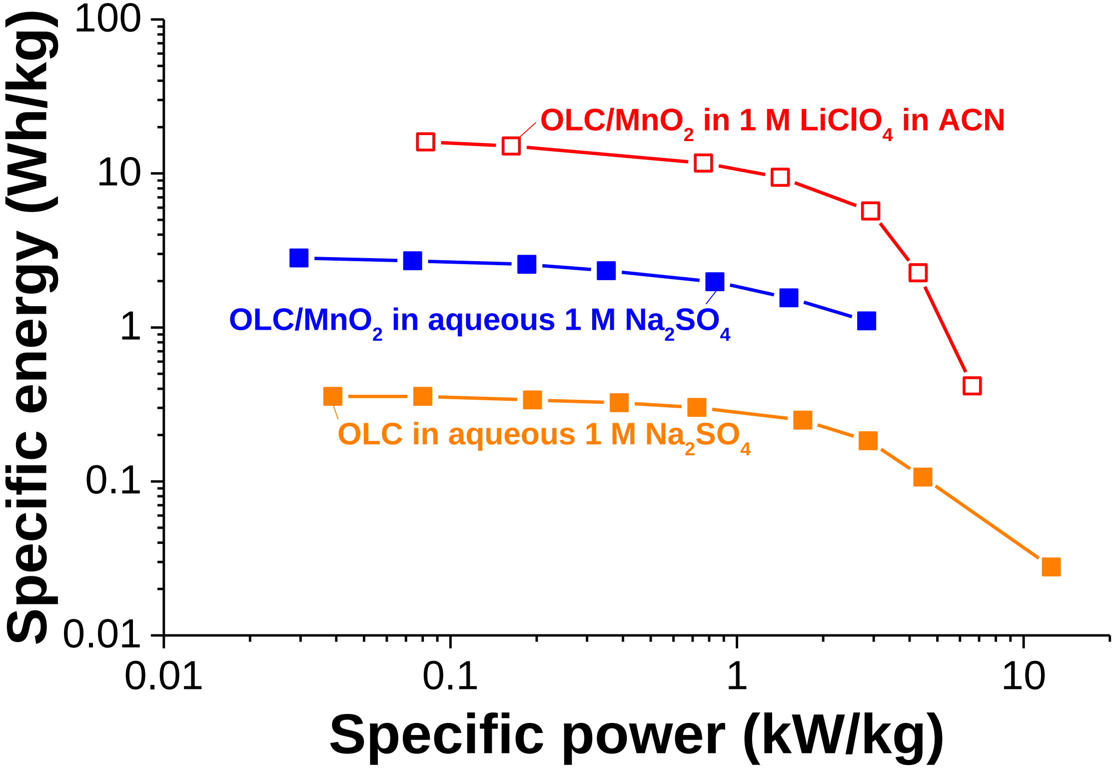
REDOX-ENABLING EDLC

METAL OXIDE / CARBON ONION HYBRID

- **Hydrothermal synthesis of MnO_2/carbon onion hybrids**





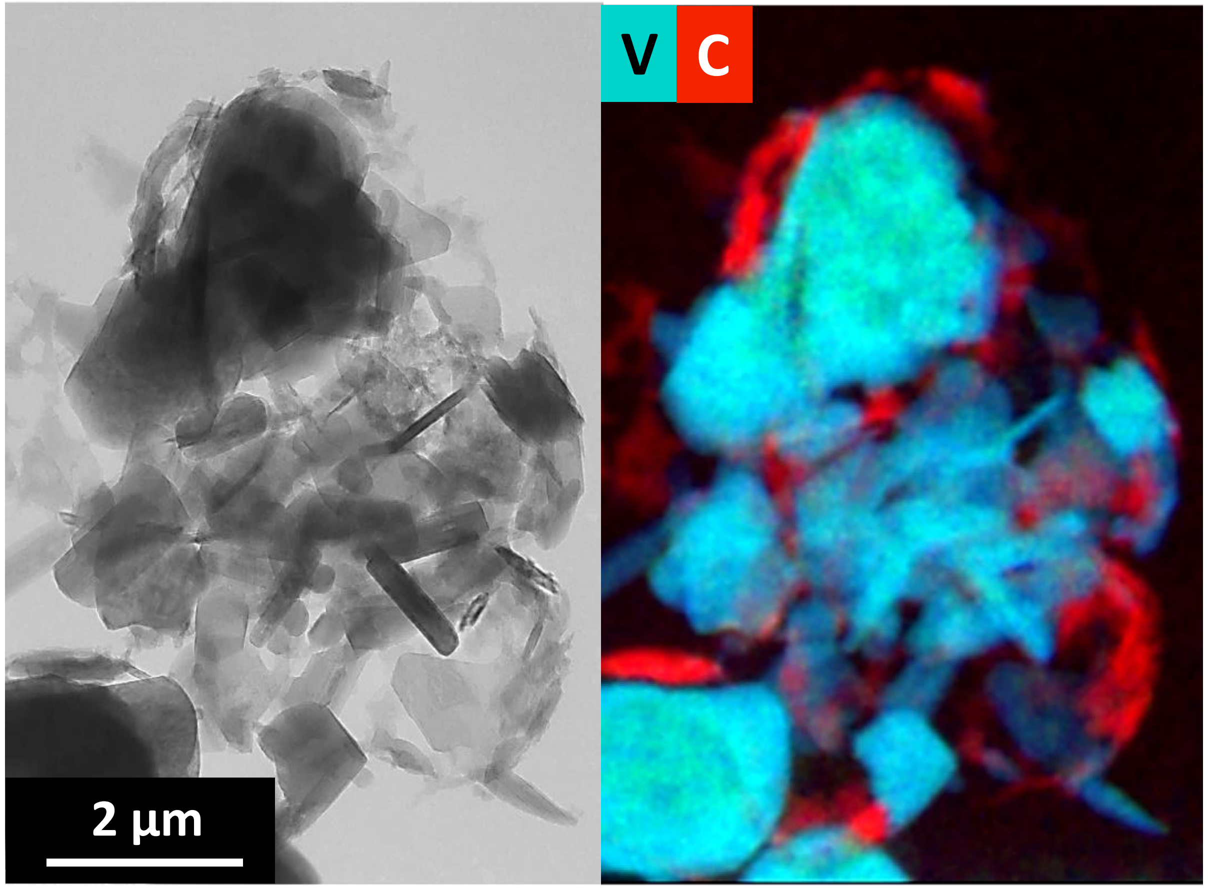


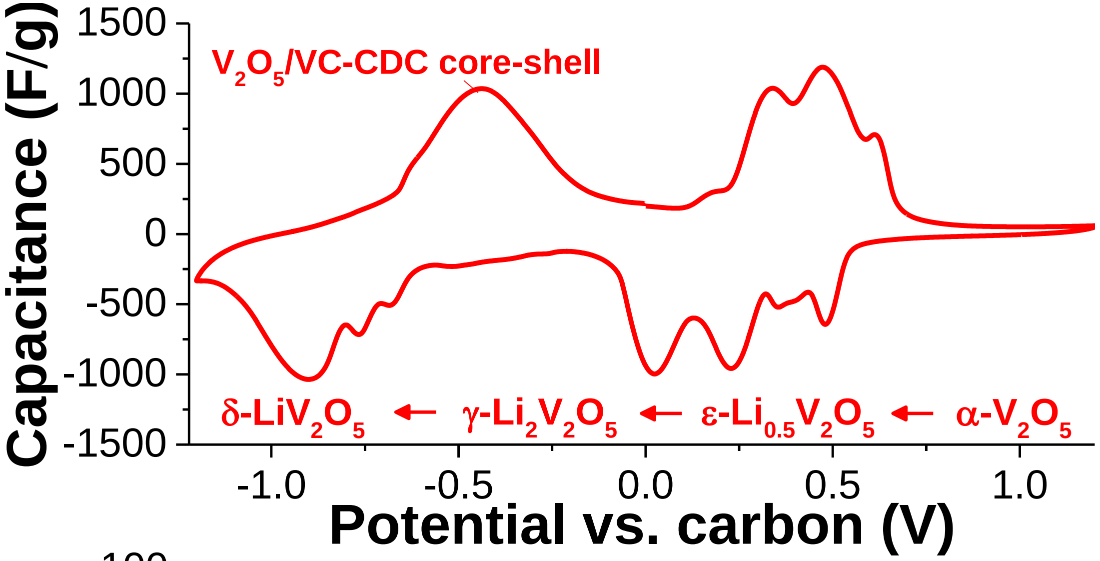
 Journal of Materials Chemistry A, 2015, 3, 3480-3490 / RSC Advances, 2016, 6, 107163-107179.

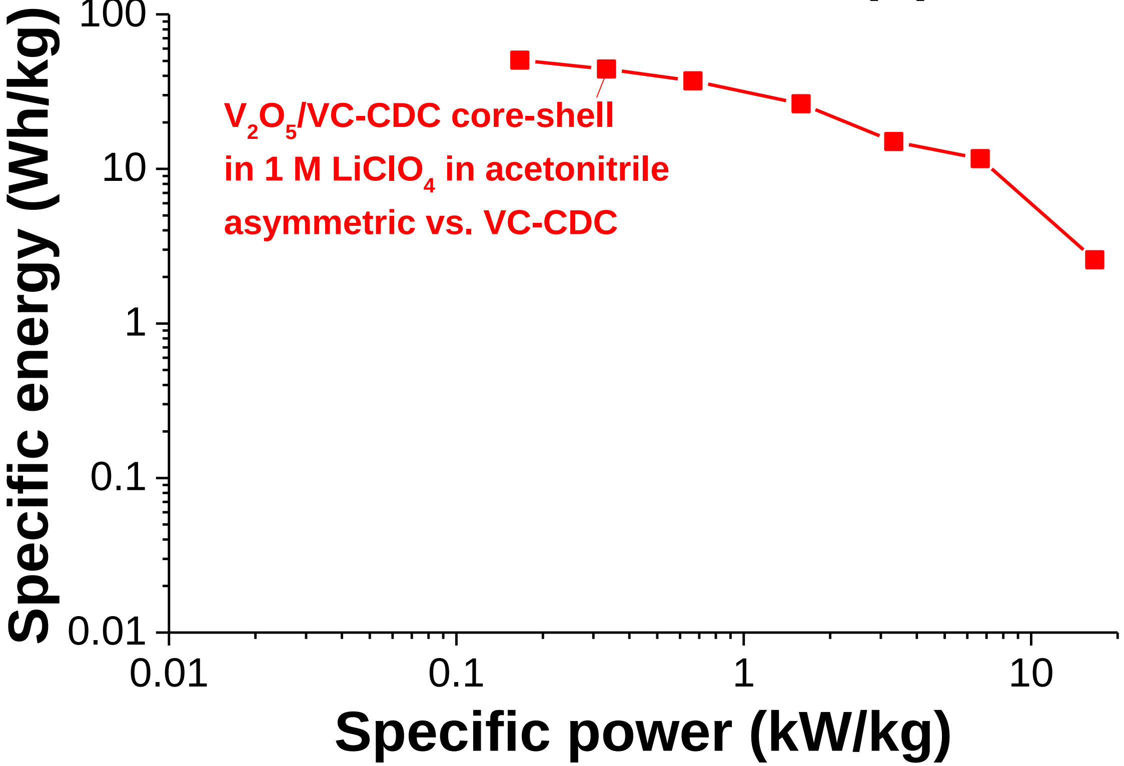
REDOX-ENABLING EDLC

METAL OXIDE / CDC HYBRID

- VC-derived V_2O_5/VC-CDC core-shell particles





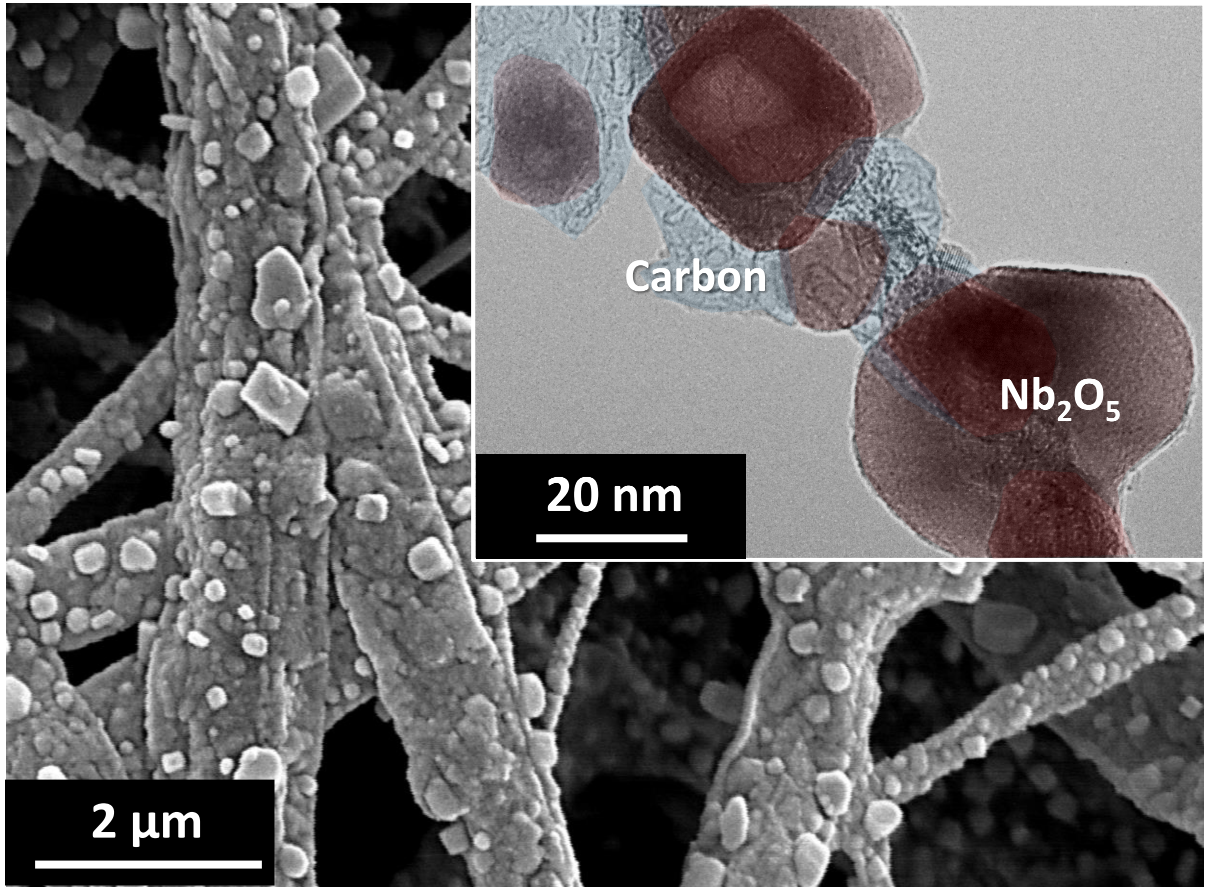


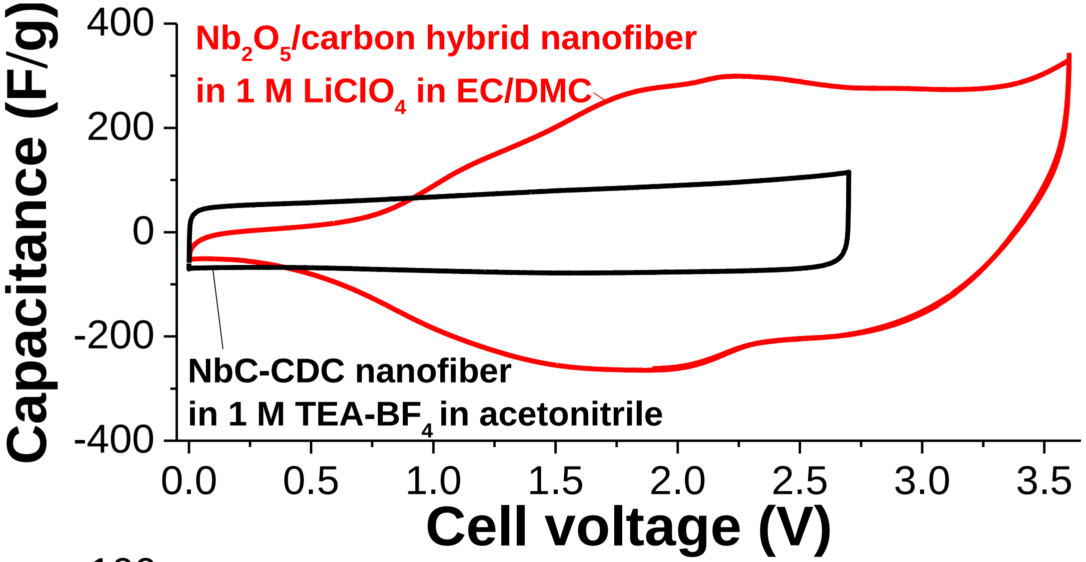
Journal of Materials Chemistry A, 2016, DOI:10.1039/C6TA08900C.

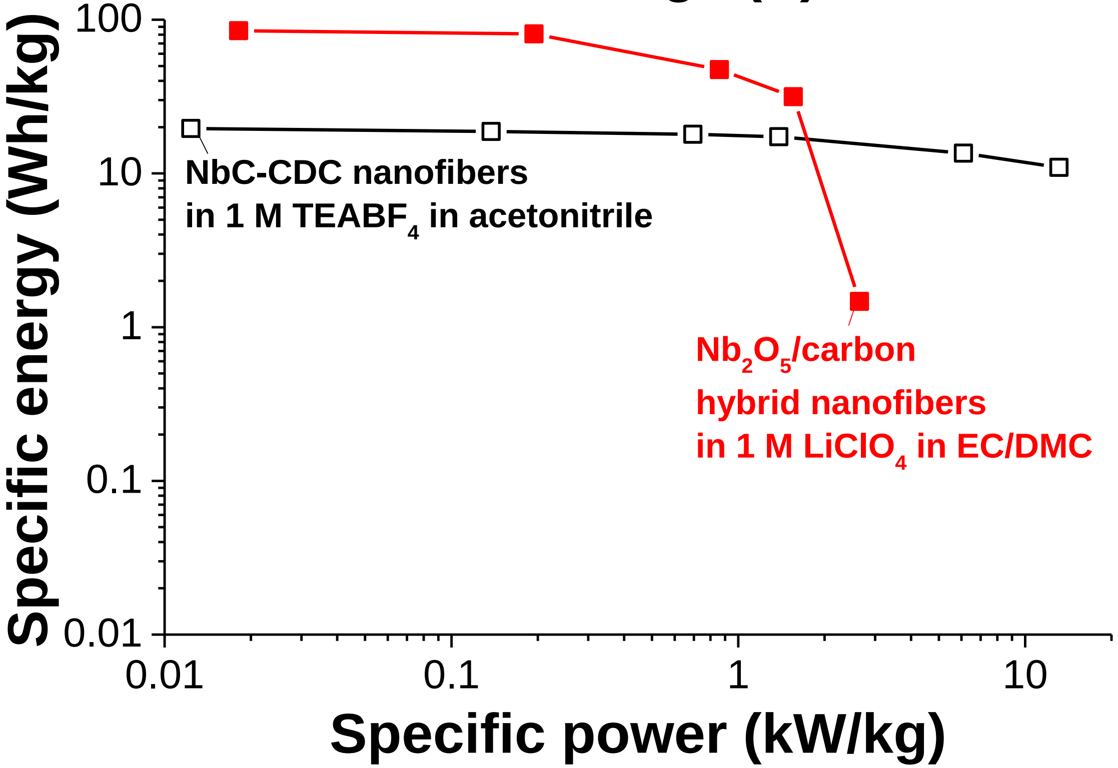
REDOX-ENABLING EDLC

METAL OXIDE / CARBON FIBER HYBRID

- **Electrospun Nb_2O_5/carbon nanofibers**





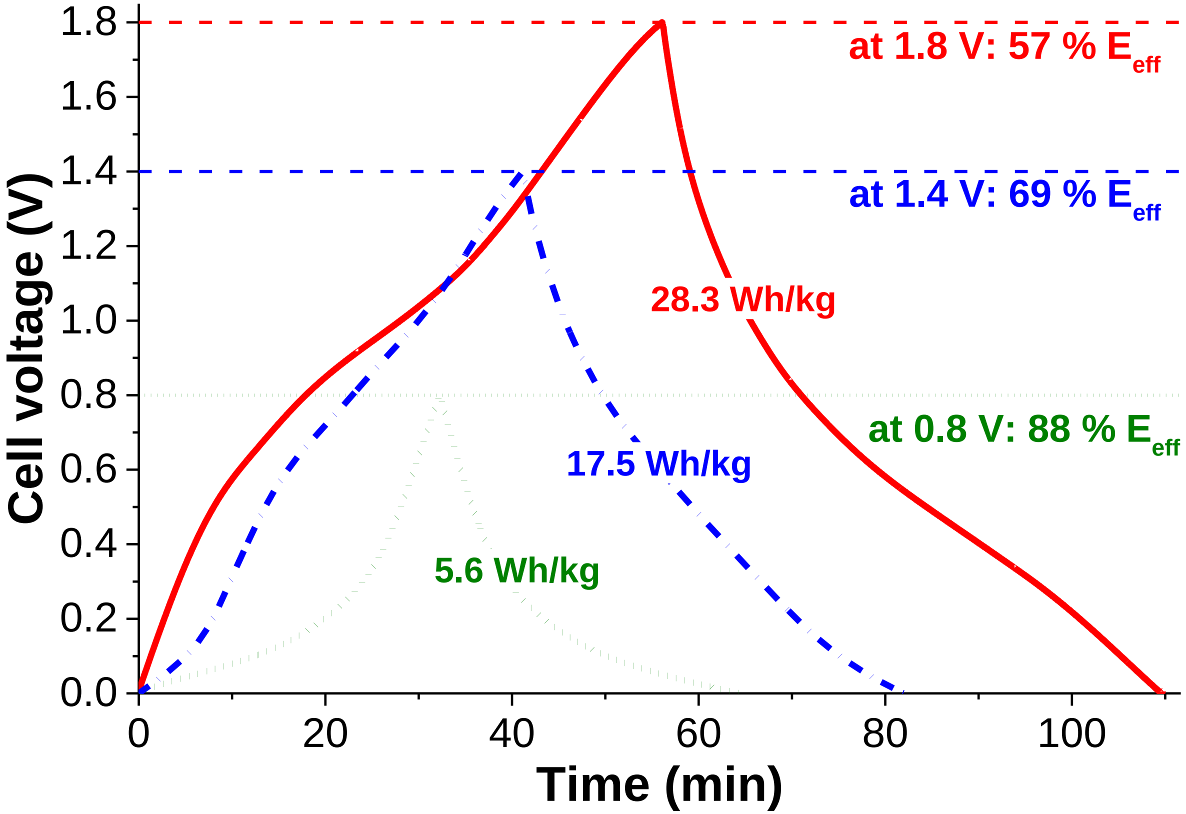


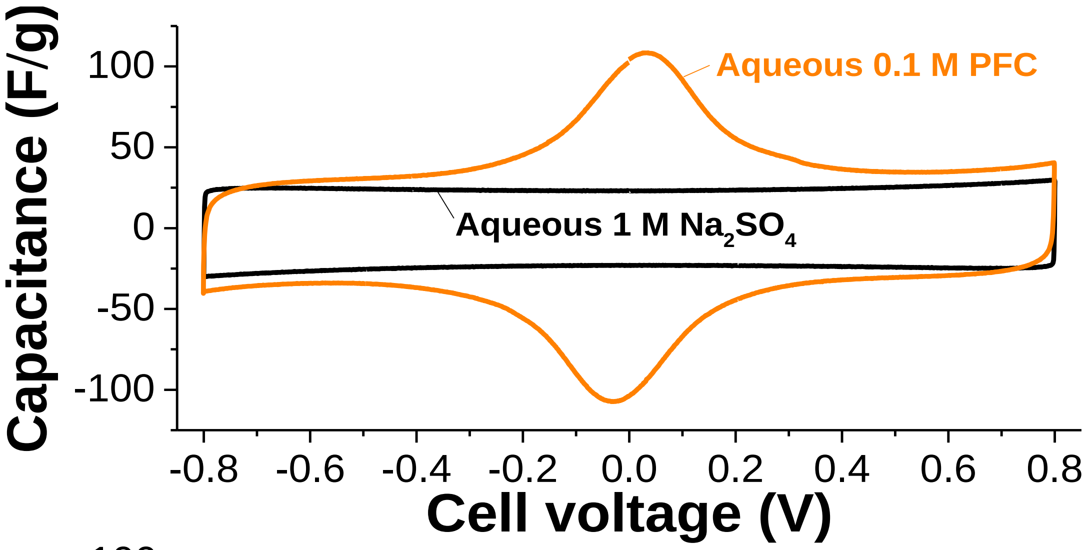
Journal of Materials Chemistry A, 2016, DOI: 10.1039/C6TA06224E.

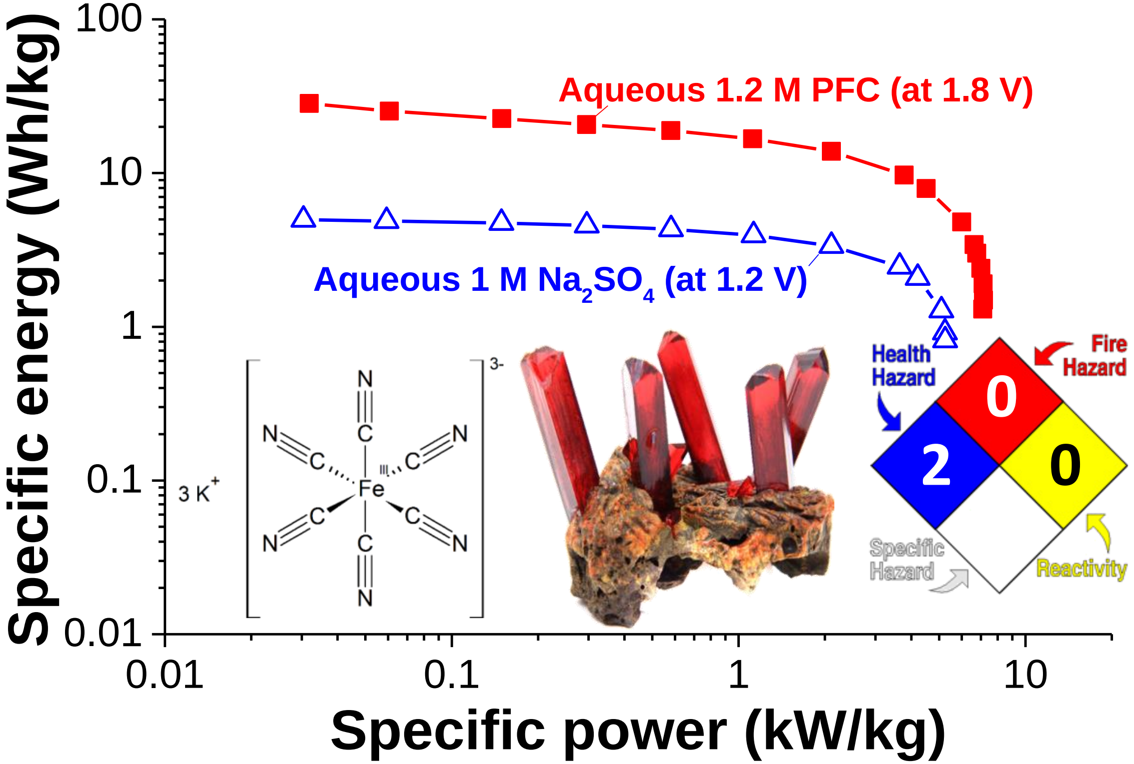
REDOX-ENABLING EDLC

POTASSIUM FERRICYANIDE (AQUEOUS)

- <u>Using conventional activated carbon (YP80)</u>





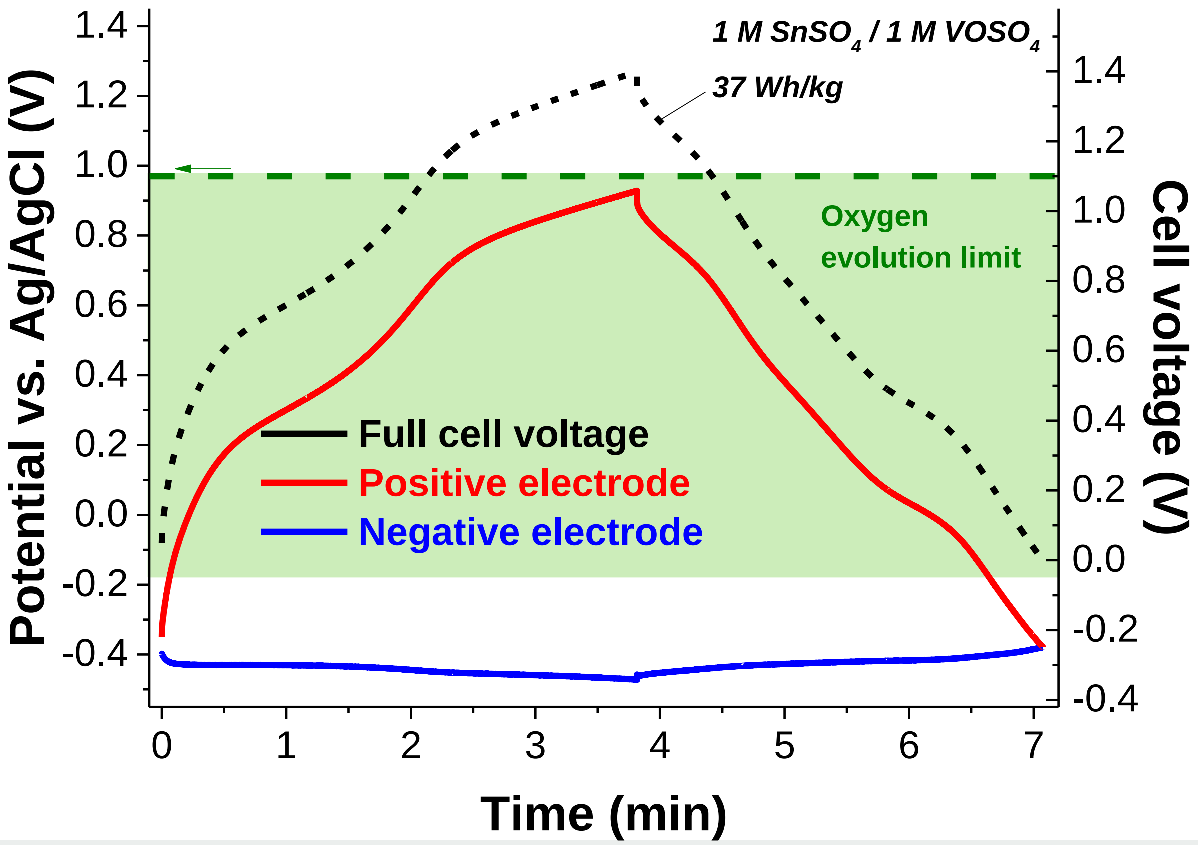


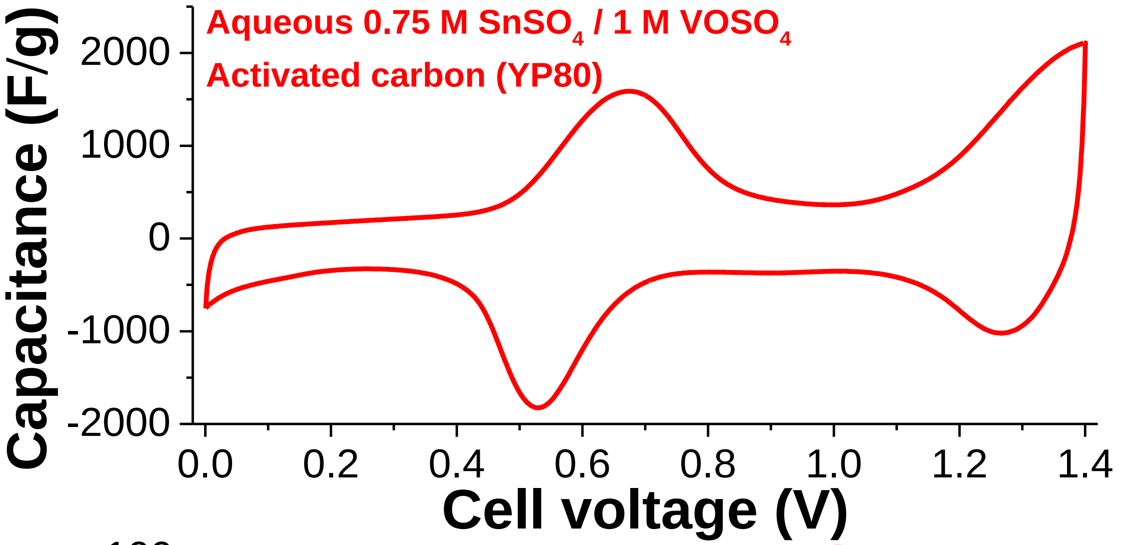
 ACS Applied Materials & Interfaces, 2016, 8, 23676-23687.

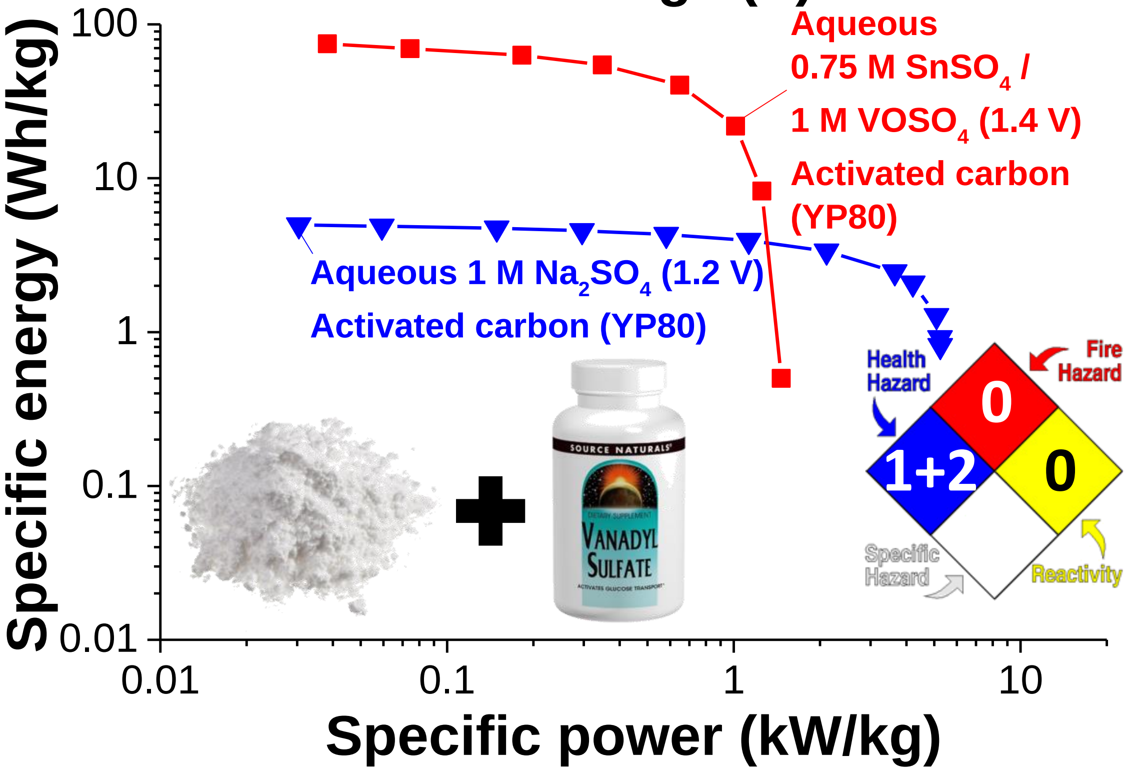
REDOX-ENABLING EDLC

TIN / VANADYL SULFATE (AQUEOUS)

- **<u>Using conventional activated carbon (YP80)</u>**





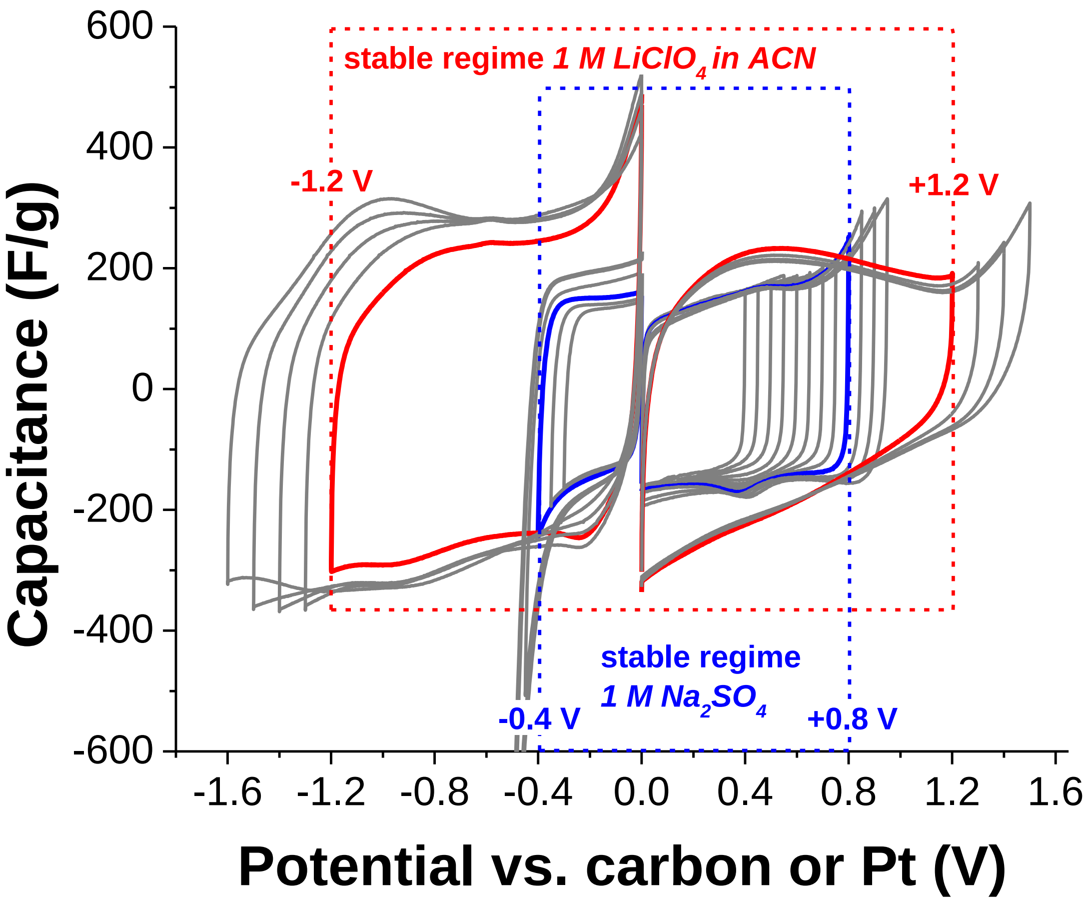


 Energy & Environmental Science, 2016, 9, 3392-3398.

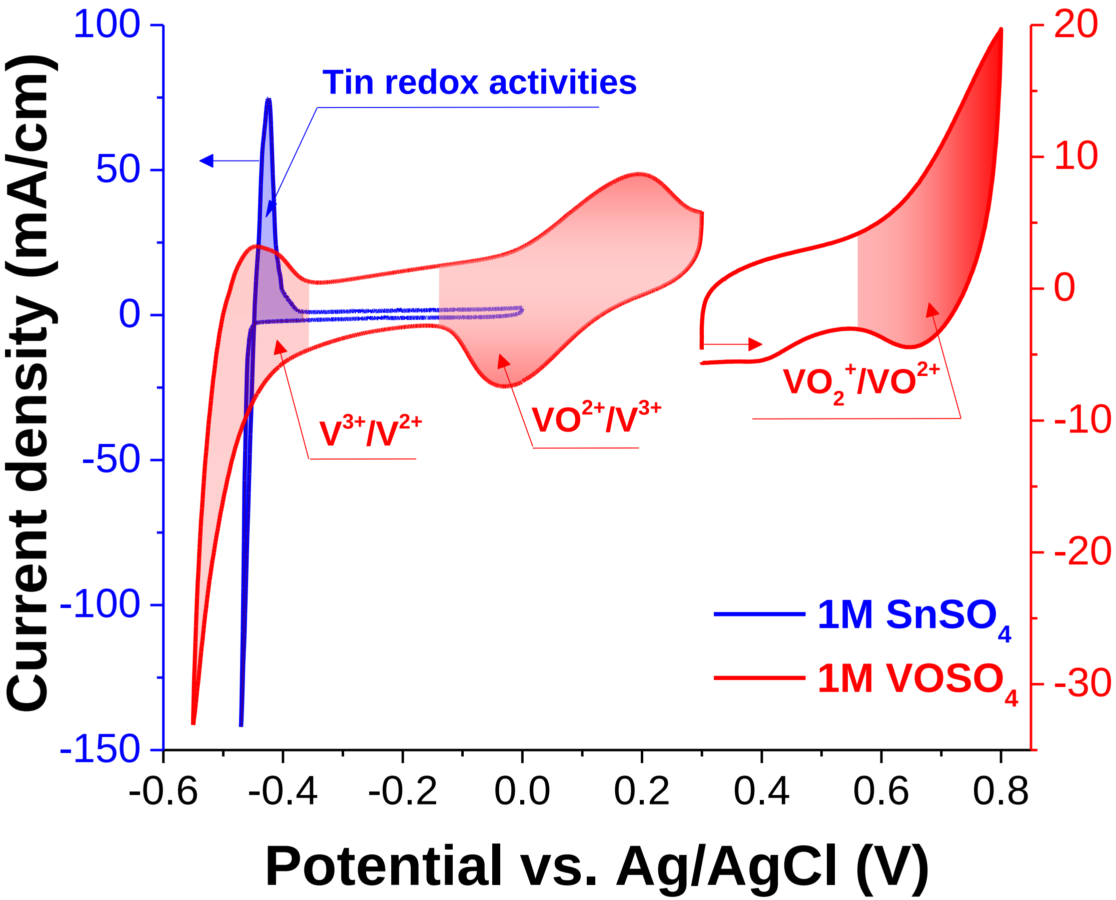
REDOX-ENABLING EDLC

CELL BALANCING AND VOLTAGE WINDOW OPTIMIZATION

Electrode balancing to compensate stability



Electrode balancing to maximize storage capacity



RSC Advances, 2016, 6, 107163-107179 / Energy & Environmental Science, 2016, 9, 3392-3398.

REDOX-ENABLING EDLC

TAKE HOME MESSAGES

- **Redox processes can severely boost the energy storage capacity**
- **Careful design of cell (electrode balancing / voltage window) is needed**
- **Redox processes in liquid phases particularly attractive**

“Green” energy storage?

“GREEN” ENERGY STORAGE?

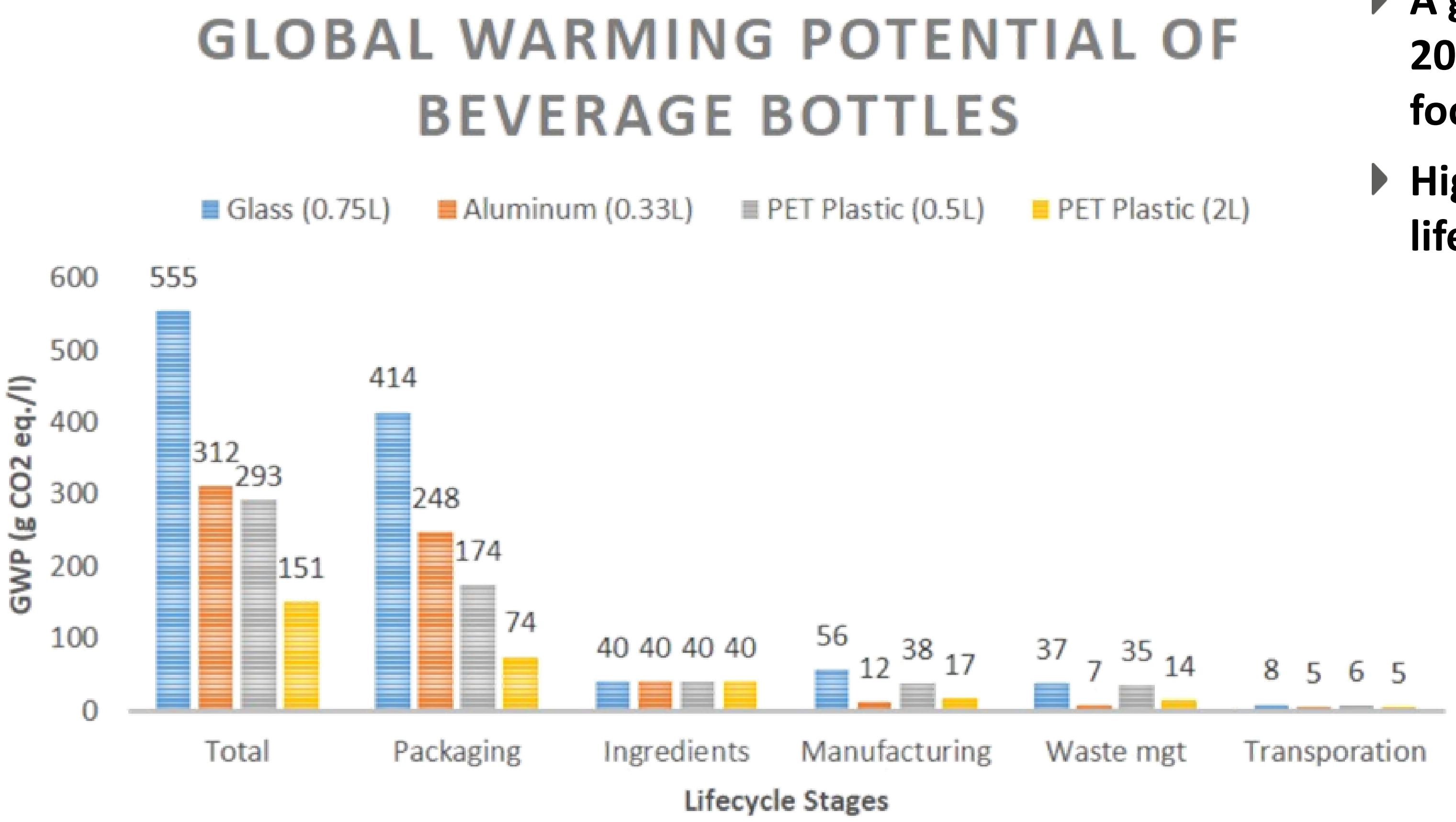
ACTUALLY, A DAILY QUESTION!

- Energy for mining / production
- Energy for packaging
- Energy for transport
- Energy for use
- Energy for recycling / disposal

- Light vs. heavy
- Abundant vs. rare
- Sustainable vs. non-renewable
- Local vs. far-far-away
- Toxin release vs. harmless

“GREEN” ENERGY STORAGE?

GLASS VS PLASTIC VS ALUMINUM



- **A glass bottle needs to be recycled at least 20-times to come down to the carbon footprint of a single-use PET bottle**
- **High need for comparable and realistic full-life-cycle assessment**

 http://verdefood.com/glass-vs-plastic/

"GREEN" ENERGY STORAGE?

LITHIUM ION BATTERY VS LEAD ACID ACCUMULATOR

For just one cycle (1 Wh)

- Energy needed for LIB is 2.7-times higher than for lead acid accumulator!
- High energy costs for lithium ion battery (LIB) processing (electrode materials)
- High energy cots for transport (esp. for lead acid battery, LAB, from Asia)

Factoring in device lifetime

- Lithium ion battery: 10.000 > Lead acid battery: 2.000

Thus, for a "normal" usage profile:

- Time for a device to turn "green" = when just the same amount of energy is stored as was needed for production:
  - LIB: 0.65 years
  - LAB: 1.86 years

→ **Light beats heavy**
Local beats long-distance

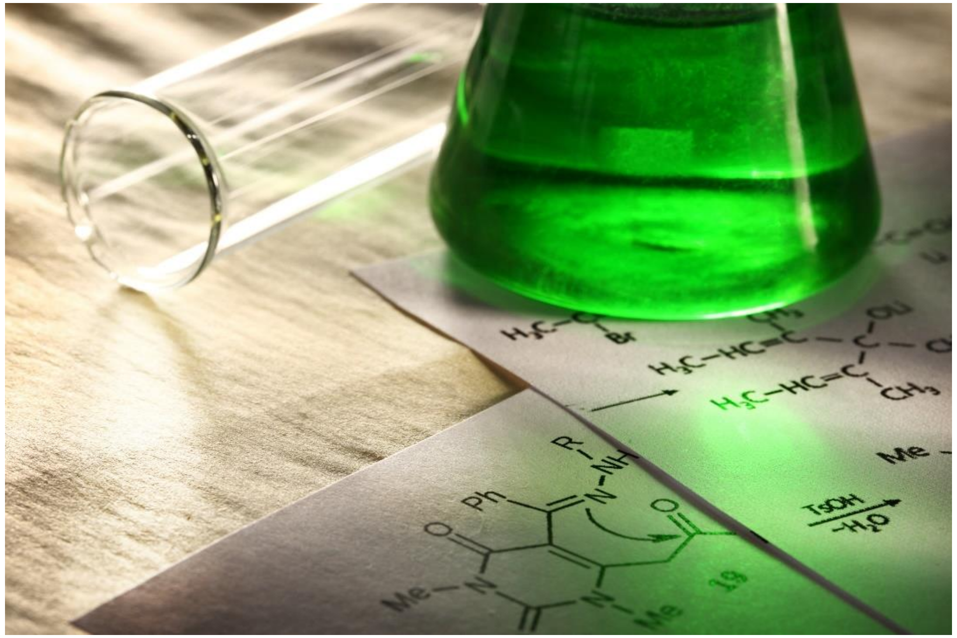
Unpublished data; for more, see the website of Prof. Dr. Karl-Heinz Pettinger at Hochschule Landshut


LOCALLY
GROWN

“GREEN” ENERGY STORAGE?

SOME GENERAL CONSIDERATIONS

- The challenge
  - Sustainability without higher price
  - Green synthesis compatible with existing processes
  - No decrease in performance (stability & ratings)



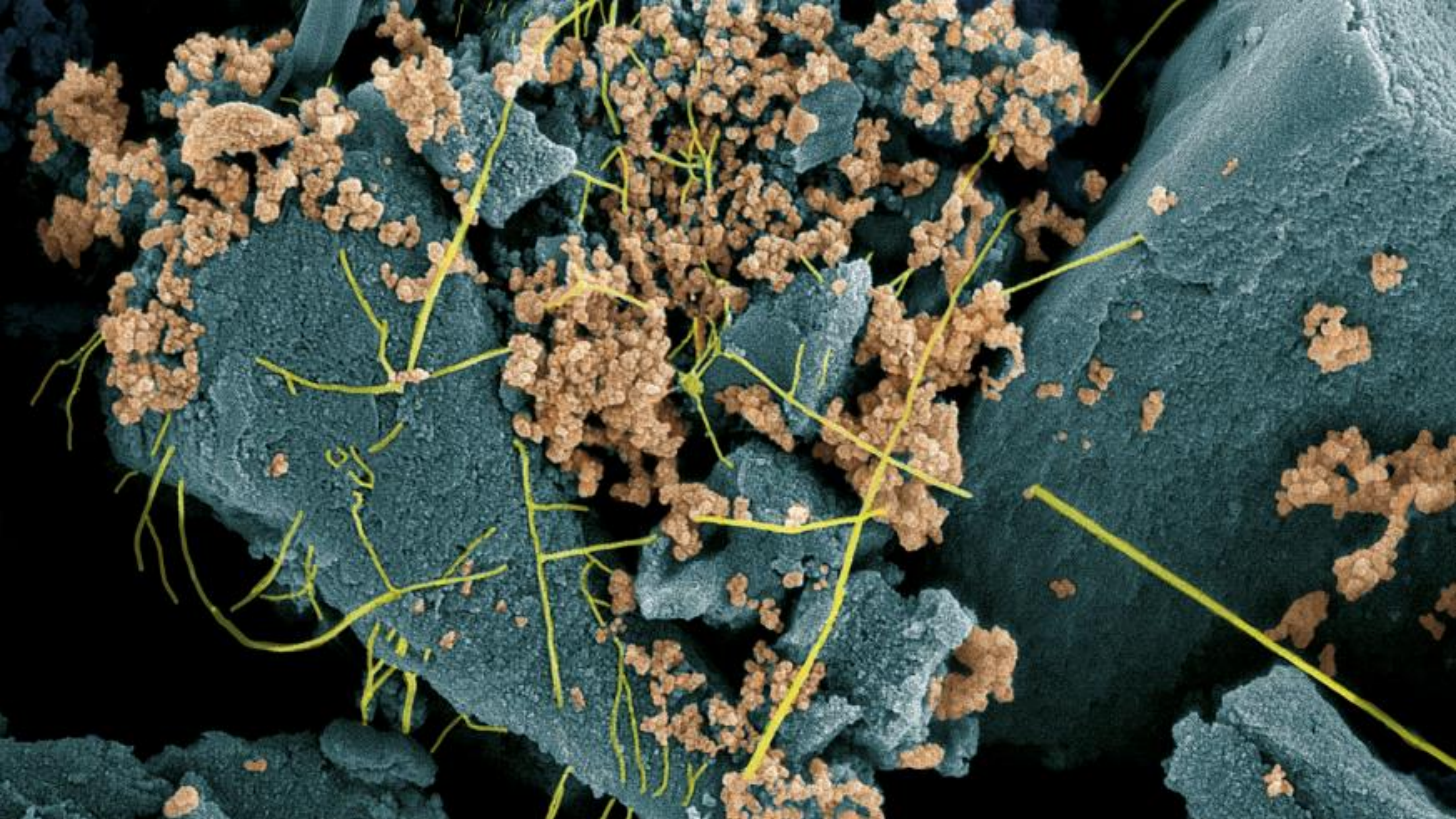
- Saving material by needing fewer cells
  - Improved energy & power ratings
  - Improved efficiency
- Saving energy related to transport
  - Lightweight construction
  - Use of local materials
- Saving energy related to production
  - Improved materials synthesis
  - Improved cell construction
- Sustainable chemistry
  - Green materials: Environmentally-friendly end-of-use
  - Green synthesis: Relaxed production processes

“GREEN” ENERGY STORAGE?

NOT ALL CARBON IS GREEN

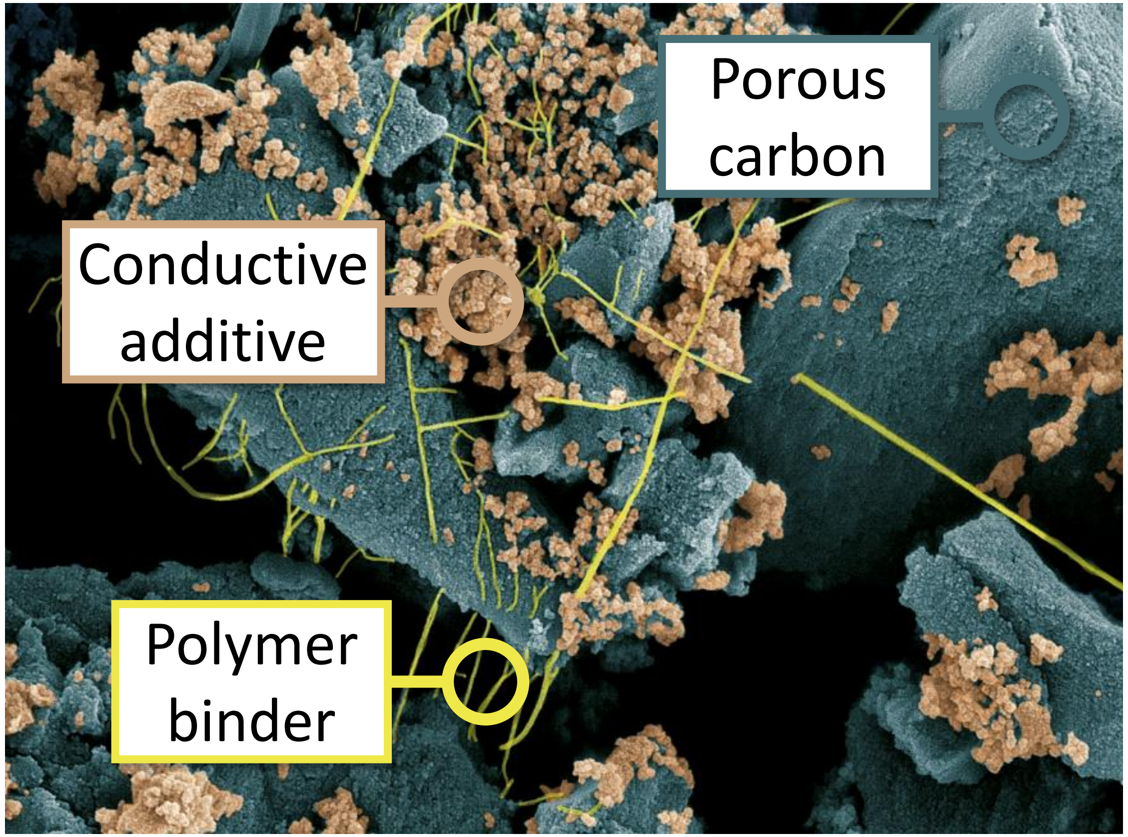
- **Palm plantation**

- **Crude oil**



"GREEN" ENERGY STORAGE?

CONDUCTIVE ADDITIVES AND BINDER MATERIALS



Conductive additive

- Improves electrode conductivity
- Usually employs carbon black or nanographite
- Commonly 5-10 mass% added
- Complications:
  - Dead mass -> reduced energy ratings
  - Lowered electrochemical stability

Binder

- Enables film coherence and processing
- Usually employs fluoropolymers
- Commonly 5-10 mass% added
- Complications:
  - Dead mass -> reduced energy ratings
  - Lowered electrical conductivity

 Jäckel N, Weingarth D, Zeiger M, Aslan M, Grobelsek I, Presser V. Journal of Power Sources. 2014;272(1):1122-33.

“GREEN” ENERGY STORAGE?

TAKE HOME MESSAGES

- Improved environmental friendliness is more realistic than targeting ideal green devices
- Greener processing is just as important as the use of green materials
- Water based electrolytes, esp. redox electrolytes, show great promise

Go green!
Go lightweight!
Go local!
Appreciate progress!