Supercapacitors

A. Balducci

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Outline

- High power applications: supercapacitors vs. batteries
- Supercapacitors
  - Components and materials
  - Techniques
- EDLC
  - Carbons
  - Electrolytes
- Pseudocapacitors
- Hybrid devices

Outline

- ➢ High power applications: supercapacitors vs. batteries
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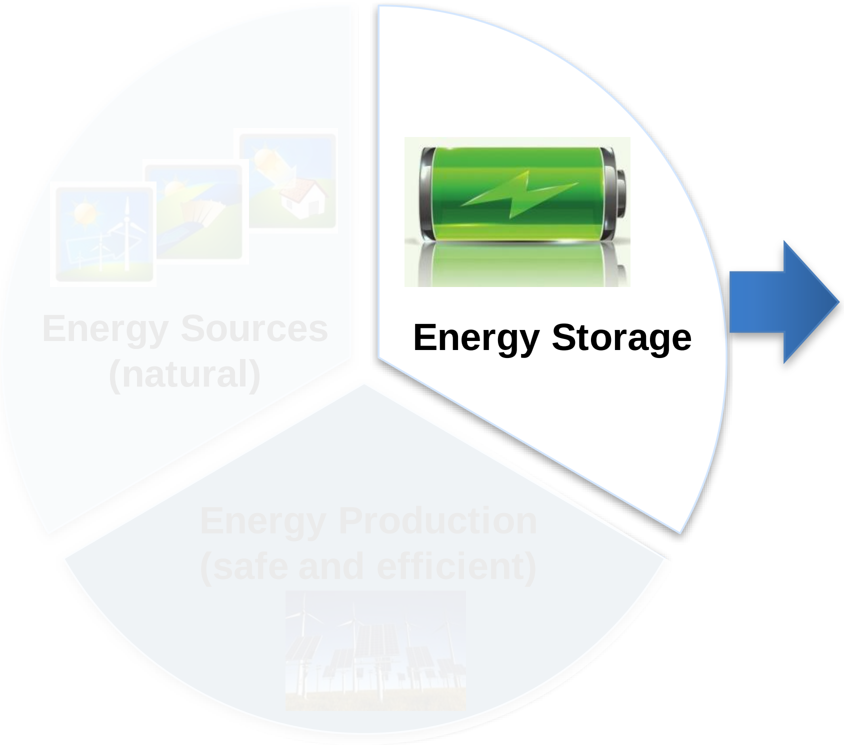
- ➢ EDLC
  - Carbons
  - Electrolytes
- ➢ Pseudocapacitors
- ➢ Hybrid devices

Energy delivering



We need to store high amount of energy

We need to deliver energy as desired

High power applications

Energy on demand

“Energy on demand”: An effective delivery is essential for an effective storage

In our daily life we are facing many different situations, and each of them requires a different **amount of energy** and, also, a different **delivery time**

There are situations in which we need:

Fast delivery/uptake: minutes or second

Repeated delivery: tens of thousands or million of times

High power applications

High power applications

Fast deliver of energy and high cycle life

High power applications

High power for emergency situations

Back-up systems in hospitals

Emergency doors in aircrafts

Fast delivery of energy, but long life is not a requirement

High power applications in transportation


“Stop and go” function


“Stop and go” in heavy vehicles


Electric vehicles


Peak power

Fast delivery of energy and high cycle life

High power applications

High power is required in public transportation

Trains

Buses

They can be charged at the station

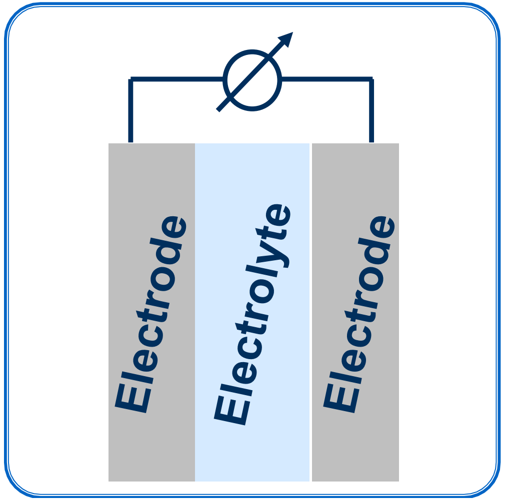
Fast delivery / uptake of energy and high cycle life

High power applications in stationary applications

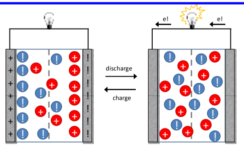
Fast delivery might be necessary to optimize the use of alternative energy sources and stabilize (smart) grid

High power and electrochemical devices

Electrochemical energy storage devices



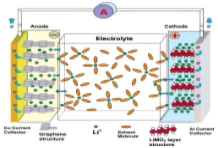
Physical storage



Double layer formation

Supercapacitors

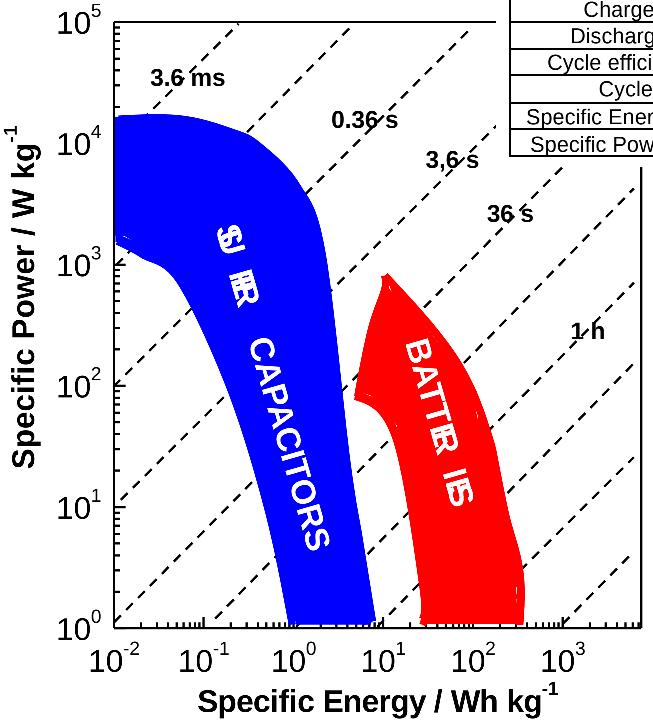
Chemical storage



Redox reaction

Lithium-ion batteries

EDLCs vs. LIBs



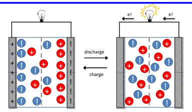
	SUPERCAPACITORS	**LITHIUM-ION BATTERIES**
Charge time	Seconds	Minutes
Discharge time	Seconds	Minutes
Cycle efficiency (%)	>95%	90%
Cycle life	>500.000	ca. 10000 @ 1C rate
Specific Energy (Wh/kg)	5	70-100
Specific Power (kW/kg)	5-10	0.5-1

Higher power

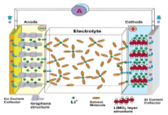
Extraordinary cycle life

Higher energy

Medium cycle life



Double layer formation



Redox reaction

Physical Storage

No charge transfer

Chemical Storage

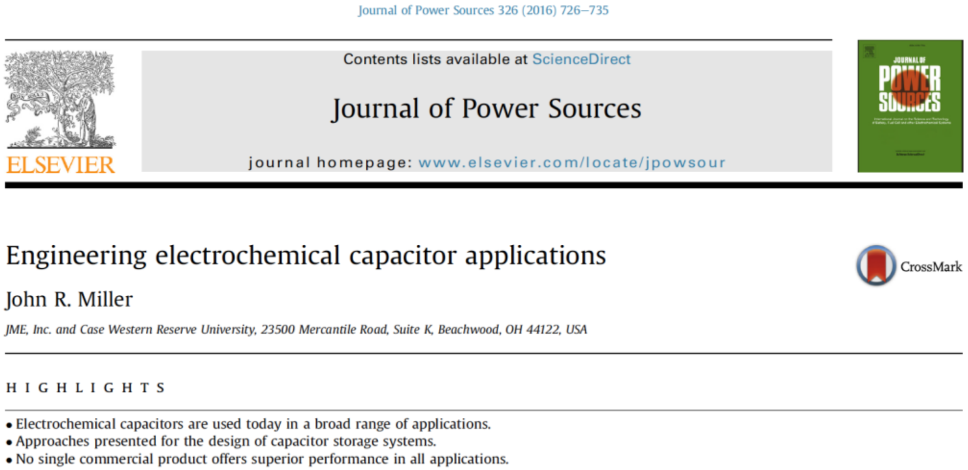
Charge transfer

EDLCs applications

Electrochemical Capacitors:
Challenges and Opportunities for Real-World Applications

by John R. Miller and Andrew F. Burke

Interface **2008**



Journal of Power Sources 326 (2016) 726–735

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Engineering electrochemical capacitor applications

John R. Miller

JME, Inc. and Case Western Reserve University, 23500 Mercantile Road, Suite K, Beachwood, OH 44122, USA

HIGHLIGHTS

- Electrochemical capacitors are used today in a broad range of applications.
- Approaches presented for the design of capacitor storage systems.
- No single commercial product offers superior performance in all applications.

EDLCs vs. LIBs

City bus with “stop and go” driving: thousand start/stop during a day

Fɪɢ. 2. *Hybrid city transit bus that uses an electrochemical capacitor energy storage system. Typical charge/discharge periods may be forty seconds in this application with continuous 16-hours-per-day operation (>1000 charge/discharge cycles each day). (Photo courtesy of ISE Corporation.)*

High cycle life
Need to dissipate the heat generation due to charge-discharge losses

Supercap: 3000F, 2,7 V
High power battery: 12Ah

EDLCs vs. LIBs

Supercap: 3000F, 2,7 V
High power battery: 12Ah

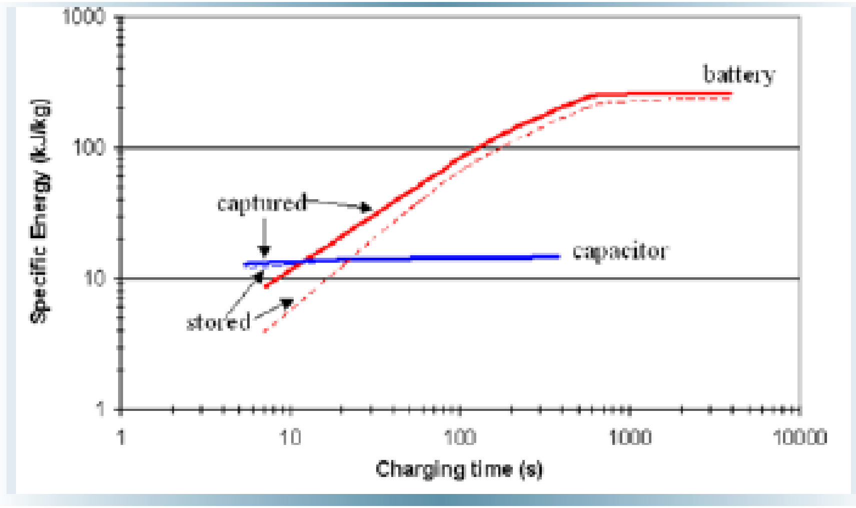
Test performed by measuring the amount of energy captured by each device for various constant-current charge times

The stored regenerative energy was the amount of energy that could be discharge after the charge

Charging:
2,7 V for supercap
2,8 V for battery

Initial state
Supercapacitor 1,35 V
Battery 10% SOC

EDLCs vs. LIBs



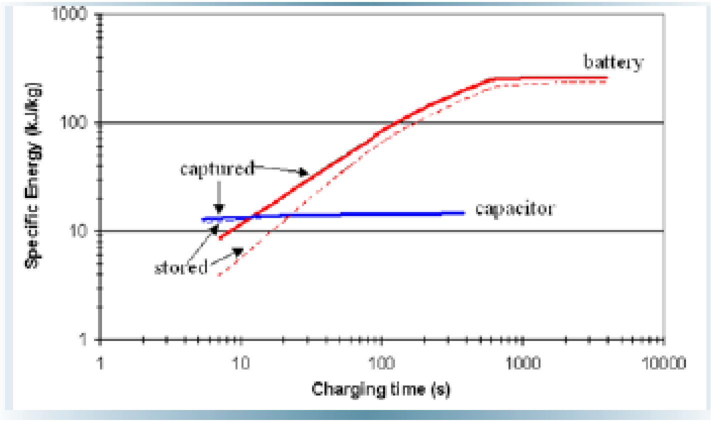
t>600 s (10 minutes)
Battery has a constant ca. 15 times higher specific energy than the capacitors

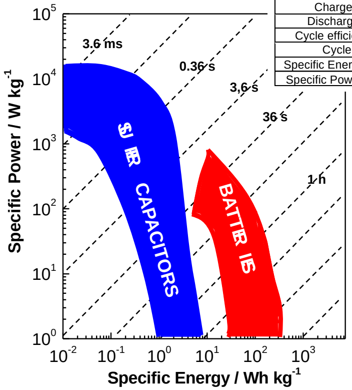
t= 100 s battery capture ca. 5 times more energy than capacitor

t= 10 s battery and supercap capture the same specific energy.
BUT, supercap can discharge ca. 95% of this amount, while the battery only ca. 50% of the amount.
The effective energy density of the capacitor is twice that of the battery (that will need larger cooling system to remove the dissipate energy)

T<10 s supercap better performance (specific energy remain flat well below 10 s)

EDLCs vs. LIBs





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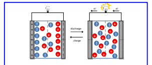
Higher power

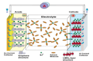
Extraordinary cycle life

Higher energy

Medium cycle life



Double layer formation



Redox reaction

Physical Storage

No charge transfer

Chemical Storage

Charge transfer

Supercaps more appropriate for high power application

Battery not well suited for high-rate cyclic operation

Only a relatively small fraction of the battery´s energy can be utilized

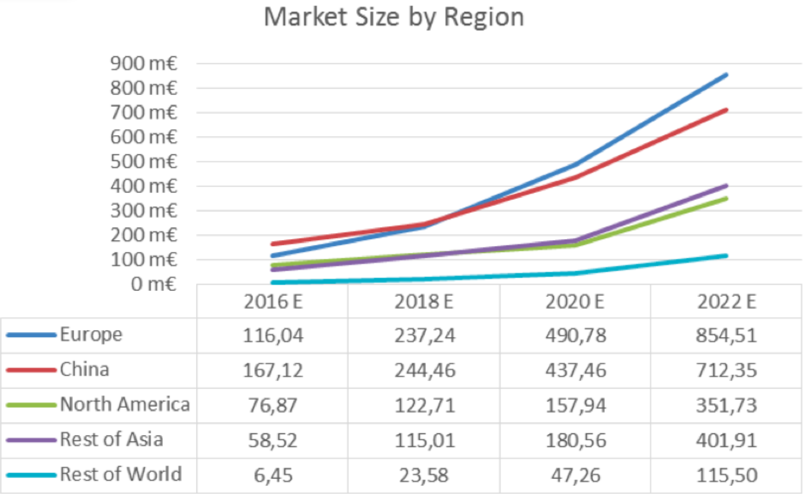
High power applications

There is a strong need of high power systems

High power systems need to display:

- High power
- Relatively high energy
- Short charge-discharge time
- High cycle life
- Reliability
- Large applicability
- High safety

Market Size by Region



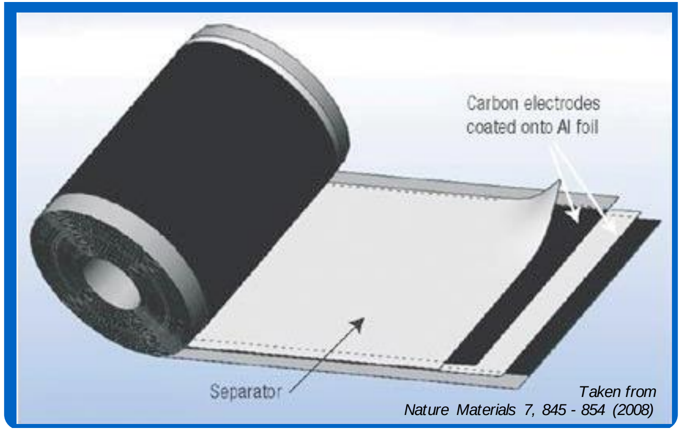
	2016 E	2018 E	2020 E	2022 E
Europe	116,04	237,24	490,78	854,51
China	167,12	244,46	437,46	712,35
North America	76,87	122,71	157,94	351,73
Rest of Asia	58,52	115,01	180,56	401,91
Rest of World	6,45	23,58	47,26	115,50

Source:IDTechEx

Global market supercapacitor in 2016 was ca. 450 million USD

Supercapacitor producers

- Maxwell (USA)
- Ioxus (USA)
- JSR Micro (Japan)
- Nippon Chemi-Con Corporation(Japan)
- Nesscap (Korea)
- Cap-XX (Australia)
- Yunasko (Russia)
- Skeleton (Estonia-Germany)



Taken from
Nature Materials 7, 845 - 854 (2008)

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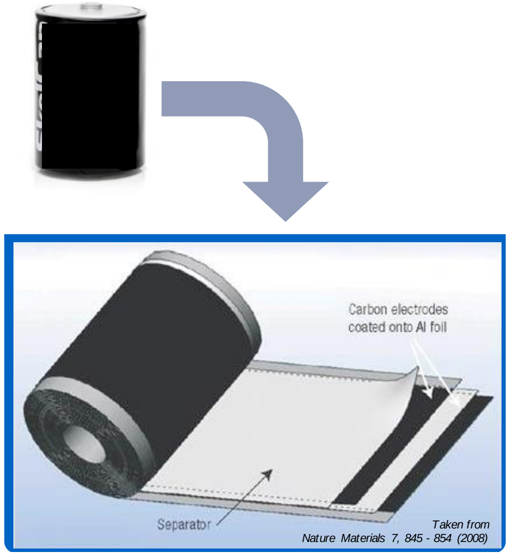
- Pseudocapacitors
- Hybrid devices

Supercapacitor components



Taken from
Nature Materials 7, 845 - 854 (2008)

CELL COMPONENTS

Casing

ELECTRODE COMPONENTS

Active material
Conducting agent
Binder
Current collectors

ELECTROLYTE COMPONENTS

Solvent
Conducting salt

ACTIVE MATERIALS

INACTIVE MATERIALS

Supercapacitor classification

- Active material
- Type of electrolyte
- “Degree of hybridization”

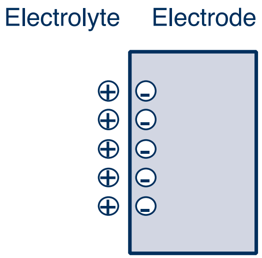
Supercapacitors

Electrochemical Capacitors

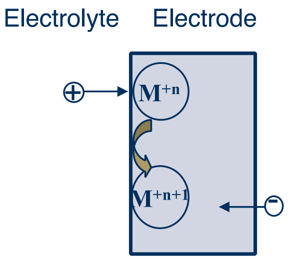
EC Double Layer Capacitor

Pseudocapacitors

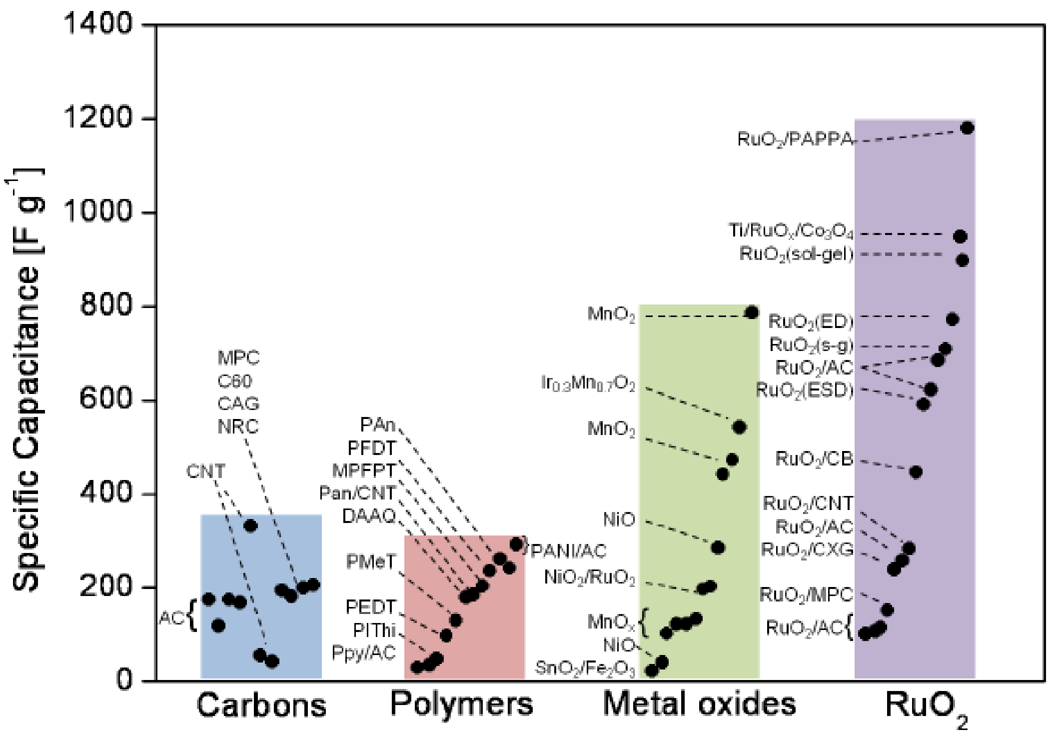
Non-Faradaic
(no transfer of charge)



Pseudocapacitance
Charge transfer through surface
Faradaic, redox reactions

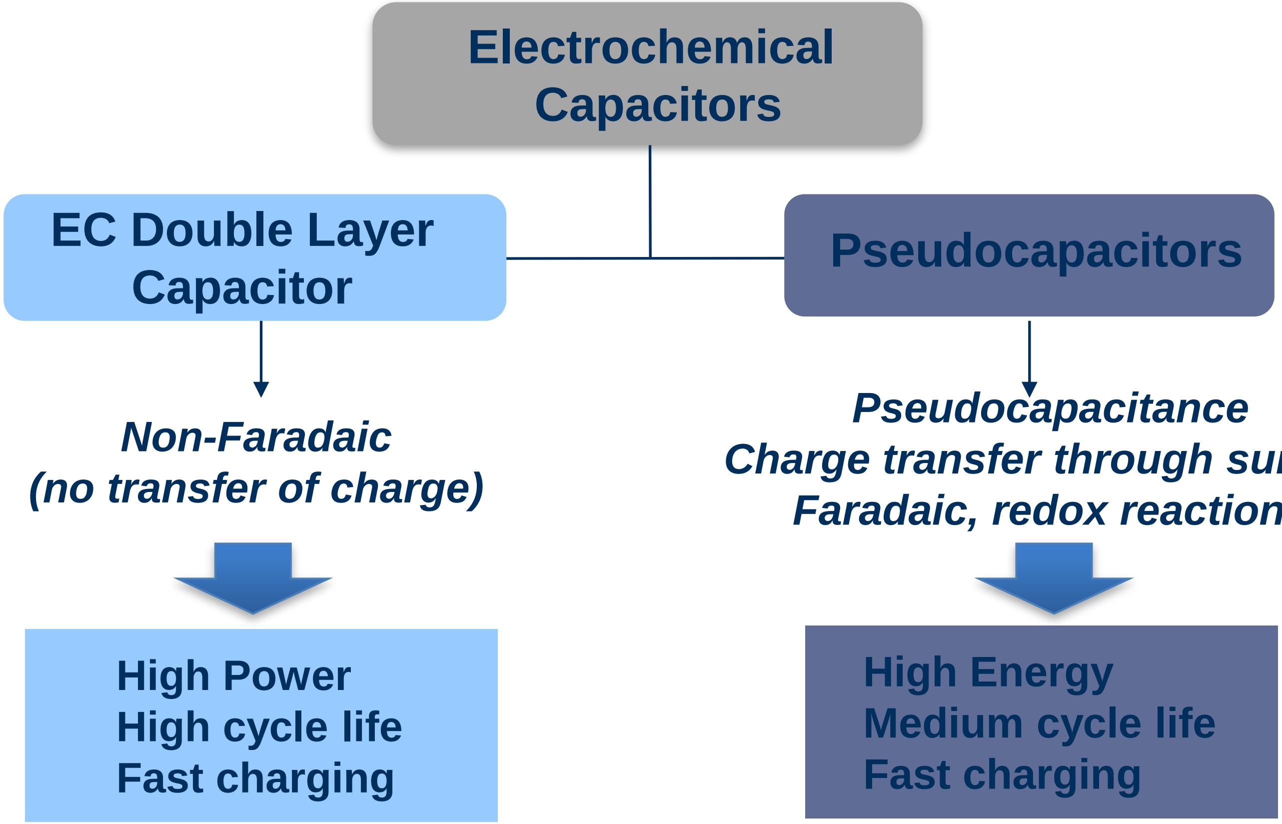


Active materials in supercapacitors



K. Naoi, P. Simon, *Interface* **2008**, 17, 34

Supercapacitors



Electrochemical Capacitors

EC Double Layer Capacitor

Non-Faradaic
(no transfer of charge)

High Power
High cycle life
Fast charging

Pseudocapacitors

Pseudocapacitance
Charge transfer through surface
Faradaic, redox reactions

High Energy
Medium cycle life
Fast charging

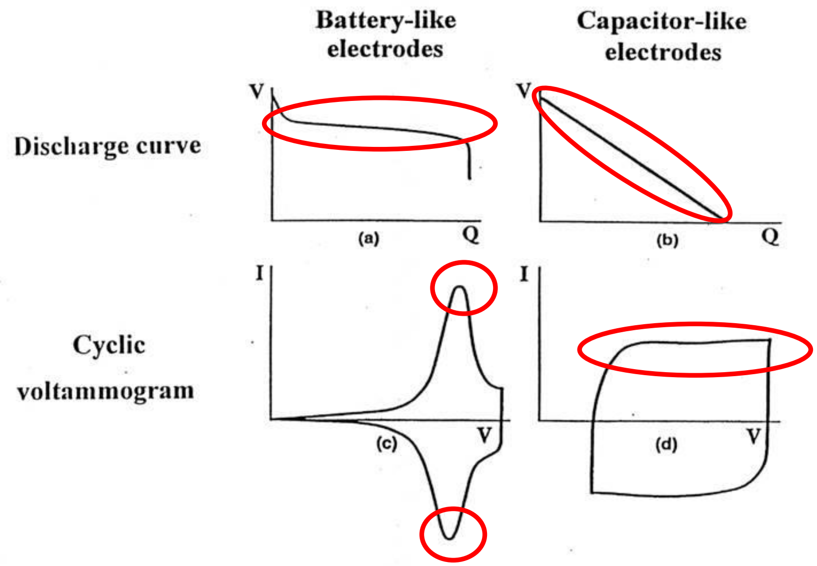
Capacitor-like and battery-like electrodes

Capacitor-like electrodes

The charge discharge process is limited only by the electrochemical stability of the electrolyte

Battery-like electrodes

The charge discharge process take place ONLY at well defined potential



Energy and power

$$\boxed{E_{max} = \frac{1}{2} C V^2}$$

$$\boxed{P_{max} = \frac{V^2}{4R}}$$

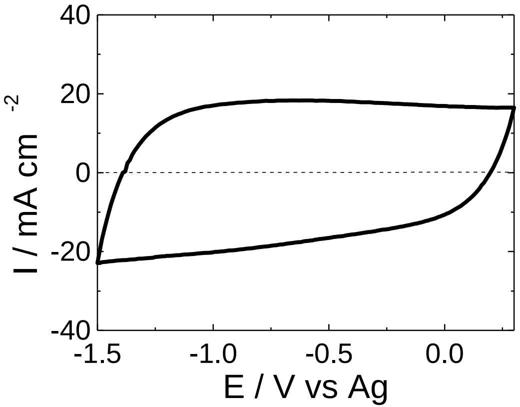
C = Capacitance
V = Maximum supercap voltage
R = Equivalent Series Resistance (ERS)

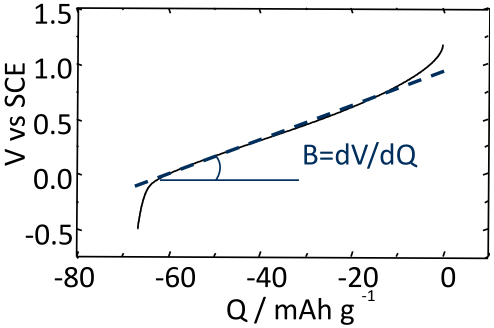
- Maximum supercapacitor voltage ($\Delta V_{max,Sc}$) $DV_{max,Sc} = V_{max,+} + | V_{max,-} |$

- Supercapacitor specific capacitance (C_{Sc}) $C_{Sc} = \left(\frac{1}{C_+ w_+} + \frac{1}{C_- w_-}\right)^{-1} / w_{Sc}$

- Equivalent Series Resistance (ESR) $ESR = R_{ionic} + R_{electronic}$

Performance metrics (from CV)





i (A/cm^2) = current density
s (V/s) = scan rate
m(g/cm^2)= electrode mass

SPECIFIC CAPACITANCE

a) $C\ (F/g) = i/(s \times m)$

b) $C\ (F/g) = 3.6 \times dQ/dV = 3.6/B$

SPECIFIC CAPACITY

$Q\ (mAh/g) = \int i dV/(s \times m \times 3.6)$

COULOMBIC EFFICIENCY

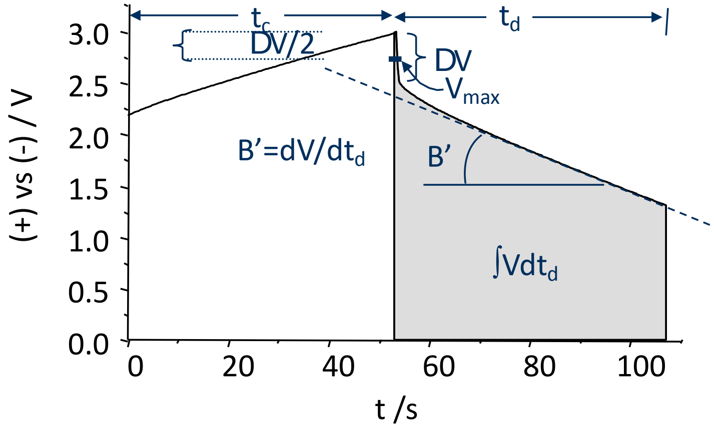
charge-discharge process

$h\% = (Q_{discharge} / Q_{charge}) \times 100$

CYCLING STABILITY

$\%$ capacity fade $= [1-(Q_{1000th\ cycle} / Q_{10th\ cycle})] \times 100$

Performance metrics (from CC)



t_c (s) = time of charge
t_d (s) = time of discharge
w_{act}(g/cm^2) =total active mass
w_{comp}(g/cm^2) =total composite mass
i (A /cm^2) = current density
V_{max}(V) = maximum cell voltage
ESR (Wcm^2) = DV/(2 × i)

DEVICE CAPACITANCE

C (F/cm^2) = i (dt_d/dV) =i/B'

MAXIMUM SPECIFIC POWER

P_{max} (W/kg)= $V_{max}{}^2$/(4*ESR*w_{comp})

COULOMBIC EFFICIENCY

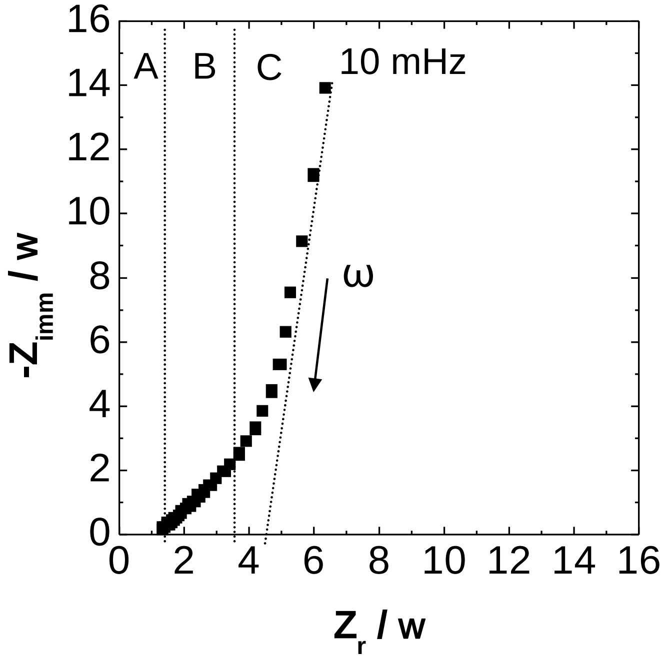
of the charge-discharge process h% = t_d/t_c×100

CYCLING STABILITY

% capacity fade = [1-($Q_{1000^{th}\ cycle}$/ $Q_{10^{th}\ cycle}$)]×100

Performance metrics (from impedance spectroscopy)

From 10KHz to 10 mHz



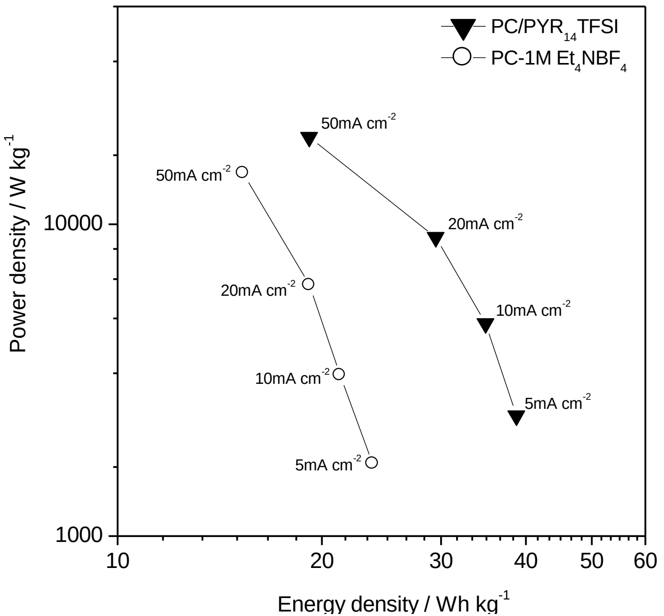
A (high frequency)= pure resistivity behaviour
Uncompensated resistance (bulk) $Z_{imm}=0$

B (intermediate frequency)= the signal “penetrate” more deeply into the porous structure of the electrodes. The capacitive behaviour appears in the diagram

C (low frequency)= the capacity behaviour dominate and it is visible in the linear part of the diagram. Limit capacitance can be calculated using:

$$C = \frac{1}{2pnZ_{imm}}$$

Energy and power



AVERAGE SPECIFC ENERGY

$$\mathbf{E_{av}}\ (\mathrm{Wh/kg}) = i\times\int V dt_S/(w_{comp}\times 3.6)$$

AVERAGE SPECIFC POWER

$$\mathbf{P_{av}}\ (\mathrm{W/kg}) = E_{av}\times 3600/t_S$$

t_S (s) = discharge time
w_{comp}(g/cm^2) = total mass composite electrode materials per cm^2
i (A /cm^2) = current density

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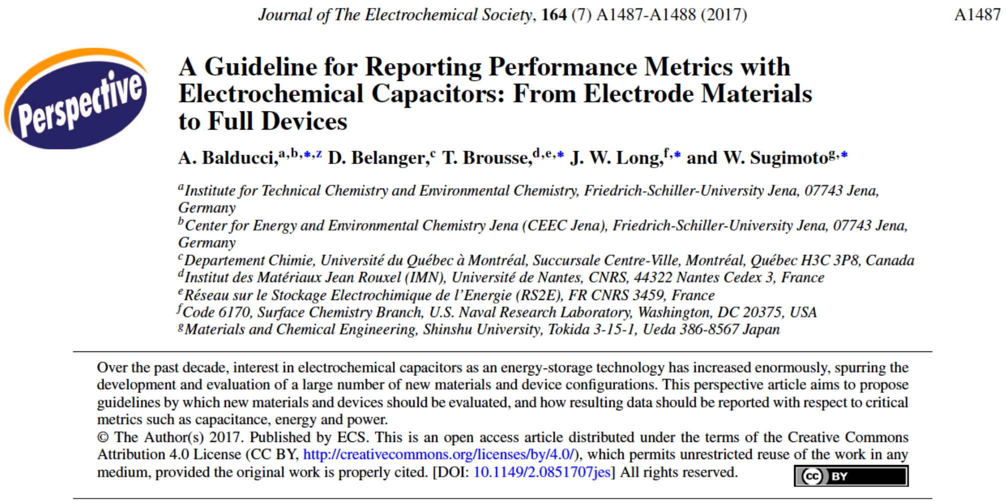
Performance metrics



Journal of The Electrochemical Society, **164** (7) A1487-A1488 (2017) A1487

Perspective

A Guideline for Reporting Performance Metrics with Electrochemical Capacitors: From Electrode Materials to Full Devices

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[b] Center for Energy and Environmental Chemistry Jena (CEEC Jena), Friedrich-Schiller-University Jena, 07743 Jena, Germany
[c] Departement Chimie, Université du Québec à Montréal, Succursale Centre-Ville, Montréal, Québec H3C 3P8, Canada
[d] Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 44322 Nantes Cedex 3, France
[e] Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France
[f] Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC 20375, USA
[g] Materials and Chemical Engineering, Shinshu University, Tokida 3-15-1, Ueda 386-8567 Japan

Over the past decade, interest in electrochemical capacitors as an energy-storage technology has increased enormously, spurring the development and evaluation of a large number of new materials and device configurations. This perspective article aims to propose guidelines by which new materials and devices should be evaluated, and how resulting data should be reported with respect to critical metrics such as capacitance, energy and power.

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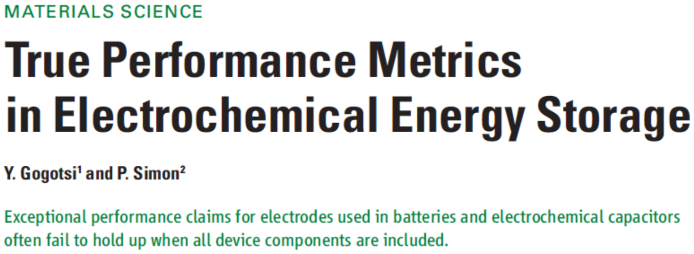

MATERIALS SCIENCE

True Performance Metrics in Electrochemical Energy Storage

Y. Gogotsi[1] and P. Simon[2]

Exceptional performance claims for electrodes used in batteries and electrochemical capacitors often fail to hold up when all device components are included.

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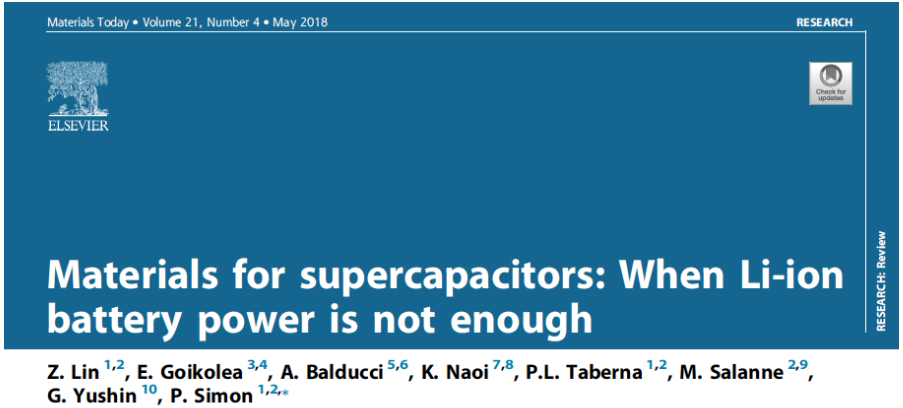
EDLCs



Materials Today • Volume 21, Number 4 • May 2018

RESEARCH

ELSEVIER

Check for updates

RESEARCH: Review

Materials for supercapacitors: When Li-ion battery power is not enough

Z. Lin [1,2], **E. Goikolea** [3,4], **A. Balducci** [5,6], **K. Naoi** [7,8], **P.L. Taberna** [1,2], **M. Salanne** [2,9], **G. Yushin** [10], **P. Simon** [1,2,*]

Materials Views

www.MaterialsViews.com

ADVANCED MATERIALS

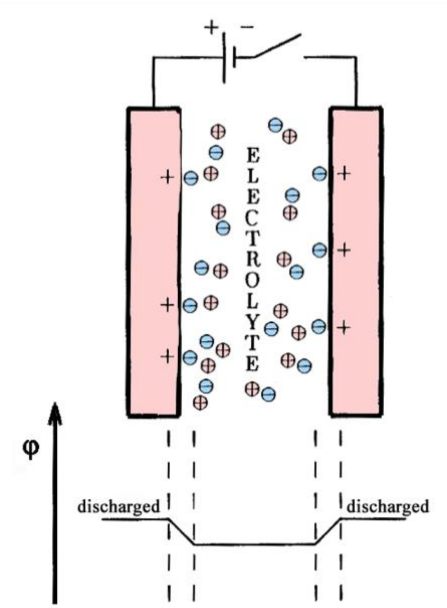
www.advmat.de

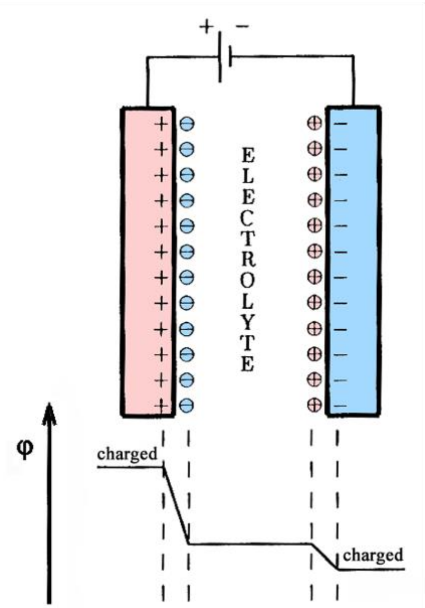
Carbons and Electrolytes for Advanced Supercapacitors

François Béguin, Volker Presser, Andrea Balducci, and Elzbieta Frackowiak*

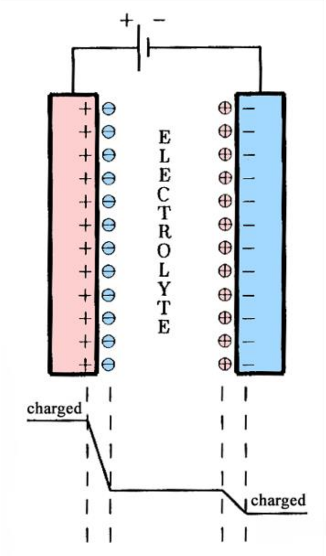
EDLCs

Electrochemical double layer capacitors (EDLCs) store the electric energy in an electrochemical double layer formed at the solid/electrolyte interface

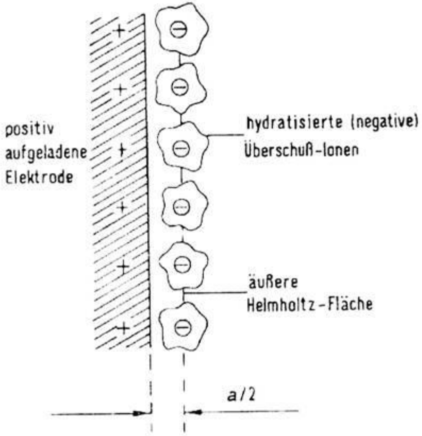




Electrical double layer



Helmholtz model



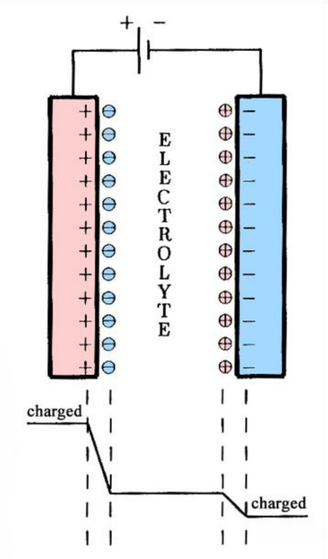
Bidimensional

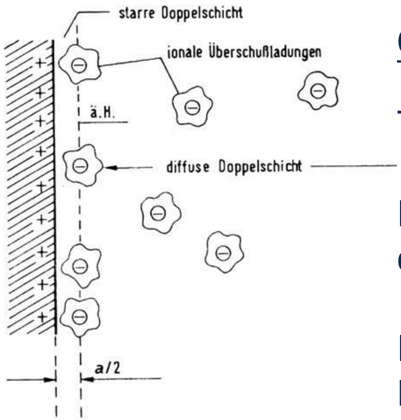
Describe the excess of charge of solvated ions at the interface metal/electrolyte.

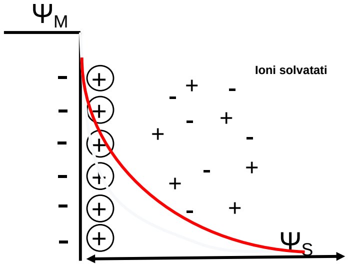
Distance between solvated ions and metal is comprise between 0.2 and 0.5 nm

After, the double layer is called external layer

Electrical double layer







Gouy-Chapman model

Tridimensional

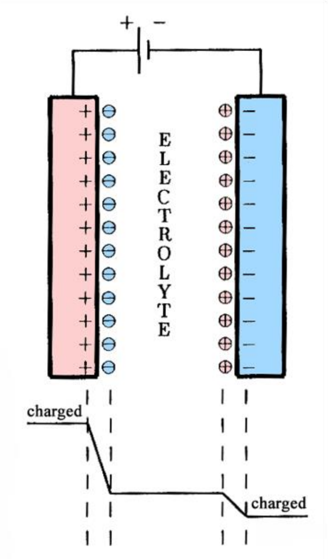
Introduce a factor related with the thermal fluctuation that consider the movement of the ions

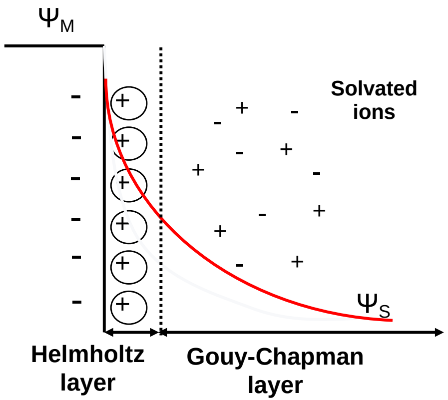
It is called diffuse layer
Describe the diffusion of the excess of charge near the electrode inside the electrolytic solution.

The ions are considered as punctual charges.

The potential associated with the diffuse layer vary exponentially with the distance from the interface

Electrical double layer





$$\boxed{\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}}}$$

Stern model

Tridimensional

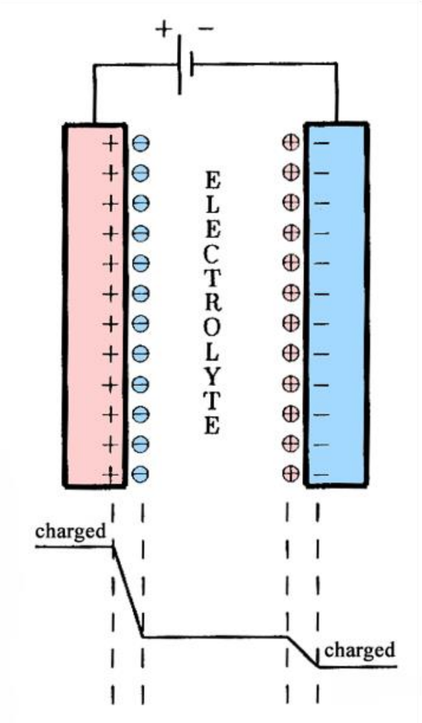
Describe the simultaneously presence of a diffuse and compact layer.

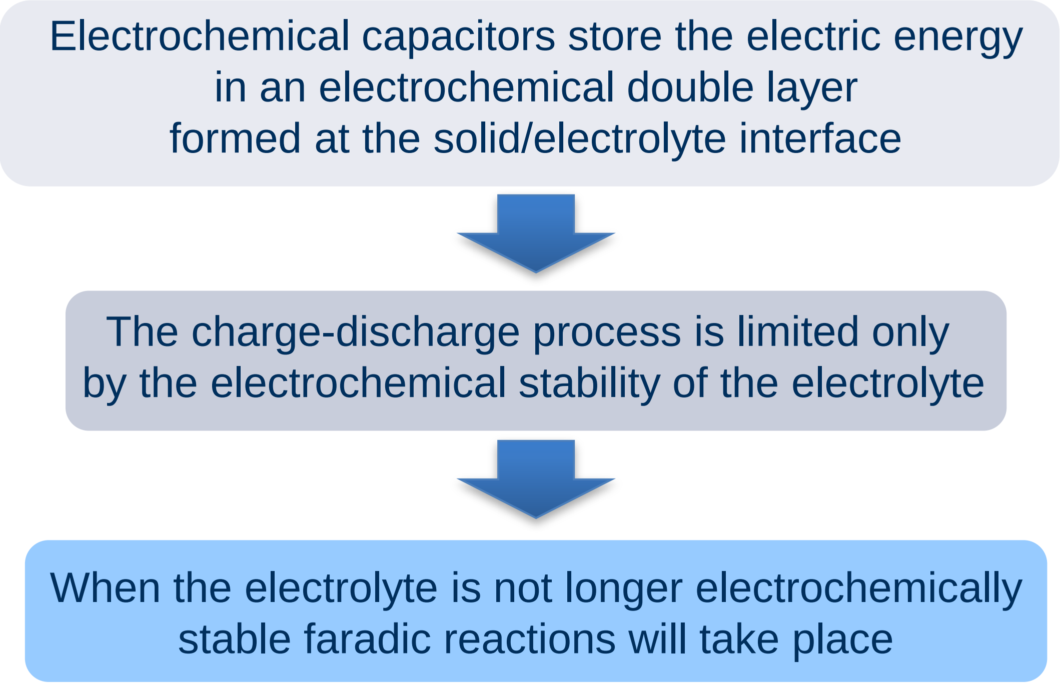
Solvated ions close to the electrode are absorbed following a Langmuir isotherm

The external region is described by a Gouy-Chapman layer

The double layer capacitance is limited by the smaller capacitance contribution and change with the potential electrode and the ions concentrations

EDLCs: storage process





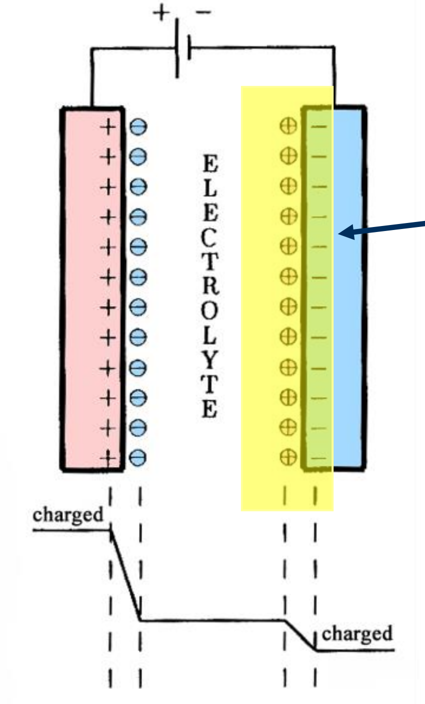
Electrochemical capacitors store the electric energy in an electrochemical double layer formed at the solid/electrolyte interface

The charge-discharge process is limited only by the electrochemical stability of the electrolyte

When the electrolyte is not longer electrochemically stable faradic reactions will take place

EDLCs: storage process

Electrostatic charge process



Positive and negative IONIC charges within the electrolyte accumulate at the surface of the solid electrode and compensate for the electronic charge at the electrode surface

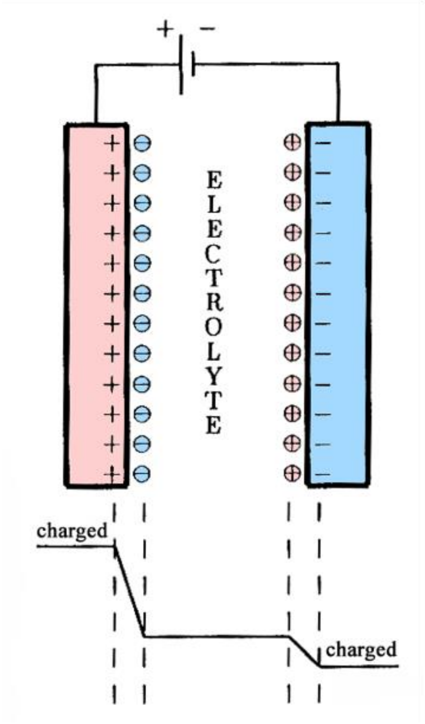
The thickness of the DL depend on the concentration of the electrolytes and on the size of the ions
(for concentrated electrolytes is in the order of 5-10Å)

The double layer CAPACITANCE can be estimated as:

$$\boxed{C=\varepsilon_r\varepsilon_o A/d}$$

C = capacitance
εr = electrolyte dielectric constant
εo = dielectric constant of the vacuum
A = electrode surface area
d = effective thickness of the double layer (charge separation distance)

EDLCs: storage process



$$C=\varepsilon_r\varepsilon_o A/d$$

The double layer capacitance is about 10-20 µF/cm^2
for a smooth electrode in concentrated electrolytic solutions

The corresponding electric field in the electrochemical double layer is very high and assumes values up to 10^6 V/cm easily

Compared to conventional capacitors the energy density stored in the electrochemical double layer display is high (Ragone plot)

In order to achieve a higher capacitance the electrode surface area is additionally increased using porous electrodes with a extremely large internal effective surface

HIGH SURFACE AREA MATERIALS

Carbons in EDLC

The attraction of carbons as a supercapacitors electrode materials arise from a unique combination of chemical and physical properties:

- High conductivity
- High surface-area range (ca. 1 to > 2000m2/g)
- Good corrosion resistance
- High temperature stability
- Controlled pore structure
- Processability and compatibility in composite materials
- Relatively low cost

- ***Activated carbon***
- Graphene
- Carbon nanotubes
- CDC
- ….

Activated carbon

Carbons can be converted into a form that has very high surface area

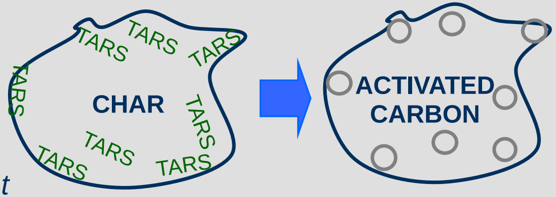
Activation is the process employed to increase surface area and porosity from a carbonised organic precursor (“CHAR”).
The resulting materials are referred as **ACTIVATED CARBONS**

CHAR have low porosity and their structure consists of elementary crystallites with a large number of interstices.

The interstices tend to be filled with disorganized carbon residues (“**TARS**”) that block the pore entrance

Activation open the pores and can create additional porosity

- Carbon precursor
- Activation condition
  - *Temperature*
  - *Time*
  - *Gaseous environment*



Control over the porosity, pore-size distribution, nature of internal surface

Activated carbon

Thermal activation (physical activation)

Modification of carbon char by controlled gasification
Usually between 700 – 1100°C in presence of oxidising gases

During gasification the oxidizing atmosphere greatly increases the pores volume and surface area of the materials through a controlled carbon “burn-off” and the elimination of volatile pyrolysis products

- Burn-off level influence the quality of the activated carbon
- It is controlled by the temperature and duration of activation

Chemical activation

Usually between 400 – 700°C.
Involves the dehydrating action of agent like KOH, H_3PO_4, ZnCl

Post activation washing of the carbon is usually required to remove residual reactant and inorganic residues

Activated carbon

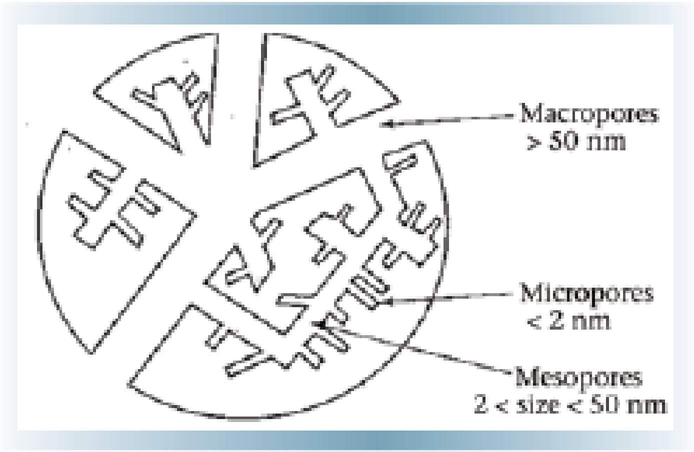


Fig. 1. Schematic diagram of the pore size network of an activated carbon grain.

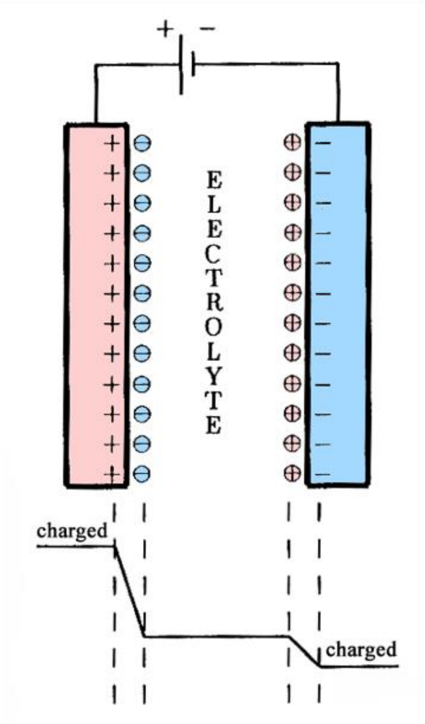
Macropores > 50nm

Mesopores 2<size<50 nm

Micropores > 2nm

Micropores give the higher contribution to the surface area
Mesopores contribute to the surface area and allows improvement accessibility
Macropores negligible contribution to the surface, but they act as transport avenue

Activated carbon



$C=\varepsilon_r\varepsilon_o A/d$

Is it the capacitance (F/g) proportional to its available surface area (m^2/g)?

NO

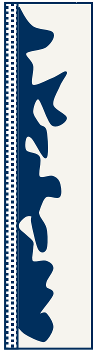
Major factor that contribute to capacitance:
- Electrode surface area
- Morphology
- Surface chemistry
- Measurement condition

Carbon and capacitance

Intrinsic resistivity (intra-particle) of a carbon material
is dependent on its chemical and structural morphology

In electrodes electrical resistance depend:

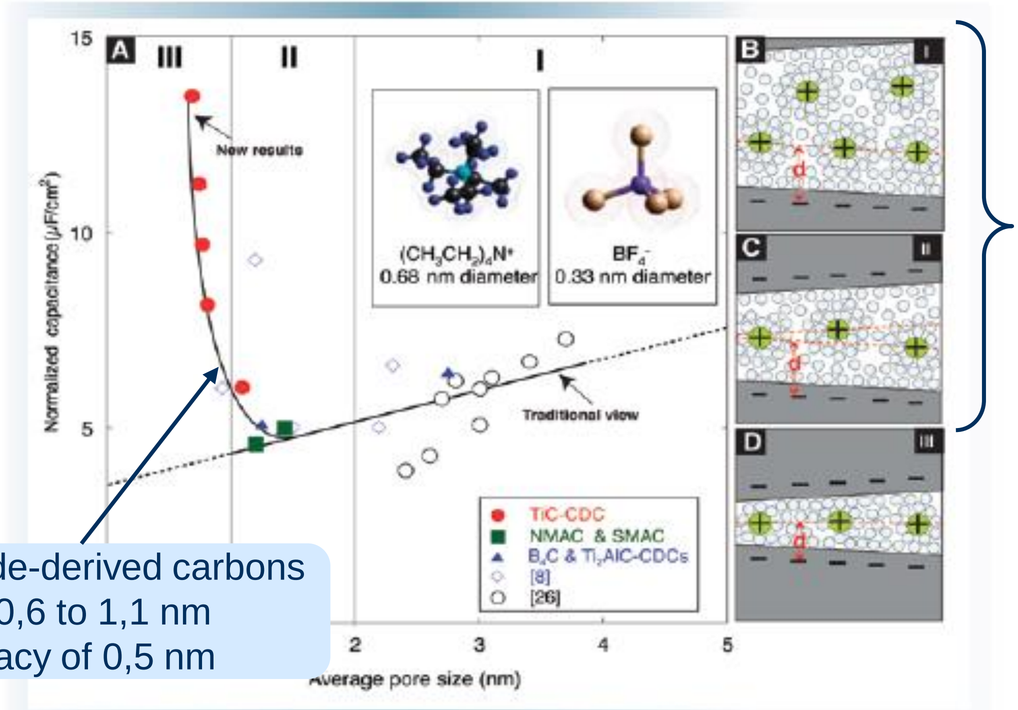
- ➢ Intra-particle resistance
- ➢ Inter-particle resistance (contact)



Resistance associated with:

- Current-carrying path
- Across carbon/carbon interface
- Across carbon/metallic current collector
- Through the metallic current collector

Carbon and capacitance



Carbide-derived carbons
From 0,6 to 1,1 nm
Accuracy of 0,5 nm

Traditional view

Distortion of the ion
solvation shell
or even desolvatation
Close approach of the ion
to the carbon surface

Fig. 2. Normalized capacitance vs. average pore size for TiC-CDC and other carbons from literature tested in the same electrolytes.[13,16] *(From Ref. 15.)*

J Chmiola, G Yushin, Y Gogotsi, C Portet, P Simon, PL Taberna Science 313 (5794), 1760-1763

Carbon and capacitance

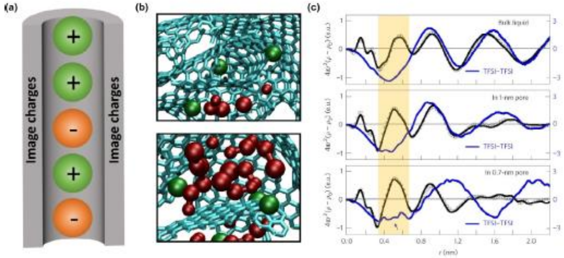


FIGURE 4

Formation of a superionic state in electrified nanopores: from theory to experiments. (a) Mean field-theory have first predicted that the presence of image charges at the surface of the nanoporous carbon exponentially screen out the electrostatic interactions of ions, leading to the packing of ions of the same sign; (b) molecular dynamics simulations of a supercapacitor formed with a CDC electrode and a BMI-PF_6 ionic liquid have displayed the formation of such structures (green: PF_6^- anions, red: BMI^+ cations, turquoise sticks: carbon–carbon bonds). Reproduced with permission from Ref. [128]; (c) Scattering experiments have finally confirmed the existence of anion-anion correlations in the nearest-neighbor region when they are adsorbed in 0.7-nm pores. Reproduced with permission from Ref. [129].

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 12403–12406

www.rsc.org/pccp

COMMUNICATION

Capacitance in carbon pores of 0.7 to 15 nm: a regular pattern†

Teresa A. Centeno,*[a] Olha Sereda[b] and Fritz Stoeckli*[b]

Received 14th March 2011, Accepted 20th May 2011
DOI: 10.1039/c1cp20748b

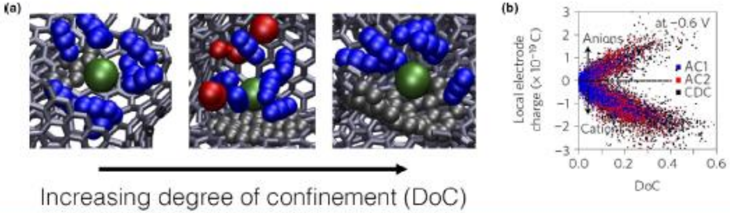
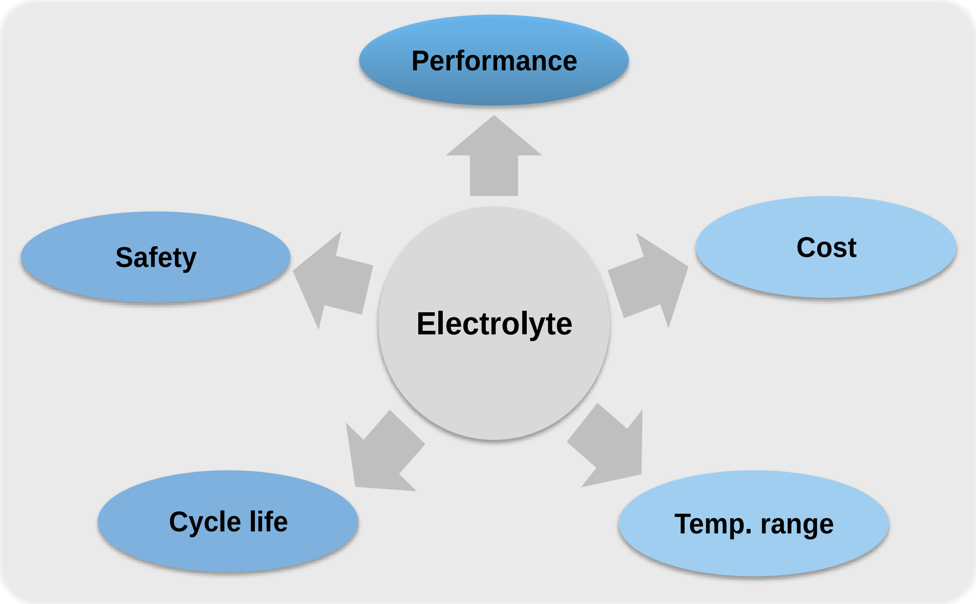


FIGURE 5

Impact of the degree of confinement of the ions on the local surface charge. (a) Molecular dynamics simulations have evidenced the existence of various adsorption sites for the ions inside nanoporous carbons, for which a degree of confinement (DoC) can be confined. Here PF6- anions (green spheres) adsorbed on sites with increasing DoC are shown from left to right (blue: ACN molecules, red: 1-butyl-3- methylimidazolium cations, gray spheres and sticks: carbon electrode). Reproduced with permission from Ref. [130]; (b) In situ small-angle X-ray scattering experiments have confirmed the correlation between the magnitude on the local electrode charge with the DoC of the adsorbed ions for a CsCl aqueous electrolyte adsorbed in various nanoporous carbons (AC1, AC2 and CDC). Reproduced with permission from Ref. [131].

Electrolytes

Electrolytes is a key component of electrochemical storage devices



Performance

Safety

Electrolyte

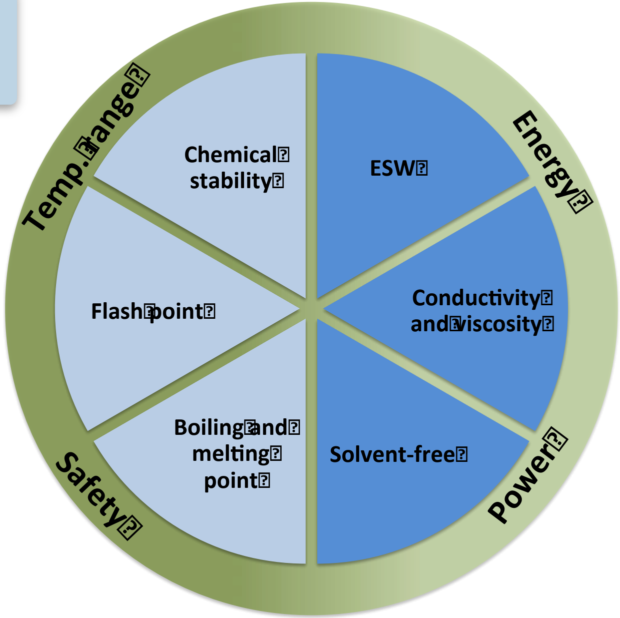
Cost

Cycle life

Temp. range

Ideal electrolyte for EDLCs

Electrolyte is
an active material



Ideal electrolyte

- Large electrochemical stability
- Solvent-free
- Low melting and high boiling points
- High thermal and chemical stabilities
- High flash point

- *Cheap (Cost)*

FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

A. Balducci, Journal of Power Sources, 326, 534-540 (2016)

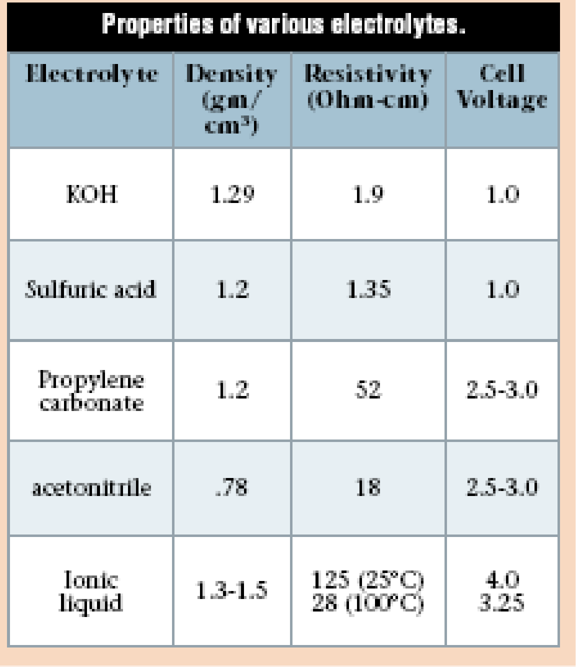
Electrolytes for EDLCs: classes

- Aqueous electrolytes
- Organic electrolytes
- Ionic liquids

Density: aqueous < organic < ionic liquids
Conductivity: aqueous > organic > ionic liquids
Cell Voltage: aqueous < organic < ionic liquids

For the same activated carbon

C in aqueous electrolyte (170 F g-1)
C in organic electrolyte (130 F g-1)
C in ionic liquid (*100* F g-1)



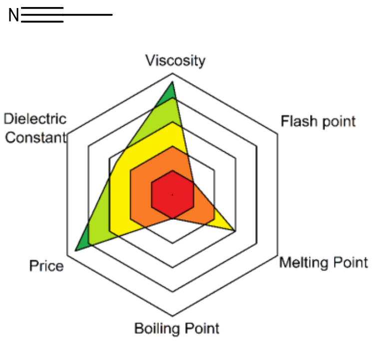
Properties of various electrolytes.

Electrolyte	Density (gm/ cm³)	Resistivity (Ohm-cm)	Cell Voltage
KOH	1.29	1.9	1.0
Sulfuric acid	1.2	1.35	1.0
Propylene carbonate	1.2	52	2.5-3.0
acetonitrile	.78	18	2.5-3.0
Ionic liquid	1.3-1.5	125 (25°C) 28 (100°C)	4.0 3.25

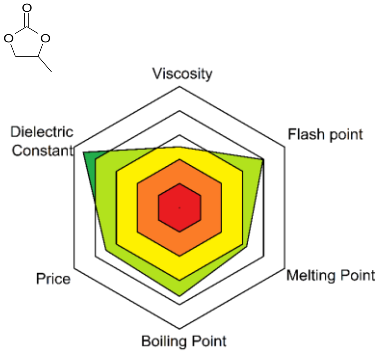
Electrolytes in EDLCs: state of the art

Solvents

Acetonitrile (ACN)



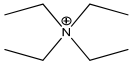
Propylene Carbonate (PC)



Conducting salt

Ammonium salt

Et_4NBF_4



BF_4^-

State of the art

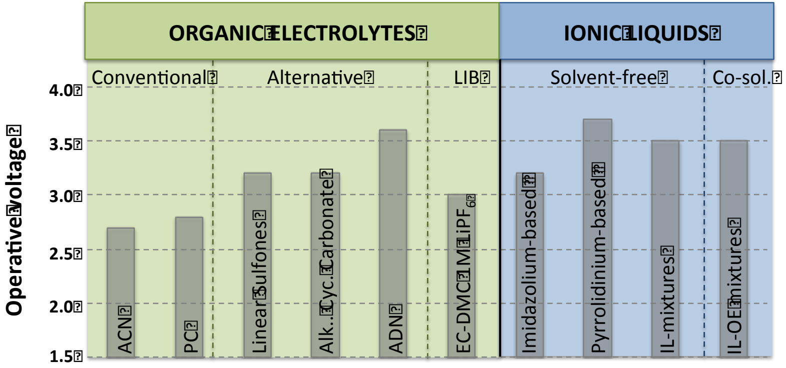
- High conductivity
- Good operative temperature range of use
- **Cell voltage: 2.7 – 2.8 V**

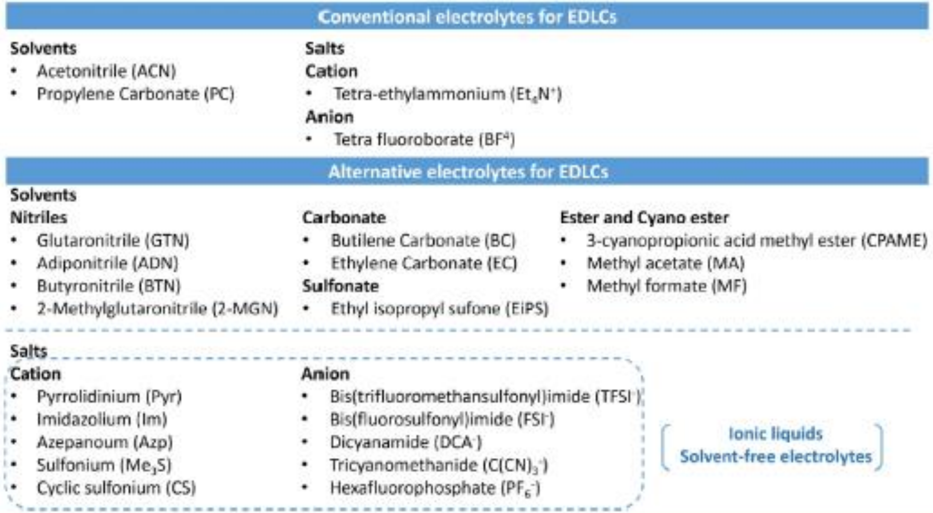
$$E_{max} = \frac{1}{2} CV^2 \qquad P_{max} = \frac{V^2}{4R}$$

Current electrolytes cannot be used for the realization of high voltage EDLC

Alternative electrolytes are needed

Alternative electrolytes





Conventional electrolytes for EDLCs

Solvents
- Acetonitrile (ACN)
- Propylene Carbonate (PC)

Salts

Cation
- Tetra-ethylammonium (Et_4N^+)

Anion
- Tetra fluoroborate (BF^4)

Alternative electrolytes for EDLCs

Solvents

Nitriles
- Glutaronitrile (GTN)
- Adiponitrile (ADN)
- Butyronitrile (BTN)
- 2-Methylglutaronitrile (2-MGN)

Carbonate
- Butilene Carbonate (BC)
- Ethylene Carbonate (EC)

Sulfonate
- Ethyl isopropyl sufone (EiPS)

Ester and Cyano ester
- 3-cyanopropionic acid methyl ester (CPAME)
- Methyl acetate (MA)
- Methyl formate (MF)

Salts

Cation
- Pyrrolidinium (Pyr)
- Imidazolium (Im)
- Azepanoum (Azp)
- Sulfonium (Me_3S)
- Cyclic sulfonium (CS)

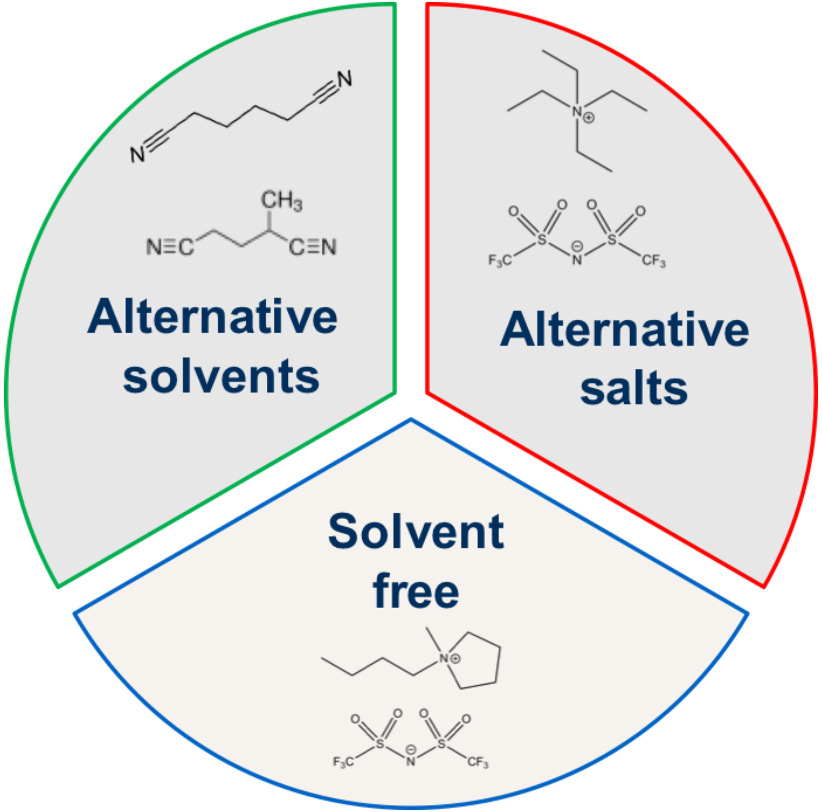
Anion
- Bis(trifluoromethansulfonyl)imide ($TFSI^-$)
- Bis(fluorosulfonyl)imide (FSI^-)
- Dicyanamide (DCA^-)
- Tricyanomethanide ($C(CN)_3^-$)
- Hexafluorophosphate (PF_6^-)

Ionic liquids
Solvent-free electrolytes

FIGURE 2

Overview of the solvents and salts utilized in conventional and alternative electrolytes for EDLCs.

Electrolyte components



Alternative solvents

Alternative salts

Solvent free

Operative voltage in alternative electrolytes

Alternative solvent ▨

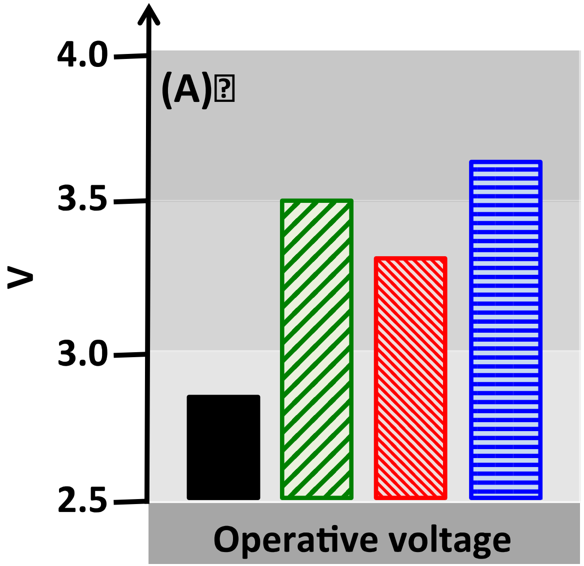
Sulfones
Adiponitrile
Carbonates

Alternative salts ▨

$PYR_{14}BF_4$
$TEMABF_4$

Solvent free ▤

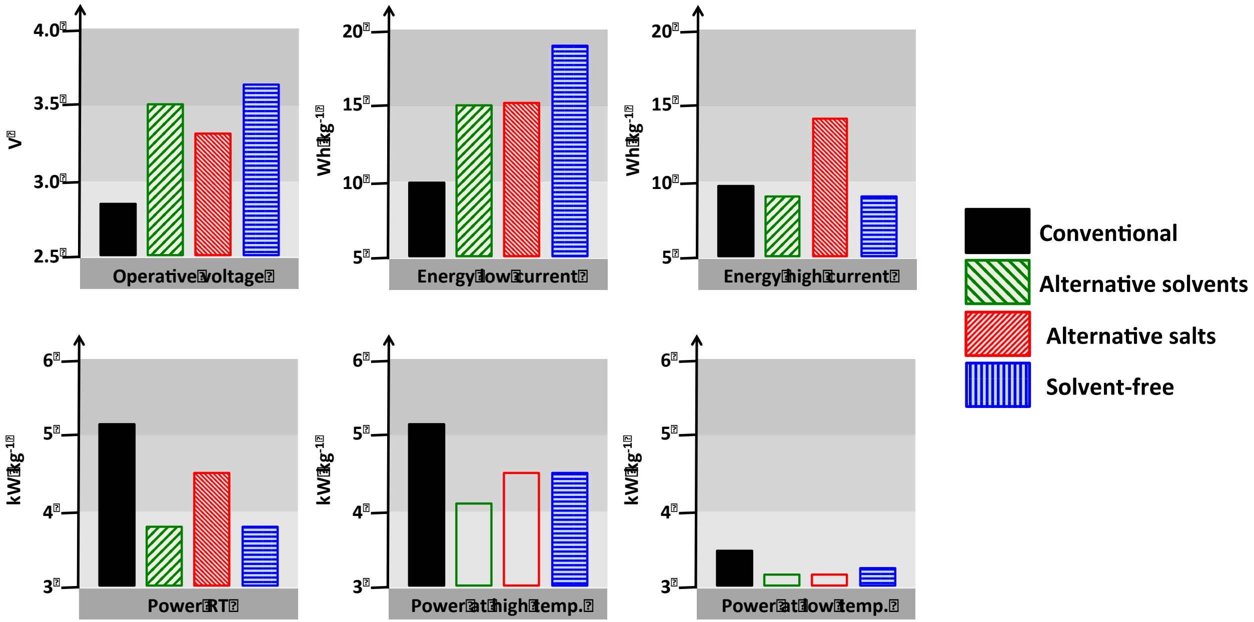
Pyrrolidinium
Imidazolium
Eutectic Mix.



The use of alternative electrolytes might lead to important increase of the operative voltage of EDLCs

F. Béguin, V. Presser, A. Balducci, E. Frackowiak, Ad. Mater.26, 2219-2251 (2014);
A. Balducci, Journal of Power Sources, 326, 534-540 (2016)

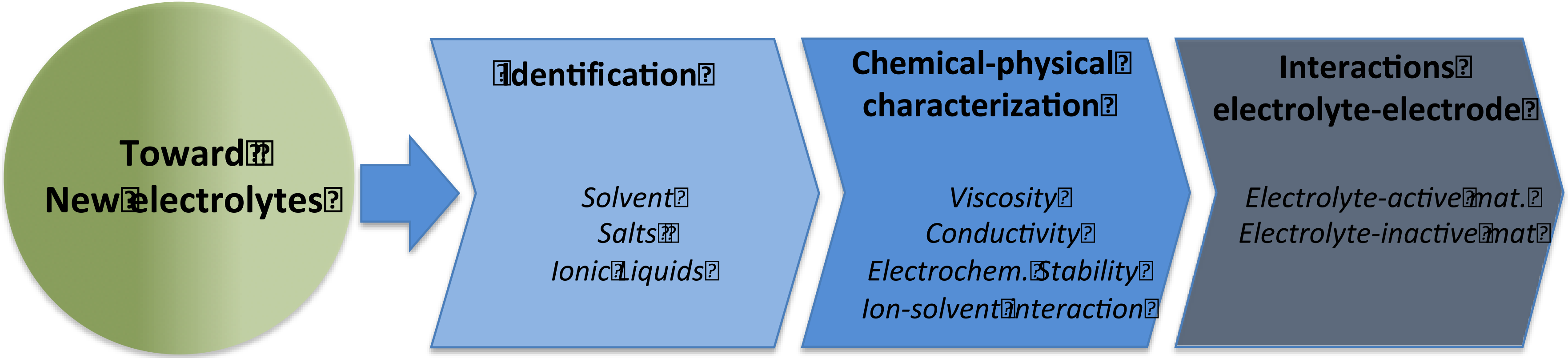
Energy and power in alternative electrolytes



The overall performance of EDLCs containing alternative electrolytes is not higher than those of systems containing conventional electrolytes

A. Balducci, Journal of Power Sources, 326, 534-540 (2016)

Development of novel electrolyte components



Toward New electrolytes

Identification

Solvent
Salts
Ionic Liquids

Chemical-physical characterization

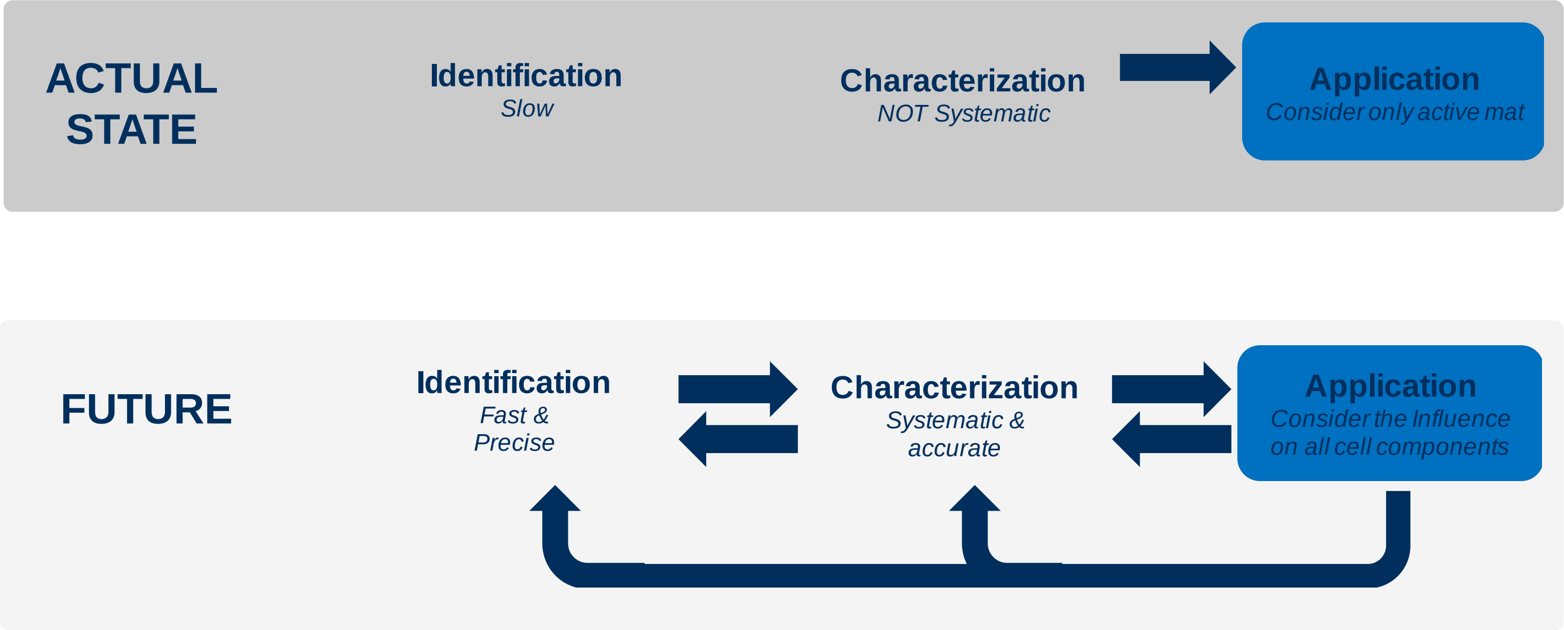
Viscosity
Conductivity
Electrochem. Stability
Ion-solvent interaction

Interactions electrolyte-electrode

Electrolyte-active mat.
Electrolyte-inactive mat

A. Balducci, Journal of Power Sources, 326, 534-540 (2016)

Develpment of novel electrolyte components



ACTUAL STATE

Identification
Slow

Characterization
NOT Systematic

Application
Consider only active mat

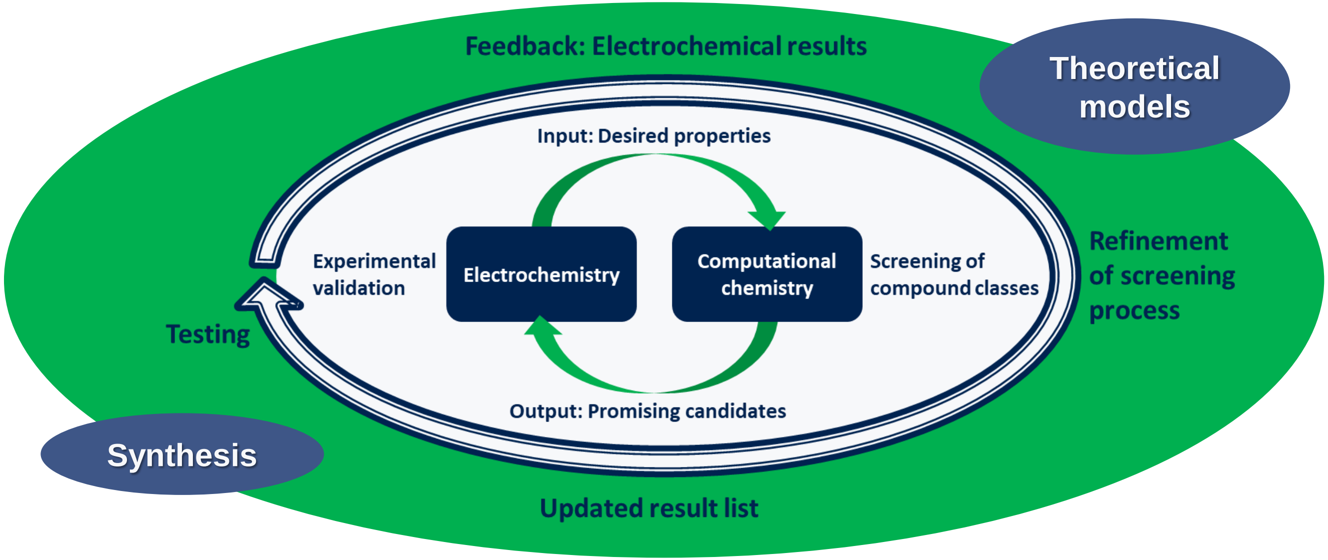
FUTURE

Identification
Fast &
Precise

Characterization
Systematic &
accurate

Application
Consider the Influence
on all cell components

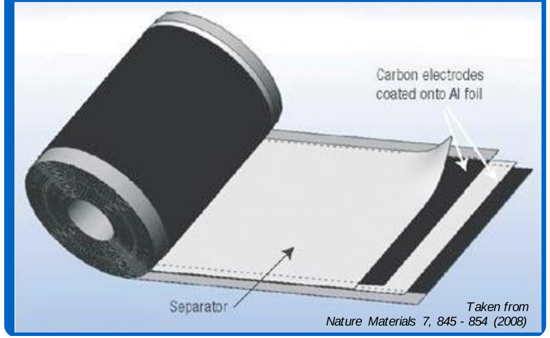
Novel electrolytes for supercapacitor



Z. Lin, E Goikolea, A. Balducci, K. Naoi, P.L. Taberna, M. Salanne, G. Yushin, P. Simon, Materials Today, 21 (4), 419-436 (2018)

Novel solvents for EDLCs and inactive electrode components

Al current collector

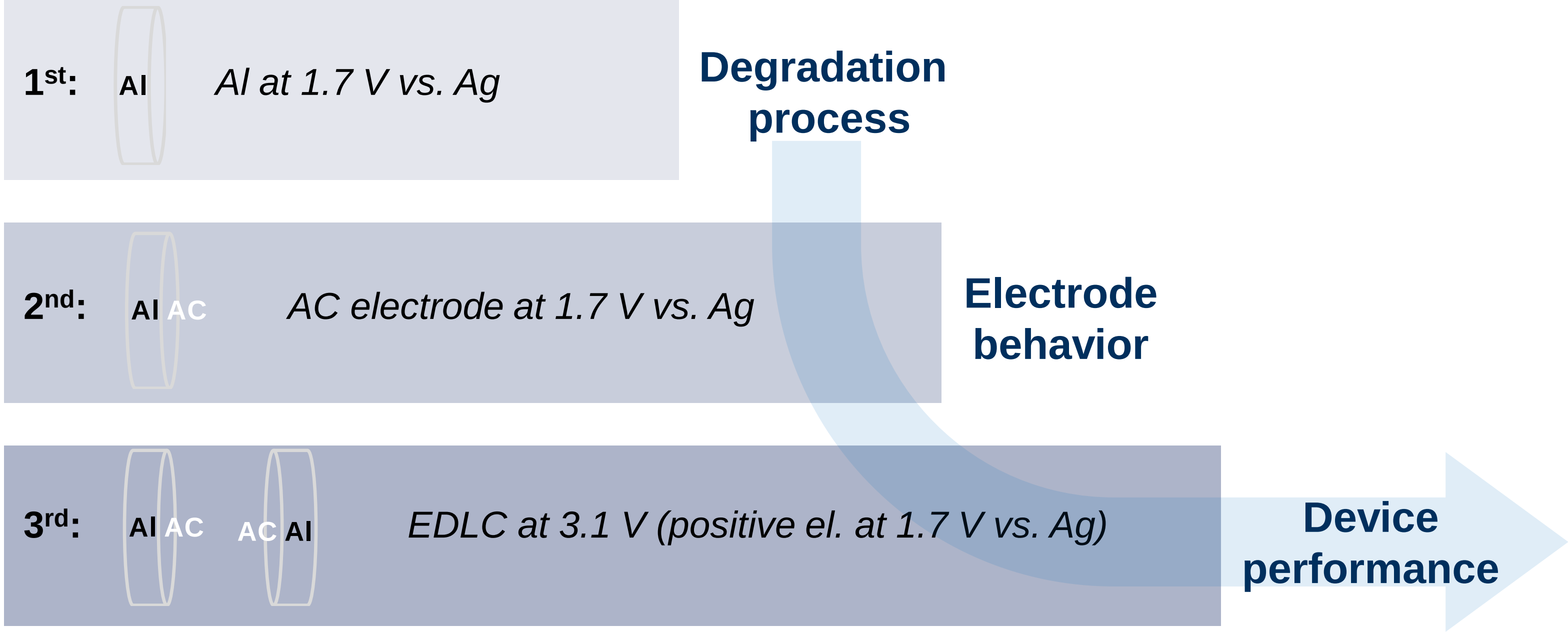


Taken from Nature Materials 7, 845 - 854 (2008)

- ❑ The degradation of the current collector has a detrimental effect on the cycling stability of EDLCs
- ❑ The composition of the salt and the ion-solvent interactions strongly affect the anodic dissolution of Al

Impact of novel electrolytes on the anodic dissolution of Al current collectors

Float tests in selected electrolytes



1st: Al — *Al at 1.7 V vs. Ag*

2nd: Al AC — *AC electrode at 1.7 V vs. Ag*

3rd: Al AC AC Al — *EDLC at 3.1 V (positive el. at 1.7 V vs. Ag)*

Degradation process

Electrode behavior

Device performance

J. Krummacher, L.H. Heß, A. Balducci, ChemSusChem DOI10.1002/cssc.201701422

Outline

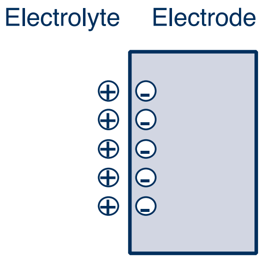
- High power applications: supercapacitors vs. batteries
- Supercapacitors
  - Components and materials
  - Techniques
- EDLC
  - Carbon
  - Electrolytes
- Pseudocapacitors
- Hybrid devices

Supercapacitors

Electrochemical Capacitors

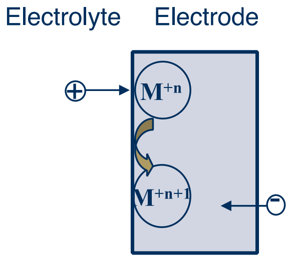
EC Double Layer Capacitor

Non-Faradaic
(no transfer of charge)

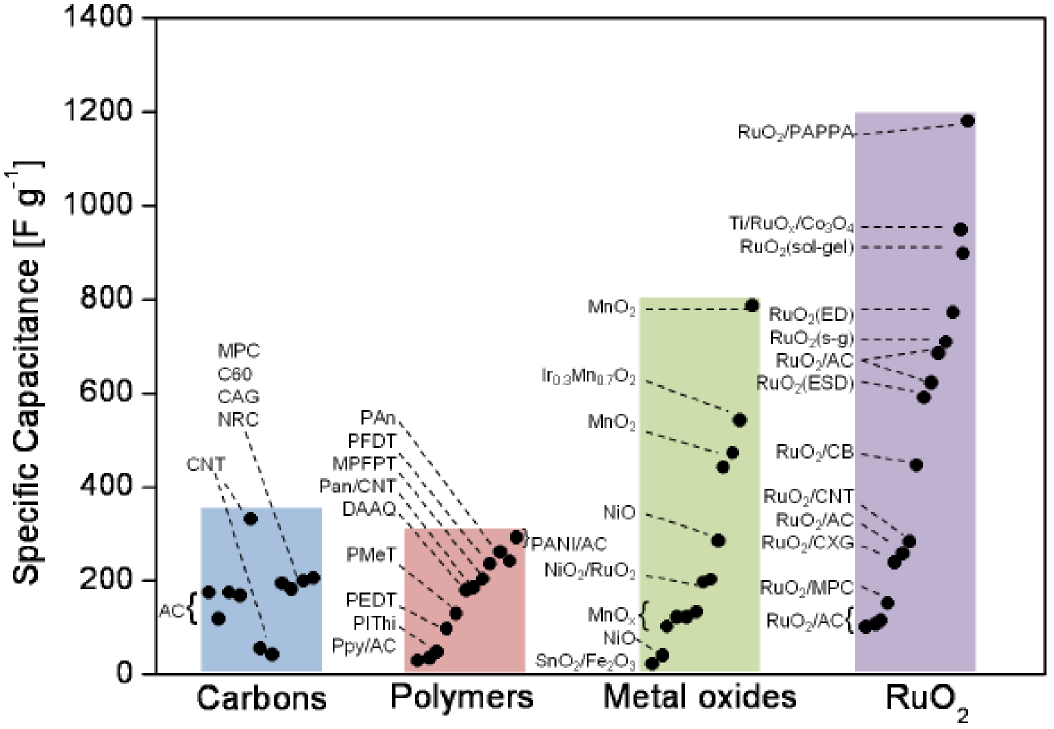


Pseudocapacitors

Pseudocapacitance
Charge transfer through surface
Faradaic, redox reactions



Active materials in supercapacitors



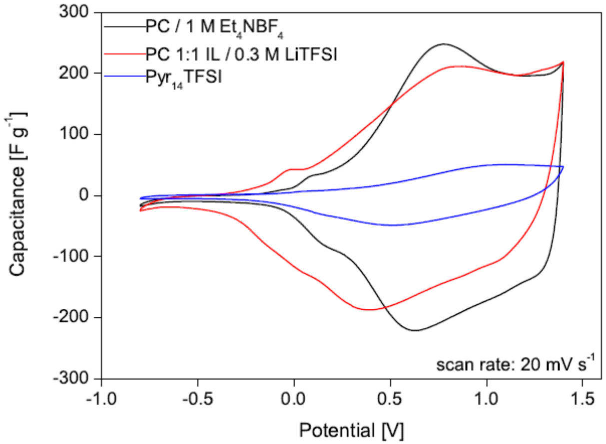
K. Naoi, P. Simon, *Interface* **2008**, 17, 34

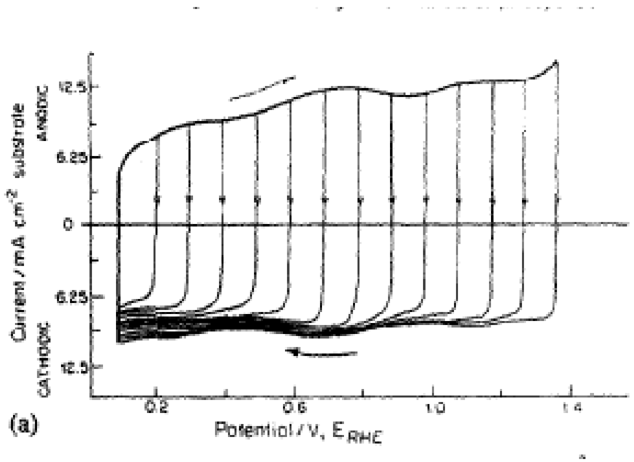
Pseudocapacitive materials

Pseudocapacitance
Charge transfer through surface
Faradaic, redox reactions

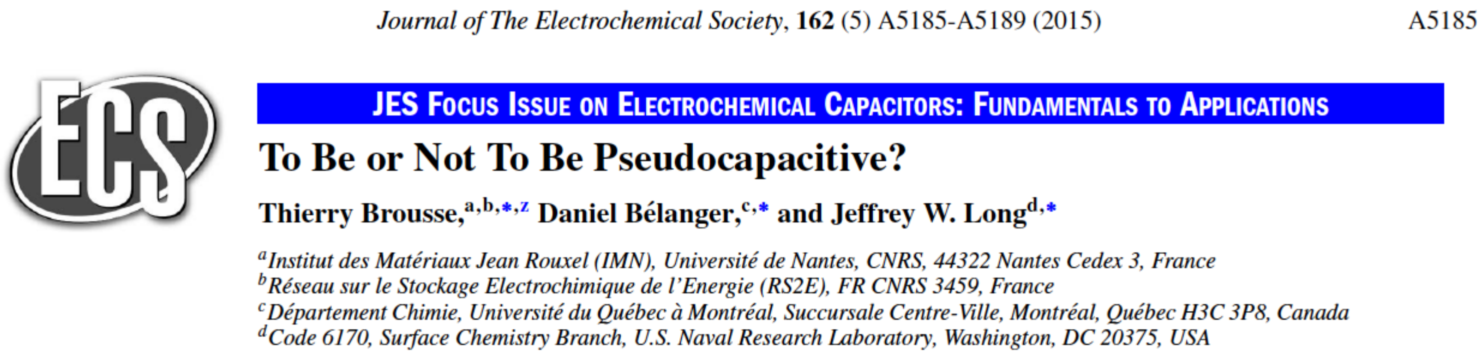
- ➢ Conducting polymers
- ➢ Metal Oxides
- ➢ RuO_2

Battery-like electrodes





Pseudocapacitive materials



Journal of The Electrochemical Society, **162** (5) A5185-A5189 (2015) A5185

ECS

JES FOCUS ISSUE ON ELECTROCHEMICAL CAPACITORS: FUNDAMENTALS TO APPLICATIONS

To Be or Not To Be Pseudocapacitive?

Thierry Brousse,[a,b,*,z] Daniel Bélanger,[c,*] and Jeffrey W. Long[d,*]

[a] *Institut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 44322 Nantes Cedex 3, France*
[b] *Réseau sur le Stockage Electrochimique de l'Energie (RS2E), FR CNRS 3459, France*
[c] *Département Chimie, Université du Québec à Montréal, Succursale Centre-Ville, Montréal, Québec H3C 3P8, Canada*
[d] *Code 6170, Surface Chemistry Branch, U.S. Naval Research Laboratory, Washington, DC 20375, USA*

In the field of electrochemical capacitors, the term “pseudocapacitance” is used to designate electrode materials (RuO2, MnO2) that have the electrochemical signature of a capacitive electrode (such as observed with activated carbon), i.e., exhibiting a linear dependence of the charge stored with the width of the potential window, but where charge storage originates from different reaction mechanisms

Pseudocapacitive materials

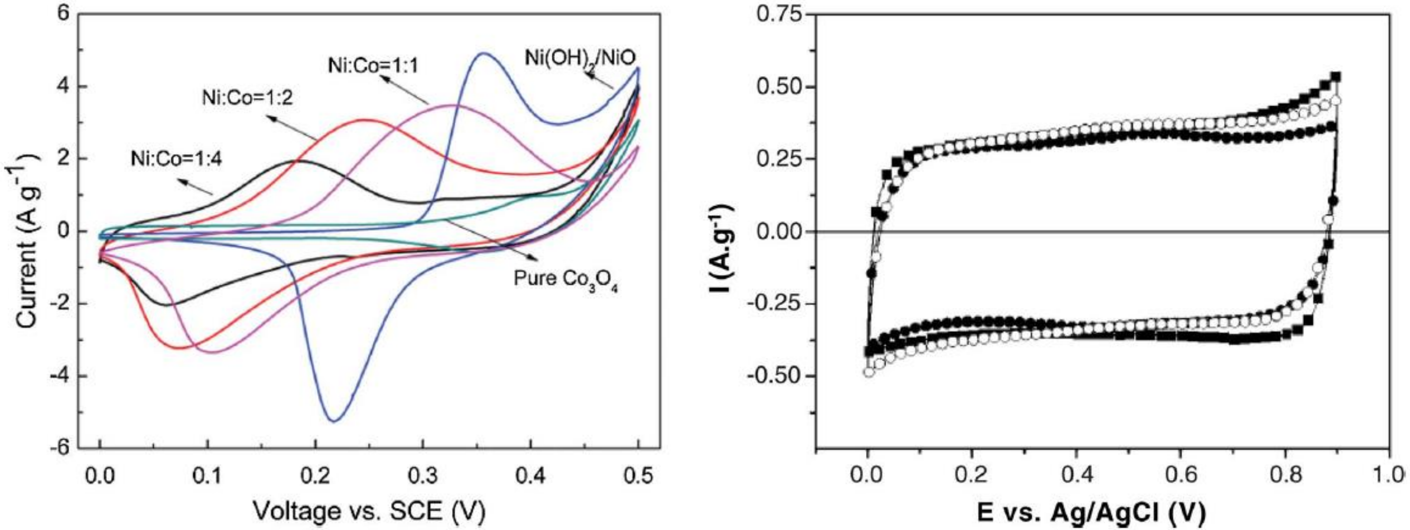
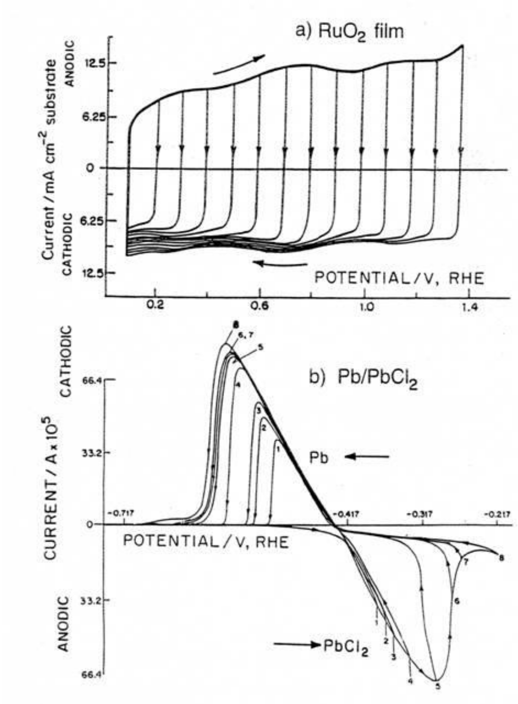


Figure 2. Cyclic voltammograms of Ni(OH)$_2$ and different cobalt doped nickel oxides[6] that exhibit pure faradaic behavior, while MnO$_2$ electrode[5] shows the rectangular shape CV typical of a pseudocapacitive oxide.

Pseudocapacitive materials



Cyclic voltammogram for RuO_2 in 1 M aqueos H_2SO_4 (298K) showing mirror-image symmetry and responses to sucessive switching along the scanned potential range

Cyclic voltammogram for Pb-$PbCl_2$ battery electrode showing typical irreversibility arising with 3-dim materials undergoing chemical phase changes

Pseudocapacitive material: MXenes

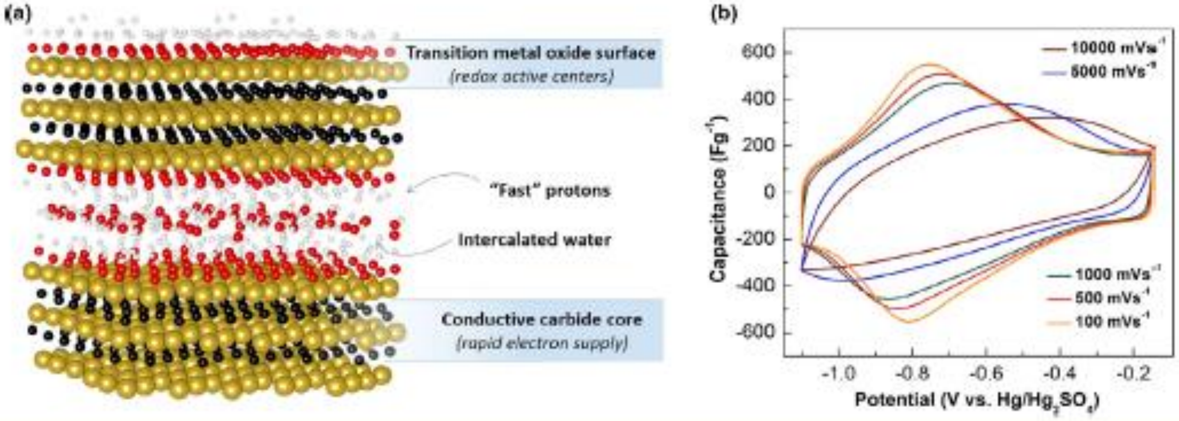


FIGURE 7

(a) Schematic illustration of MXene structure: MXenes possess excellent conductivity owing to a conductive carbide inner layer along with transition metal oxide-like surfaces. Intercalated water molecules enable high accessibility of the redox-active sites on MXene surfaces to ions, i.e., protons; (b) cyclic voltammetry profiles of macro-porous $Ti_3C_2T_x$ film with 0.43 mg cm^{-2} loading and 13-μm thickness collected in 3 M H_2SO_4 at scan rates from 100 to 10,000 mV s^{-1}. Adapted with permission from Ref. [177].

Pseudocapacitive material: Conducting polymers

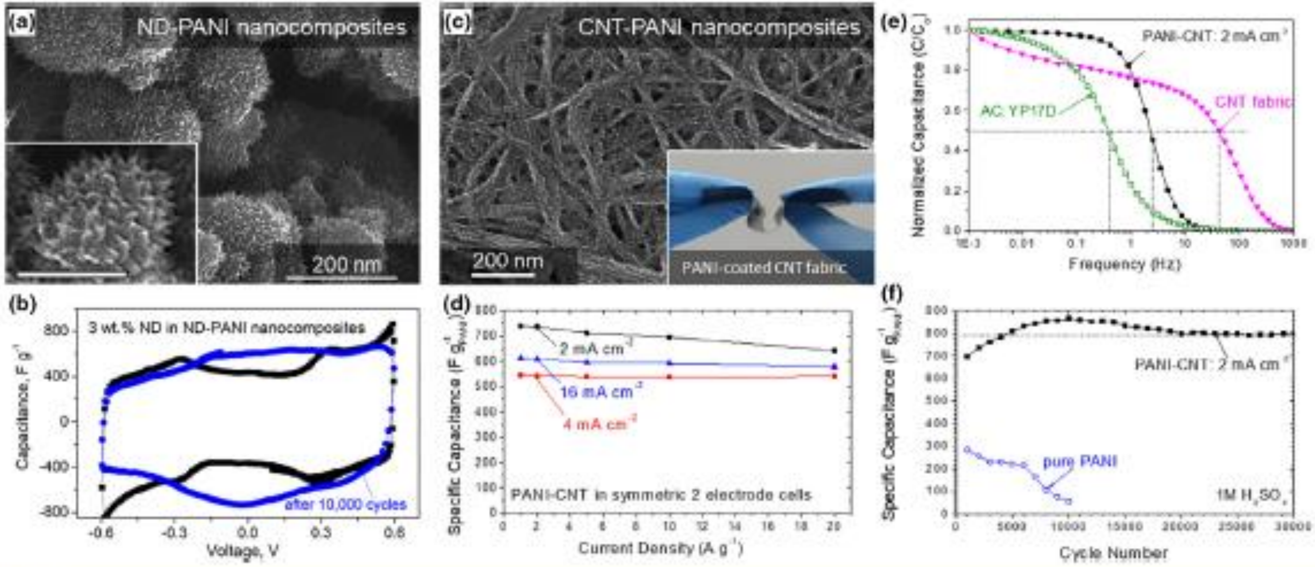


FIGURE 8

Selected examples of the conductive polymer-carbon composites and their electrochemical behavior, such as (a) SEM micrographs of PANI with 3 wt.% of nanodiamond (ND) soot incorporated into the PANI particles during synthesis; and (b) CV of a symmetric pseudocapacitor with ND-PANI electrodes; (c) SEM of PANI electrodeposited on CNT fabric at the smallest current density of 2 mA cm^{-2}; (d) its capacitance retention at high current densities; (e) frequency response in comparison with commonly used AC (YP-17D) and CNT fabric with no PANI; and (f) cycle stability showing over 30,000 stable cycles in H_2SO_4 aqueous electrolyte. Adapted with permission from Refs. [184,190].

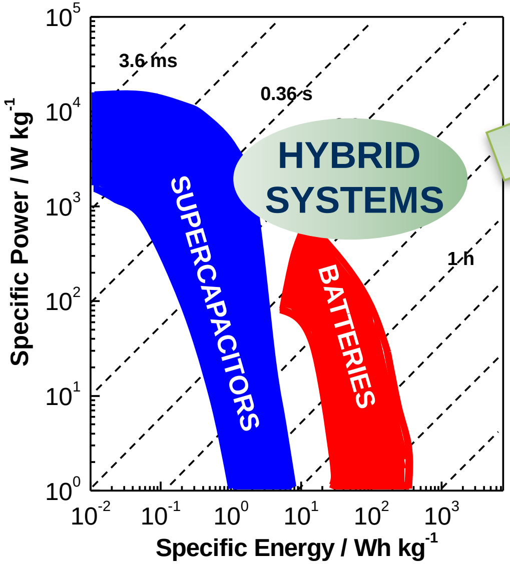
Outline

- ➢ High power applications: supercapacitors vs. batteries
- ➢ Supercapacitors
  - Components and materials
  - Techniques
- ➢ EDLC
  - Carbon
  - Electrolytes
- ➢ Pseudocapacitors
- ➢ Hybrid devices

Hybrid devices

Supercapacitors and batteries

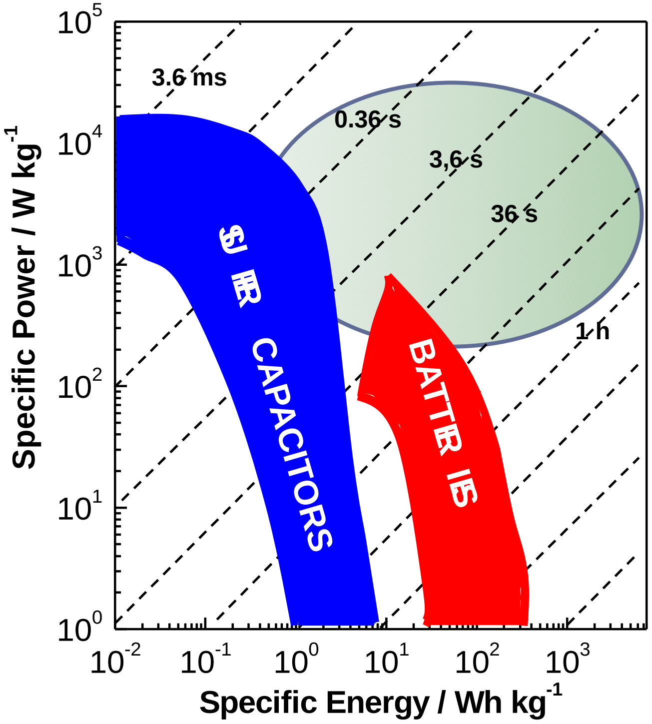
will remain different



High Energy
High Power
Medium-high cycling stability

Hybrid devices

Hybrid devices



New type of high power devices

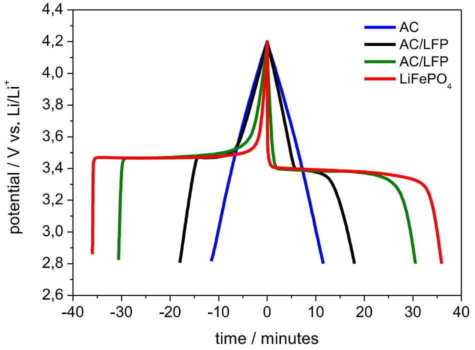
- High energy (40-60 Wh kg^{-1})
  (higher than supercaps)
- High power (5-8 kWkg^{-1})
  (higher than batteries)
- Medium-high cycling stability
  (hundred of thousand cycles)

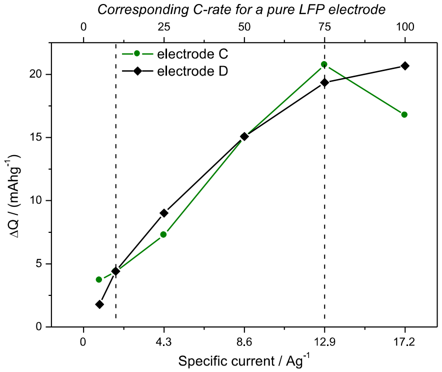
Hybridization

Active material hybridization

Combination into one electrode of supercapacitors and battery material

Interaction of $LiFePO_4$ (LFP) and Activated Carbon





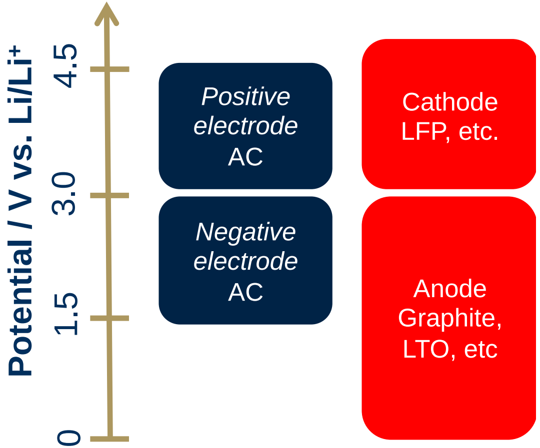
AC improves the performance of LFP at high specific current

N. Böckenfeld et al., Electrochimica Acta, 76, 130– 136 (2012)

Hybridization

Electrode combination

Combination of supercapacitors and battery electrodes into one devices



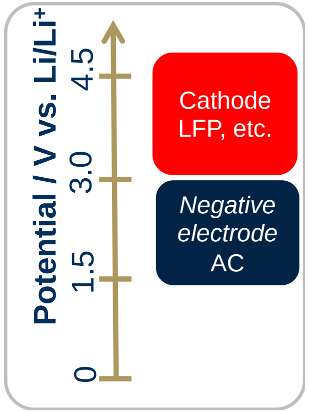
2 processes occur simultaneously during charge-discharge:

- Li insertion-extraction
- Double layer formation and deplation

Hybridization

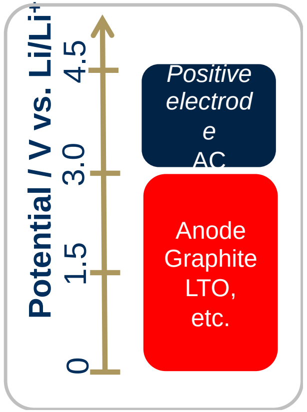
Electrode combination

Type 1



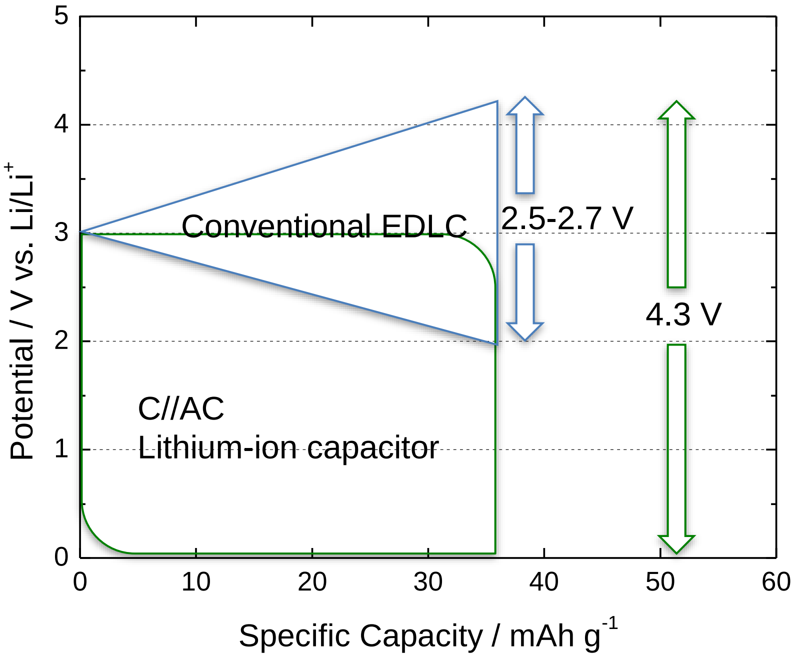
Lower operative voltage
Contain lithium (cathode)

Type 2



Higher operative voltage
Does not contain lithium (pre-lithiation)

Type 2 device: lithium-ion capacitors



- High voltage (4.3 V)
- High power
- High energy (25 Wh/kg)
- High cycle life (>50.000 cycles)
- Low self discharge

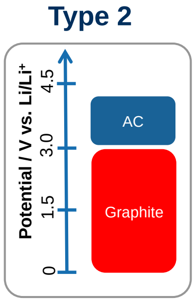
Key technology:
Pre-doping of Li to the carbon anode

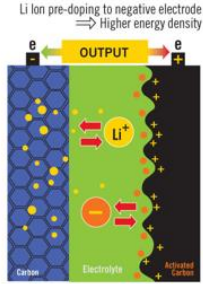
FRIEDRICH-SCHILLER-
UNIVERSITÄT
JENA

K. Naoi, P. Simon, *Interface* **2008**, 17, 34

Type 2 device: lithium-ion capacitors

Commercially available devices (JSR Micro)





Positive electrode:
Activated carbon

Negative electrode
Graphite

Electrolyte
State-of-the-art LIBs

Graphite displays poor capacity retention during intercalation processes at high currents

Alternative materials for the negative electrode of LIC would be beneficial

Conclusions

- Supercapacitors are important (and commercially available) energy storage devices which are used in a large number of applications
- The energy of supercapacitors should be improved
  - Active materials
  - Electrolytes
  - Inactive components
- We need new ideas and new scientists