TUM CREATE Centre for Electromobility, Singapore

The Importance of Electrochemistry for the Development of Sustainable Mobility

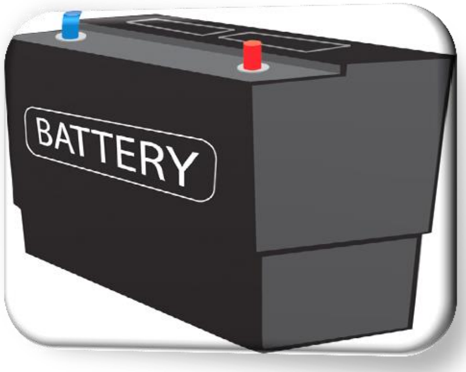
Jochen Friedl, Ulrich Stimming

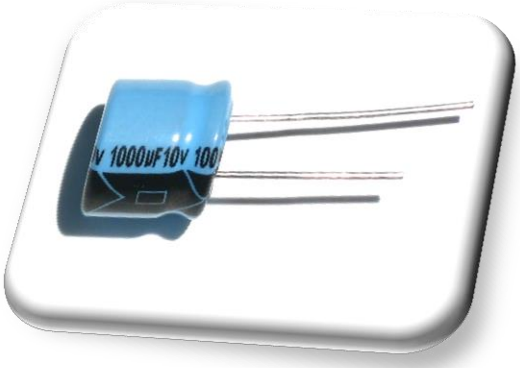
DPG-Frühjahrstagung, Working Group on Energy, 18.03.2014

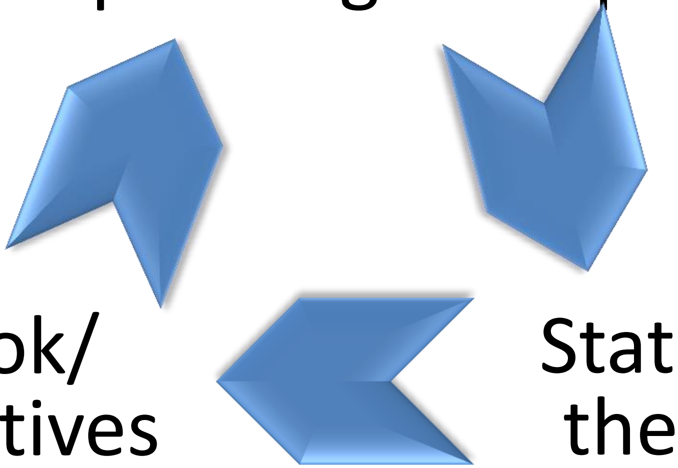
TUM CREATE
TUM Department of Physics E19
TUM Institute for Advanced Study

Bridging East and West

Outline



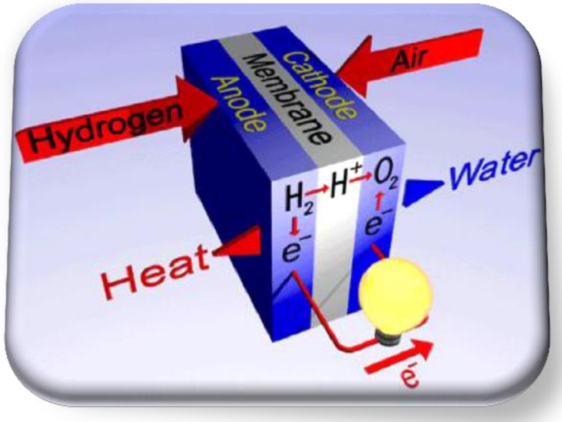




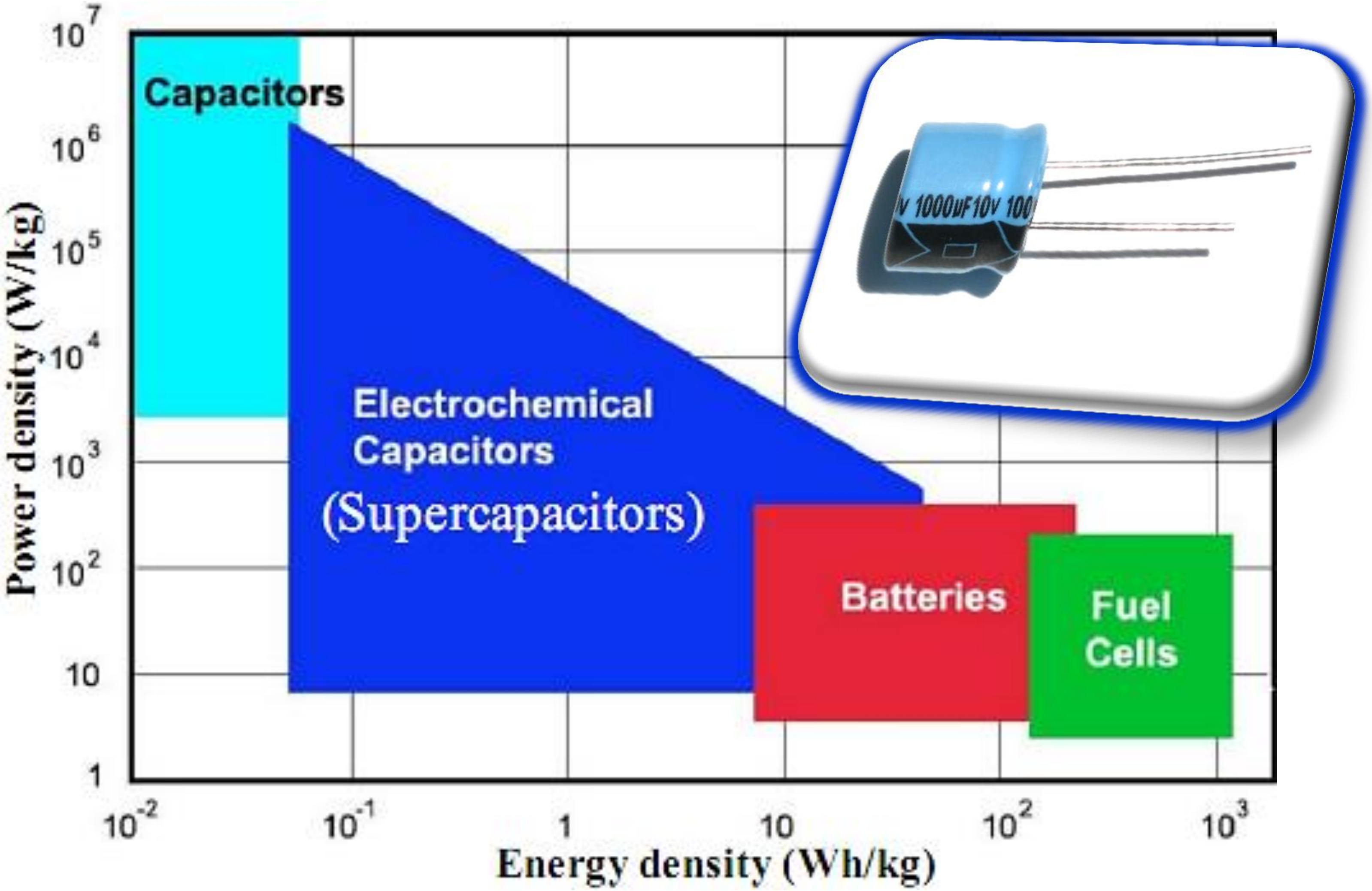
Physical Background/ Operating Principle

State of the Art

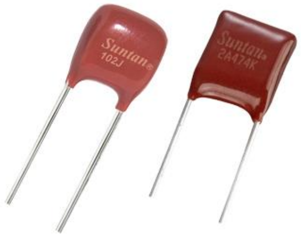
Outlook/ Perspectives



Electrochemical Double Layer Capacitor



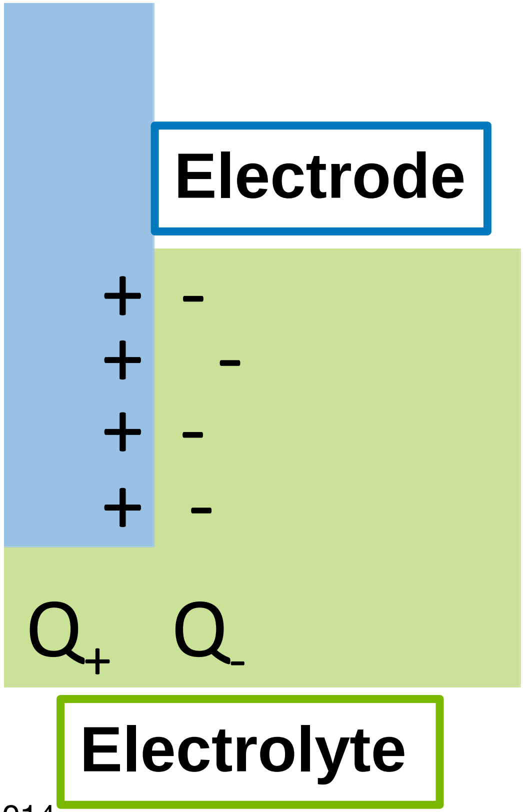
Electrochemical Double Layer Capacitor



S.O. Kasap: Principles of Electrical Engineering Materials and Devices, McGraw-Hill Higher Education, 2000

$$C_{pf} \approx 1\,nF\,cm^{-2}$$

$$C_{DL} = \frac{dQ}{d\varphi} \approx 10\mu F\,cm^{-2}$$



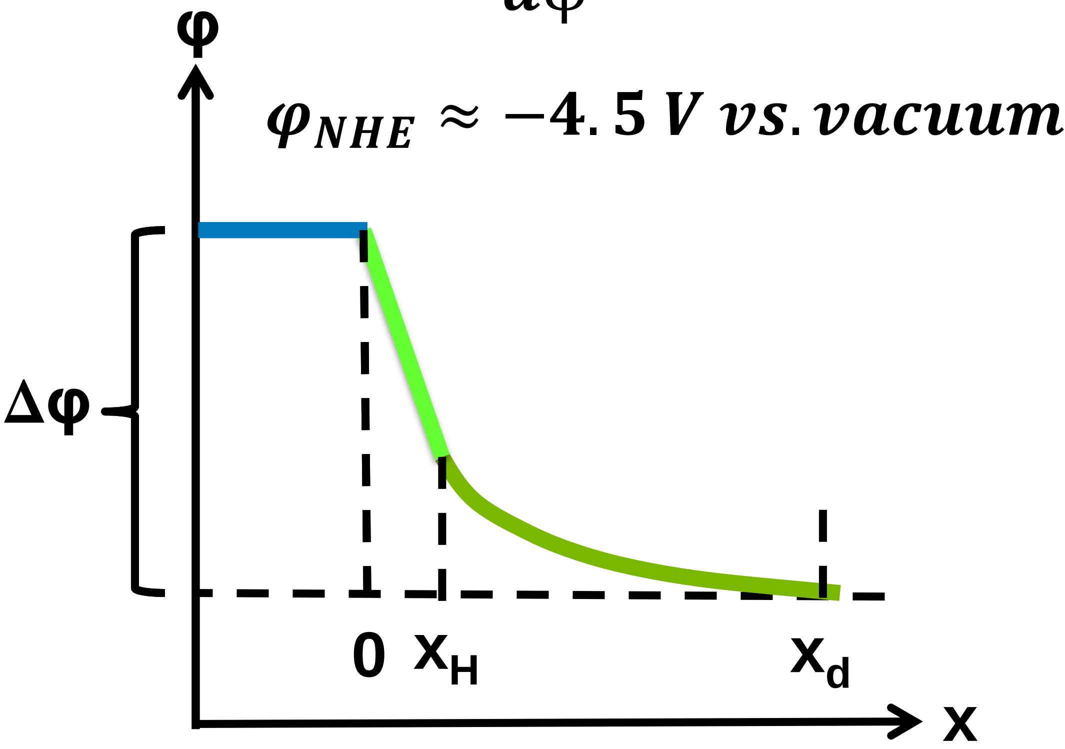
Electrode

+ + + +

- - - -

Q_+ Q_-

Electrolyte



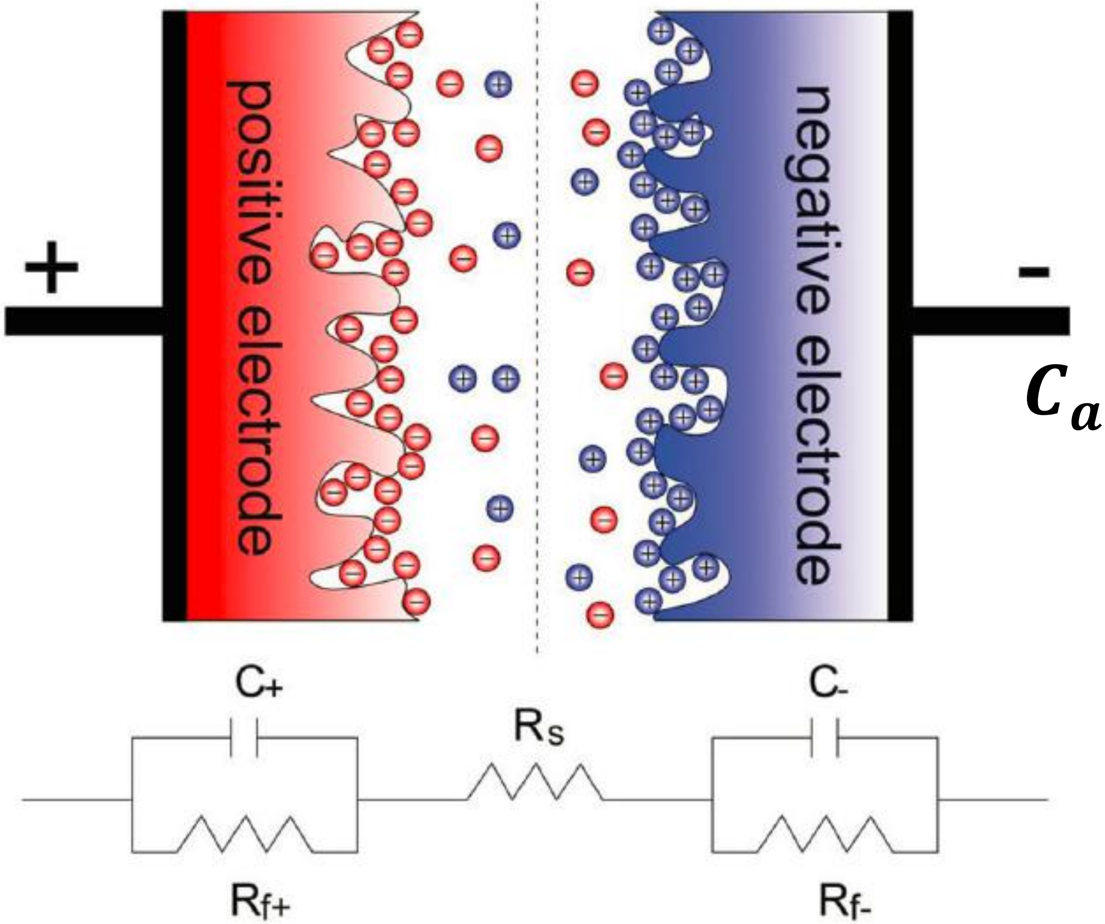
$$\varphi_{NHE} \approx -4.5\,V\ vs.\,vacuum$$

Kolb DM. Angew Chem Int Ed Engl 2001;40:1162–81.

Klaus J. Vetter: Electrochemical Kinetics, Academic Press Inc., 1967

Electrochemical Double Layer Capacitor

Béguin F et al. Adv Mater 2014:1–33.



$$C_{+/-} = \frac{dQ}{dU}$$

$$C_{act} = \left(\frac{1}{C_+} + \frac{1}{C_-}\right)^{-1} \equiv \mathbf{C}$$

$$E = \frac{1}{2} C\, U^2$$

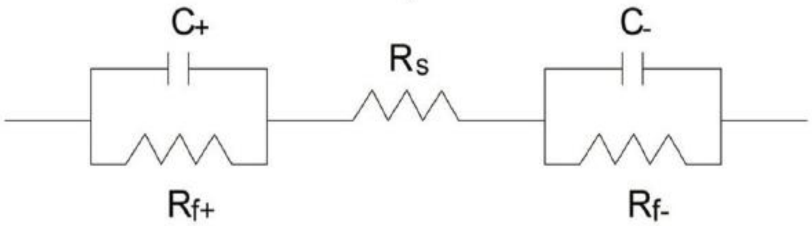
$$P = \frac{1}{4\, ESR} U^2$$

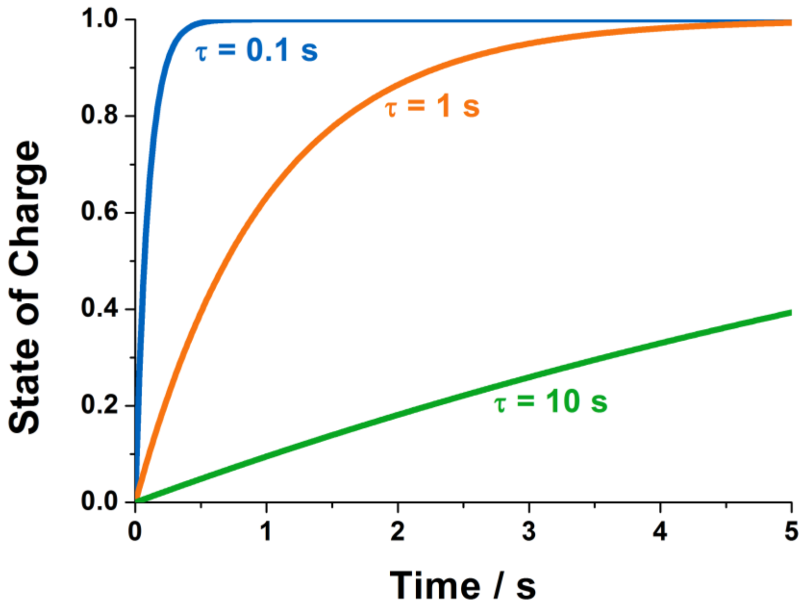
Energy stored in Electrochemical Double Layer (inner & diffuse)

Electrochemical Double Layer Capacitor

Power Density

$$U(t) = U_0\left(1 - exp\left[-\frac{t}{\tau}\right]\right)$$





No charge transfer,
no reaction: $\tau = C \cdot R_s$

➡ Small τ

➡ ≈ 10 kW kg^{-1}

Simon P, Gogotsi Y. Nat Mater 2008;7:845–54.
CAP-XX Supercapacitors for Micro-Hybrid Automotive Applications (2013).

Electrochemical Double Layer Capacitor

Energy Density

$$E = \frac{1}{2} C(1\ V)^2$$

aqueous

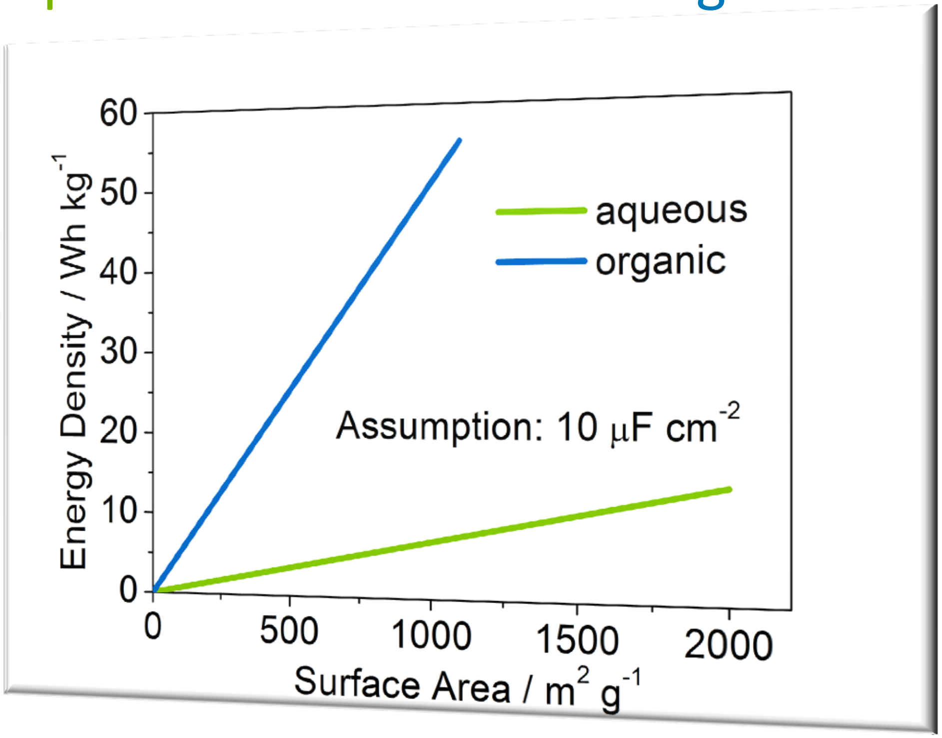
$$E = \frac{1}{2} C(2.7\ V)^2$$

organic

High Conductivity

Electrochemical Stability

High Surface Area



Carbonaceous material: 5 - 20 µF cm^{-2}

Pandolfo AG, Hollenkamp AF. J Power Sources 2006;157:11–27.

Simon P, Gogotsi Y. Nat Mater 2008;7:845–54.

CAP-XX Supercapacitors for Micro-Hybrid Automotive Applications (2013).

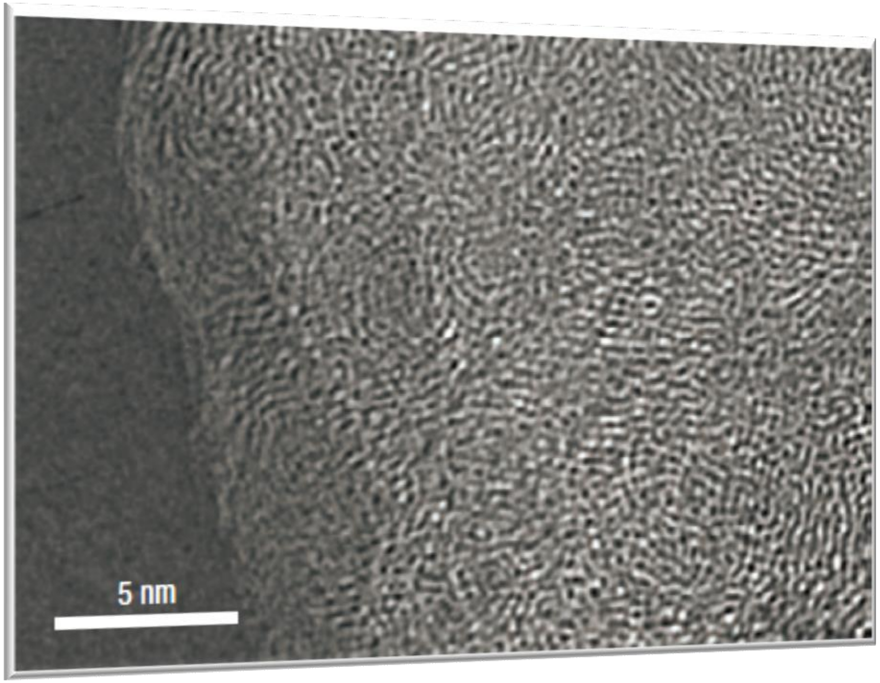
Electrochemical Double Layer Capacitor

High conductivity

Electrochemical stability

High surface area

Carbon



Béguin F et al. Adv Mater 2014:1–33.

TEM of typical Disordered Microporous (<2 nm) Carbon

S_{BET} ~ 2000 $m^2\ g^{-1}$

Above S_{BET} ~ 1200 $m^2\ g^{-1}$ gravimetric C_{DL} exhibits plateau.

Béguin F et al. Adv Mater 2014:1–33.

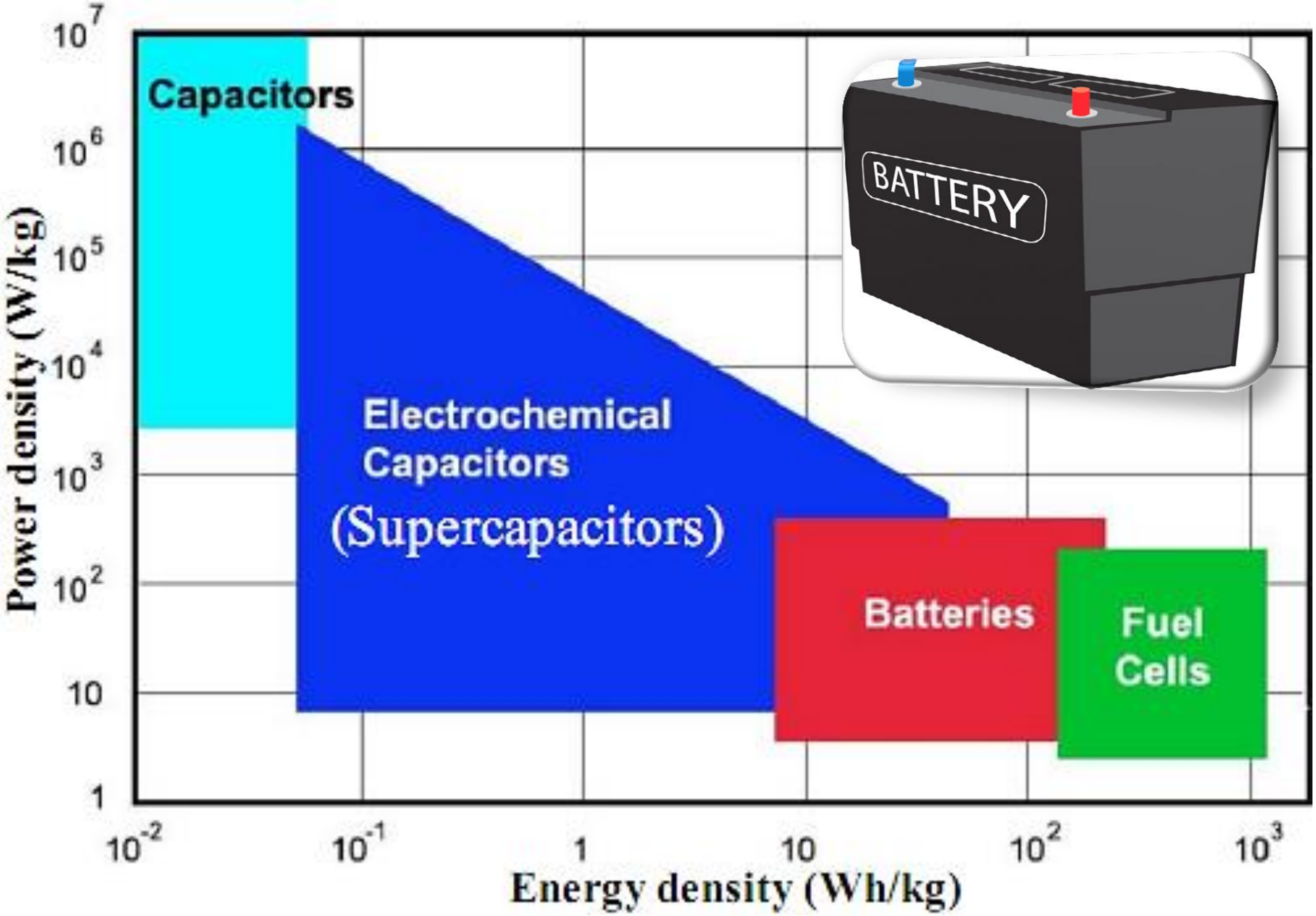
Simon P, Gogotsi Y. Nat Mater 2008;7:845–54.

Electrochemical Double Layer Capacitor

Applications for Mobility:

Simon P, Gogotsi Y. Nat Mater 2008;7:845–54.
TOYOTA HYBRID: Hybrid at the Heart of Toyota Racing in 2014 (2014);
CAP-XX Supercapacitors for Micro-Hybrid Automotive Applications (2013).

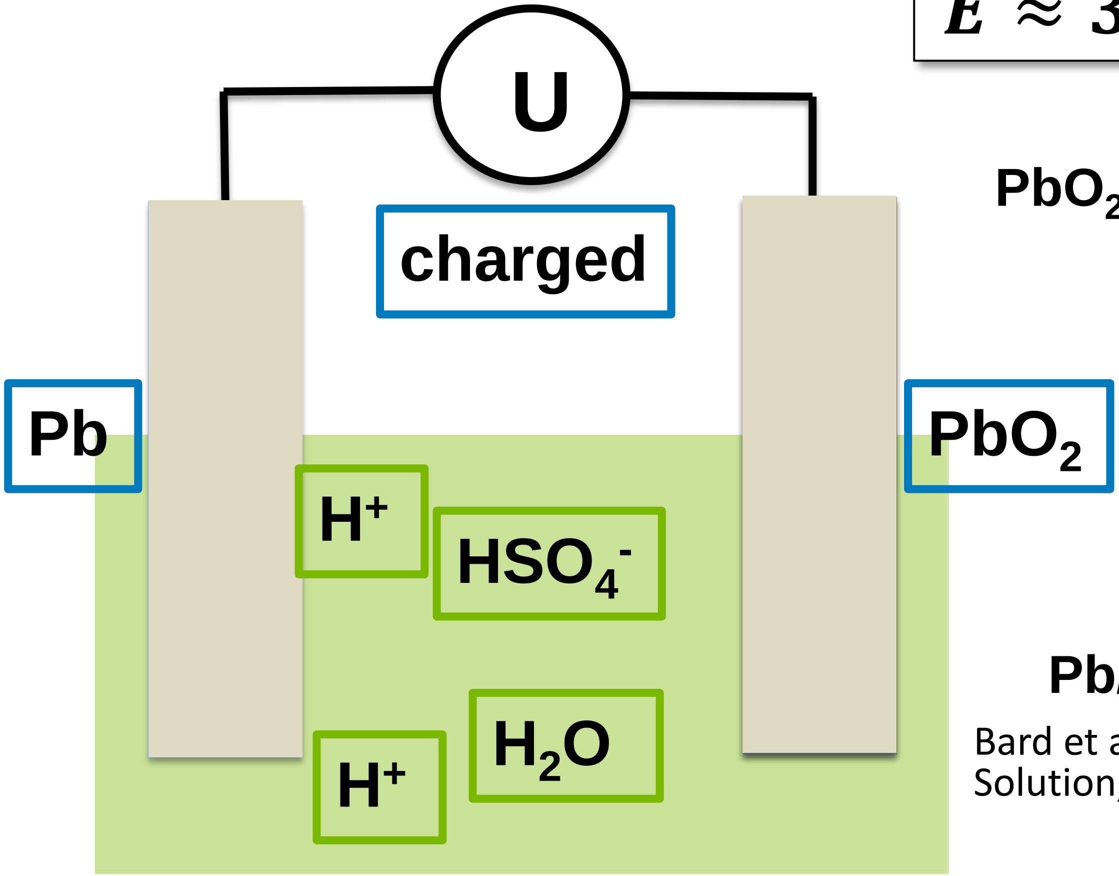
Batteries

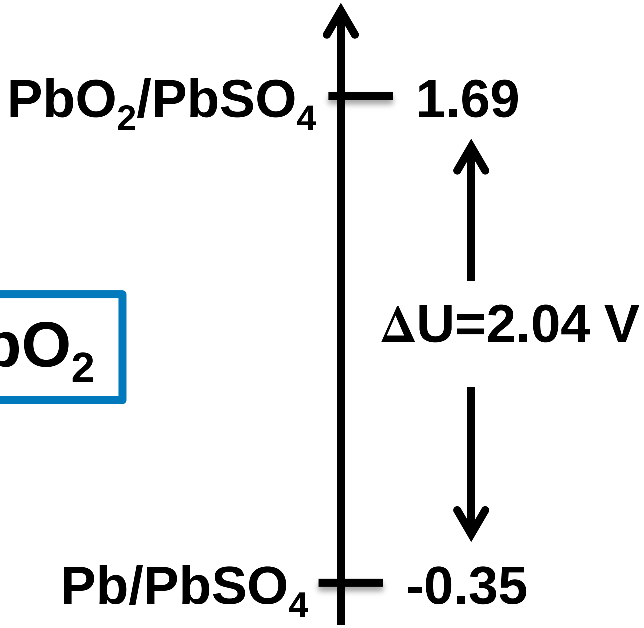

Capacitors
Electrochemical Capacitors
(Supercapacitors)
Batteries
Fuel Cells
BATTERY
Power density (W/kg)
10^7
10^6
10^5
10^4
10^3
10^2
10
1
Energy density (Wh/kg)
10^-2
10^-1
1
10
10^2
10^3

Lead-Acid Battery

$$\boxed{E = Q\,\Delta U}$$

$$\boxed{E \approx 35\,Wh\,kg^{-1}}$$





Bard et al: Standard Potentials in Aqueous Solution, CRC Press, 1985

Energy stored in Electrodes

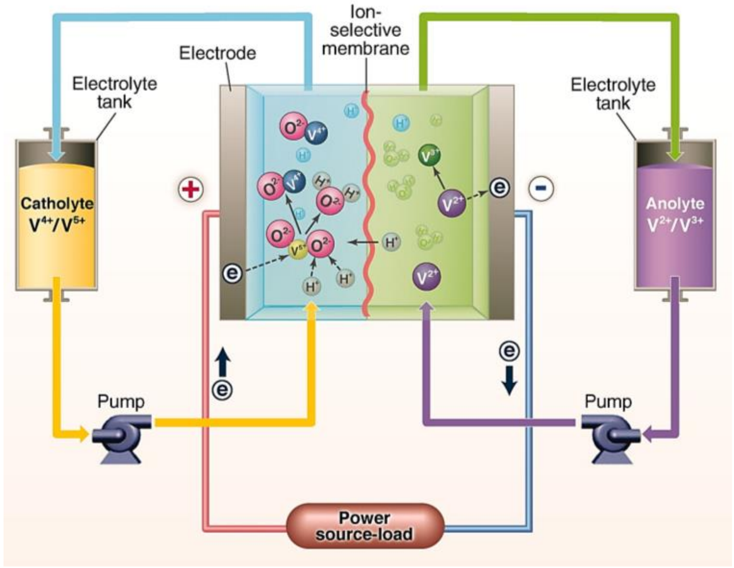
$$Pb(s) + HSO_4^- \longrightarrow \mathrm{PbSO_4(s)} + H^+ + 2e^-$$

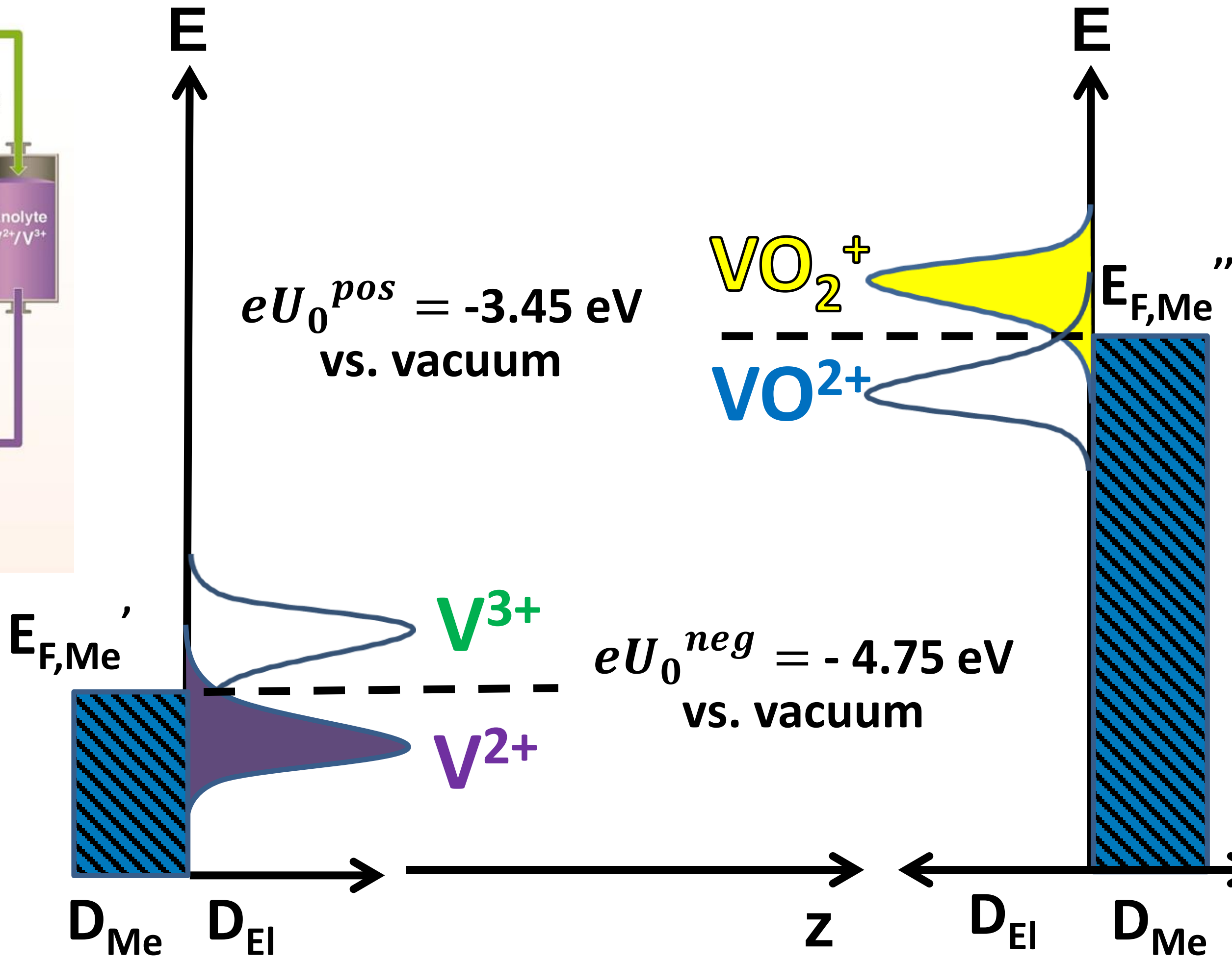
$$PbO_2(s) + HSO_4^- + 3H^+ + 2e^- \longrightarrow \mathrm{PbSO_4}(s) + 2H_2O$$

Batteries

Redox Flow Batteries

$$E = Q\,\Delta U$$





$eU_0^{pos} = -3.45$ eV vs. vacuum

$eU_0^{neg} = -4.75$ eV vs. vacuum

Negative Electrode

Positive Electrode

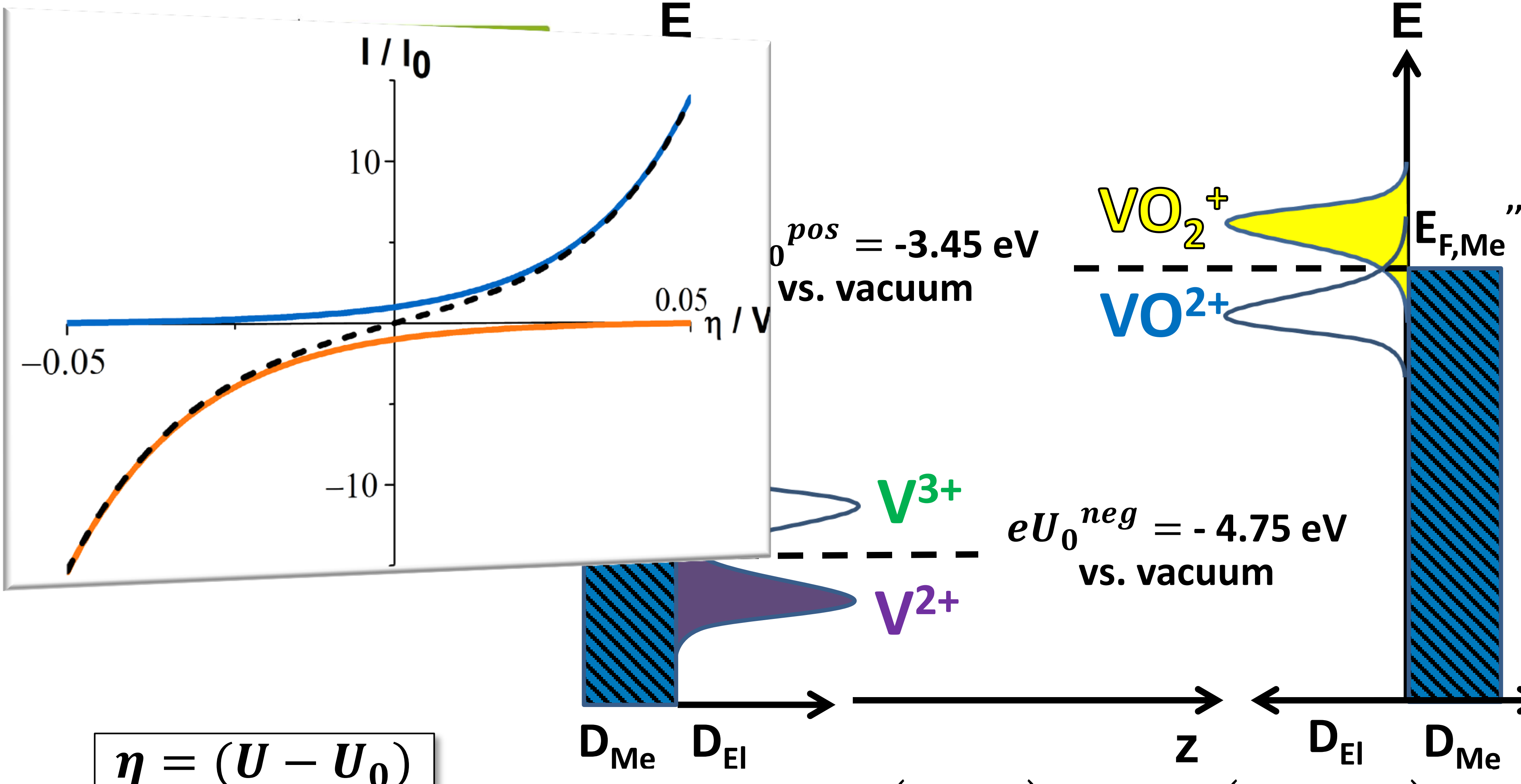
Energy stored in Electrolyte

18 March 2014

Batteries

Redox Flow Batteries

$$\boxed{E = Q\,\Delta U}$$



$_0{}^{pos}$ = -3.45 eV vs. vacuum

$eU_0{}^{neg}$ = - 4.75 eV vs. vacuum

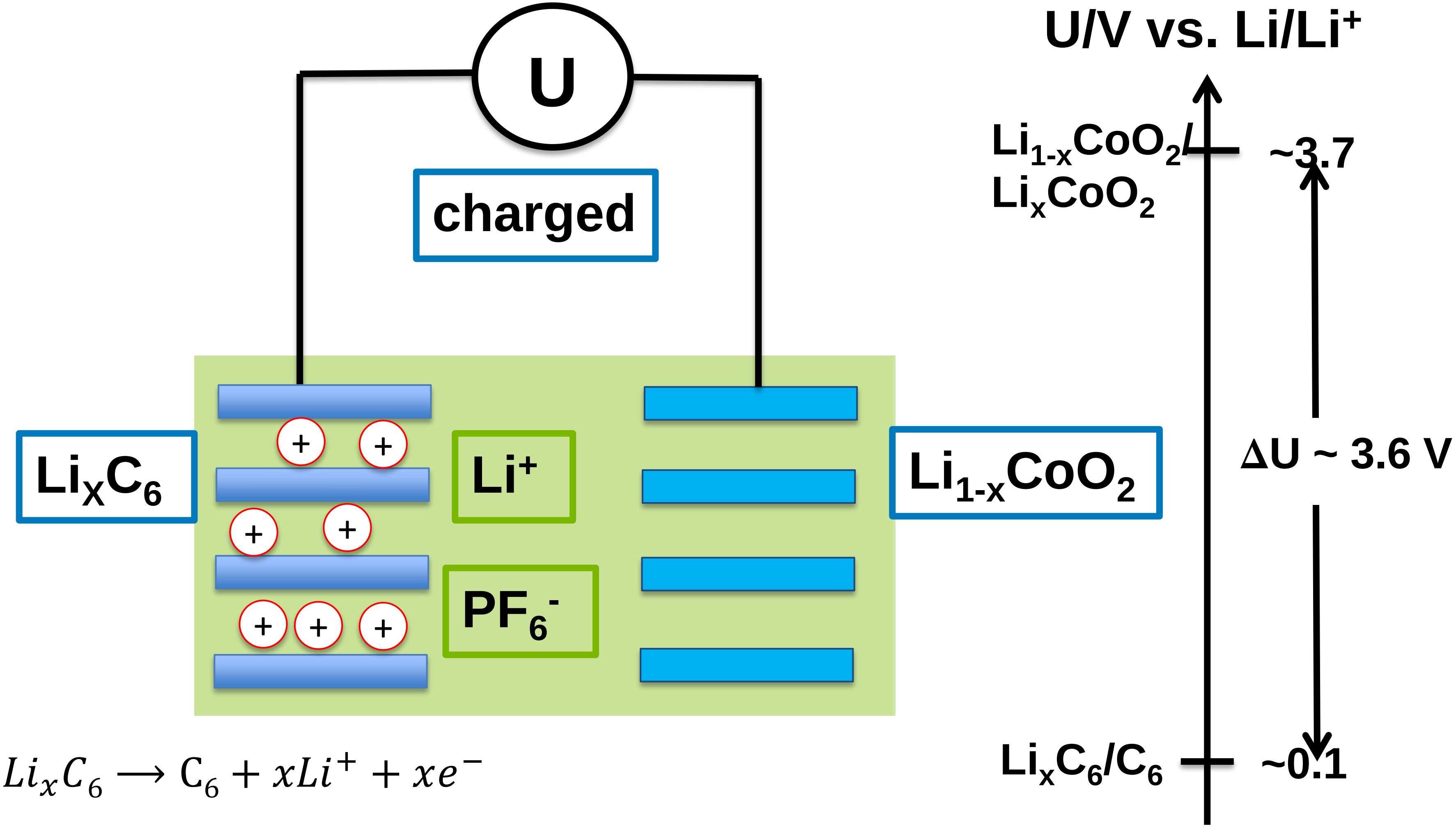
$$\boxed{\eta = (U - U_0)}$$

$$\mathrm{I} = \mathrm{I}_0\left(\exp\left(\frac{\alpha_a \mathrm{F}}{\mathrm{RT}}\eta\right) - \exp\left(-\frac{\alpha_c \mathrm{F}}{\mathrm{RT}}\eta\right)\right)$$

Batteries

$\boxed{E \approx 200\ Wh\ kg^{-1}}$ $\boxed{E = Q\,\Delta U}$

Lithium-Ion Battery



U/V vs. Li/Li^+

U

charged

$Li_{1-x}CoO_2/Li_xCoO_2$ ~3.7

ΔU ~ 3.6 V

Li_xC_6/C_6 ~0.1

Li_xC_6

Li^+

PF_6^-

$Li_{1-x}CoO_2$

$$Li_xC_6 \longrightarrow C_6 + xLi^+ + xe^-$$

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \longrightarrow Li_xCoO_2$$

Batteries

EVA

Battery:
170 Wh kg^{-1}
Pack:
101 Wh kg^{-1} 200 Wh kg^{-1}

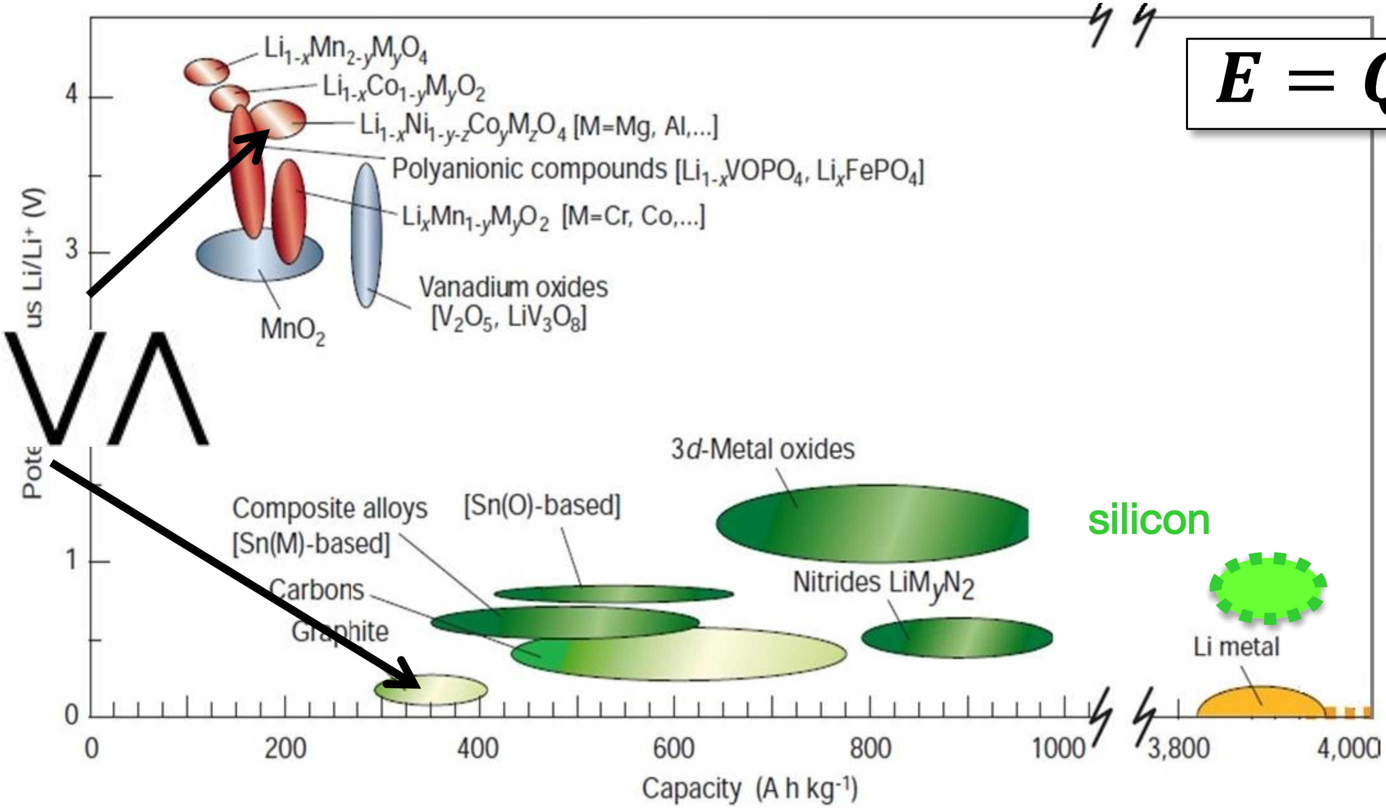
United States Advanced Battery Consortium

Battery Pack:

- 200 km range in 15 min charging;
- 50 kWh energy content;
- 300 kg battery weight;
- 495 kg pack weight;
- 216 Li-Ion NMC cells;
- 400 V nominal voltage;
- 360 A max. current.

Energy Density

$$\boxed{E = Q\,\Delta U}$$



$$x\,\mathrm{Li} + \mathrm{MX_y} \leftrightarrows \mathrm{Li_xMX_y}$$

Insertion

$$x\,\mathrm{Li} + \mathrm{MX_y} \leftrightarrows \mathrm{Li_xX_y} + \mathrm{M}$$

Conversion/Alloying

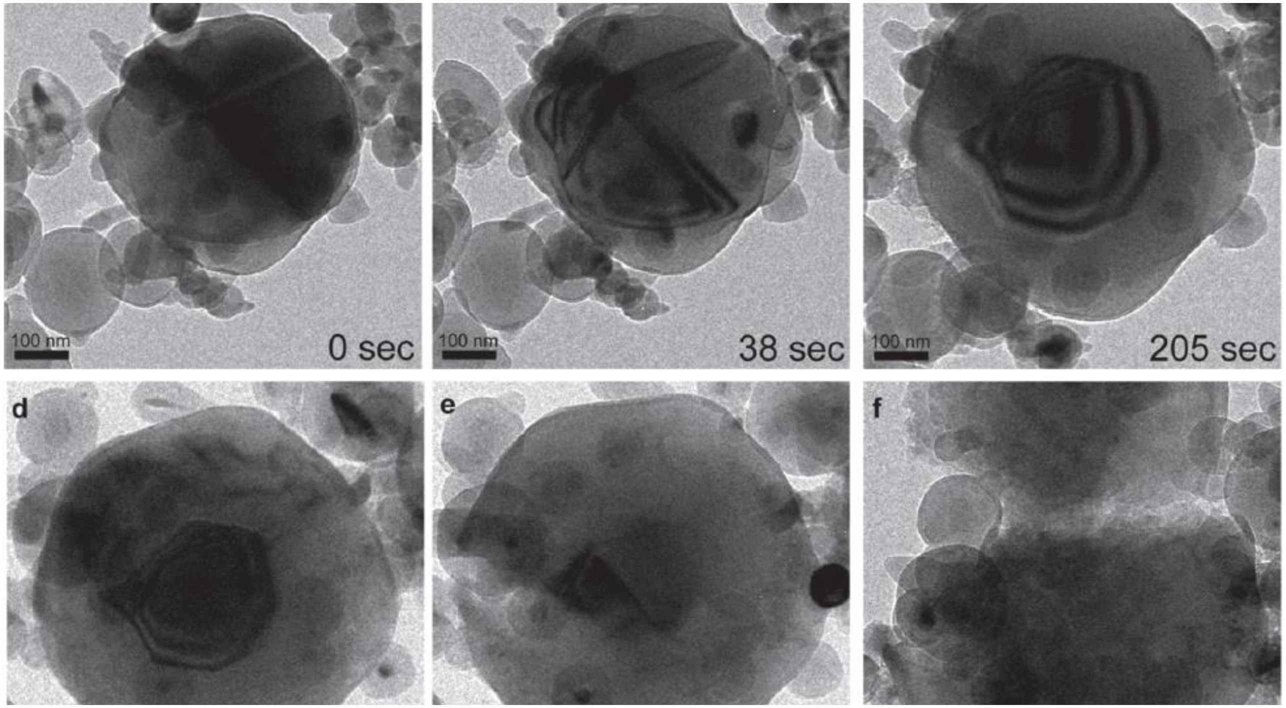
Scrosati B, Garche J. J Power Sources 2010;195:2419–30. J.-M. Tarascon, M. Armand, Nature, 2001, 414, 359

Alloying Anode: Silicon

Full Discharge: **$Li_{22}Si_5$ ➔ 4200 mAh g^{-1}** **LiC_6 ➔ 372 mAh g^{-1}**

Problem: Extreme Volume change ➔ Capacity decay

Possible Approach: Nanostructures with facile strain relaxation

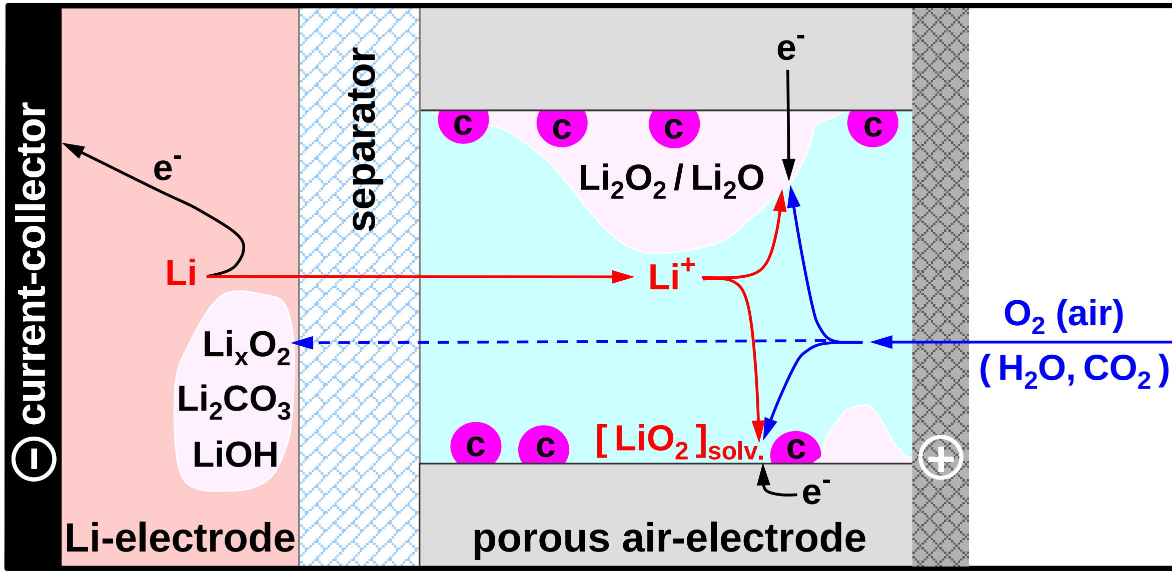


Nanostructured Si anodes are promising, but quantitative understanding is still missing and nature of SEI needs to be understood.

Wu H, Cui Y. Nano Today 2012;7:414–29. McDowell et al. Adv Mater 2013;25:4966–85.

Novel Cathode: Li-O_2

Discharge Mechanism: $2\,\mathrm{Li} + O_2 \leftrightharpoons Li_2O_2$ Up to 1200 mAh g^{-1}

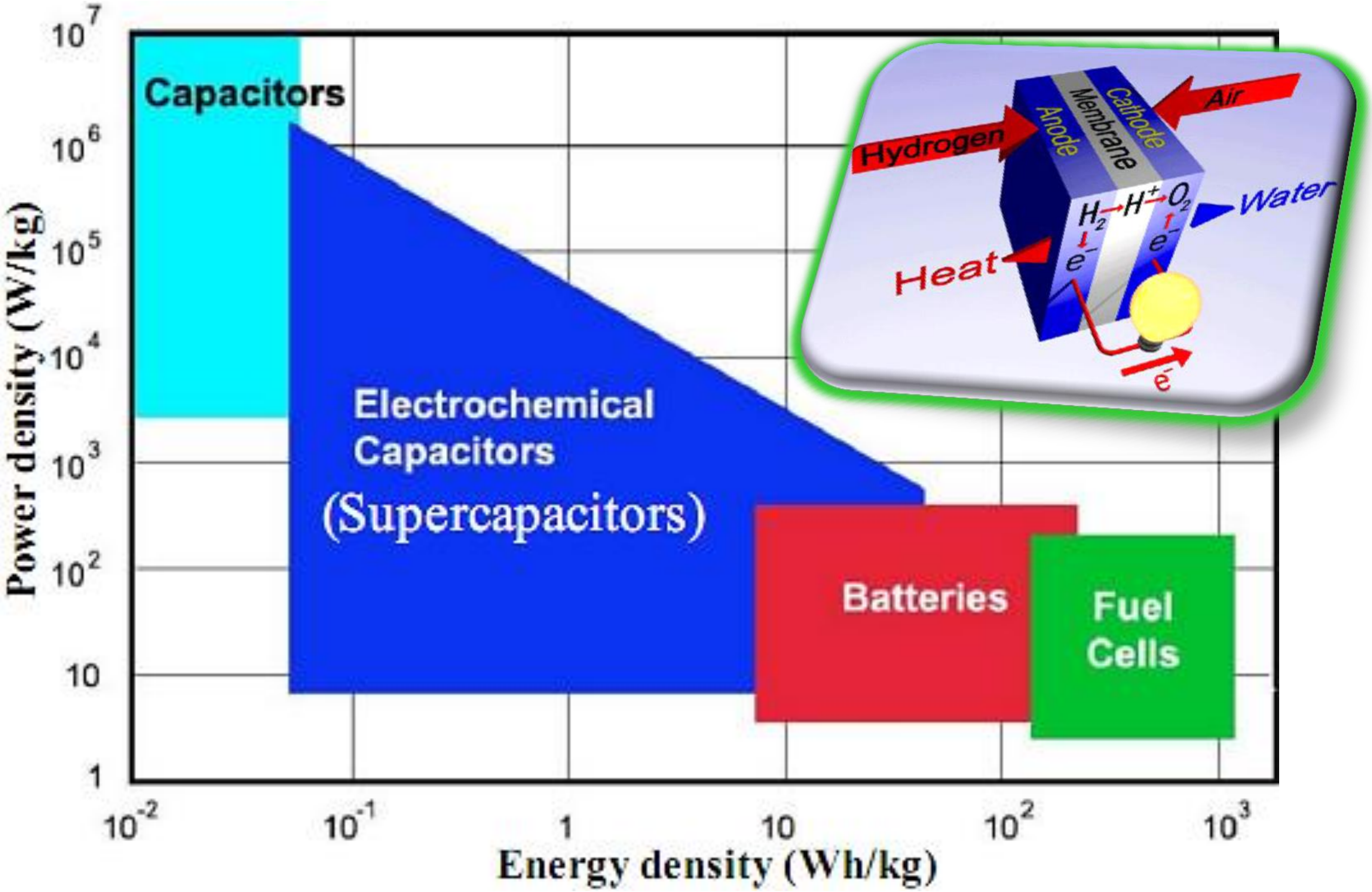


Challenges:

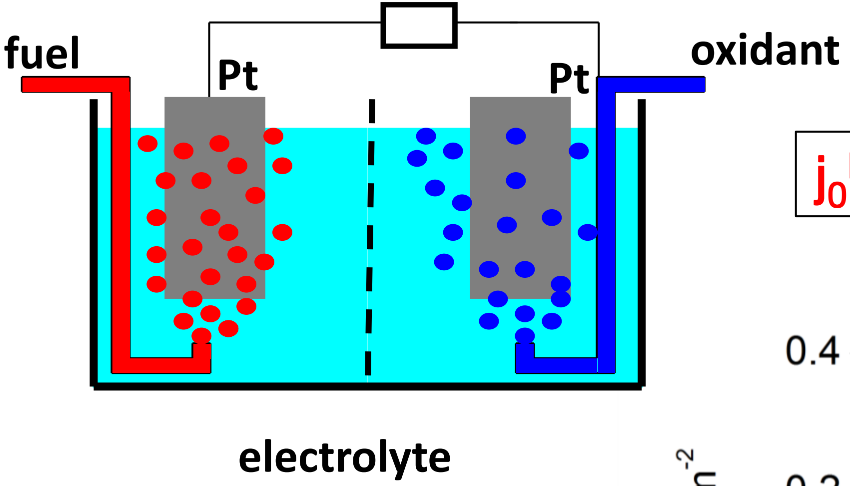
- Electrolyte stability;
- Blockage of porous carbon cathode with discharge products ("clogging");
- Slow kinetics for charging.

Y.-C. Lu,et al, Electrochem. & Solid-State Lett., 2010, 13, A69

Fuel Cells

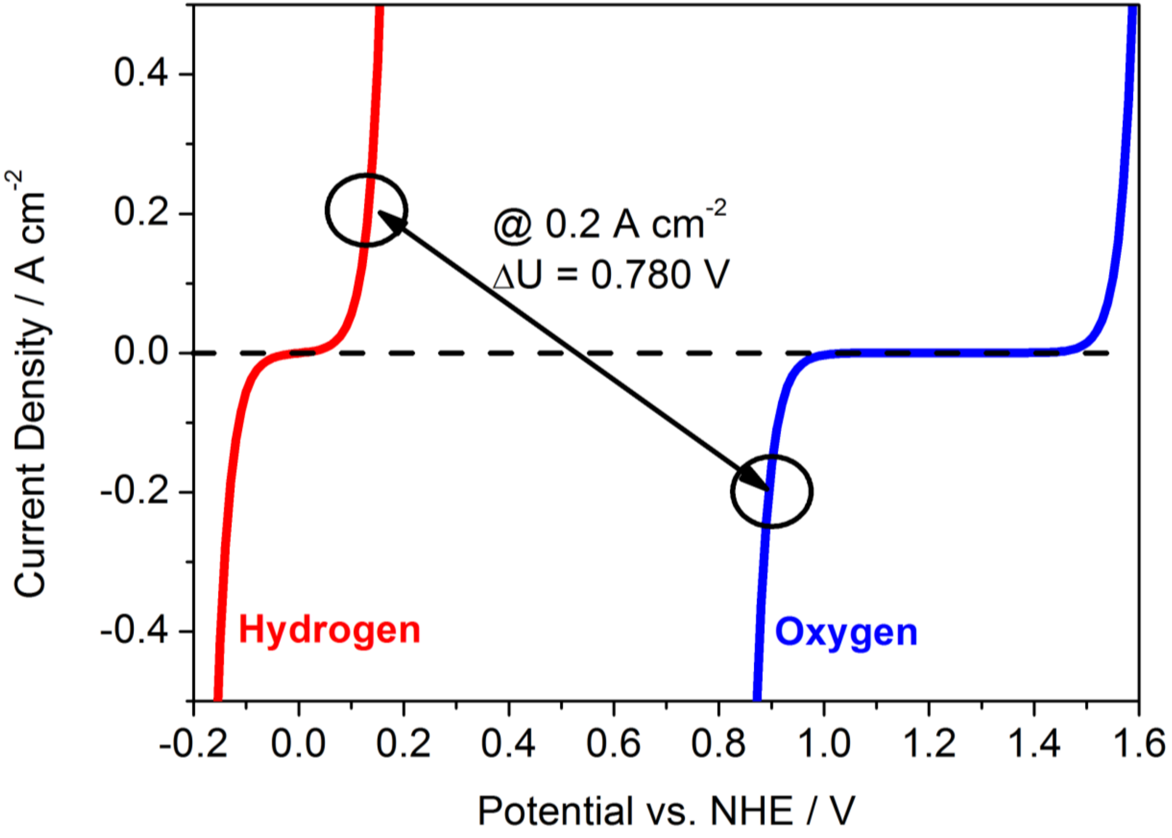

Capacitors
Electrochemical Capacitors
(Supercapacitors)
Batteries
Fuel Cells
Power density (W/kg)
Energy density (Wh/kg)
10^7
10^6
10^5
10^4
10^3
10^2
10
1
10^{-2}
10^{-1}
1
10
10^2
10^3
Hydrogen
Air
Anode
Membrane
Cathode
$H_2 \rightarrow H^+ \rightarrow O_2$
Water
Heat
e^-
e^-
e^-

Fuel Cells



$j_0^{Pt} \approx 1 \text{mA cm}^{-2}$

$j_0^{Pt} \approx 2.8\ 10^{-4} \text{mA cm}^{-2}$



- Direct conversion of chemical into electrical energy;
- Constant supply of fuel and oxidant.

Energy Conversion

$$j_0 = \frac{R\,T}{nF\,R_f\,A}$$

$$j = j_0\left(\mathrm{Exp}\left[\frac{\alpha_a nF}{RT}\eta\right] - \mathrm{Exp}\left[-\frac{\alpha_c nF}{RT}\eta\right]\right)$$

Fuel Cells

Complicated reaction mechanism

Hydrogen related reactions:

$H_2 + 2\ * \leftrightarrows 2\ H_{ad}$ Tafel

$H_2 + * \longrightarrow H_{ad} + H^+ + e^-$ Heyrovsky

$H_{ad} \longrightarrow * + H^+ + e^-$ Volmer

$j_0^{Pt} \approx 1\,\text{mA cm}^{-2}$

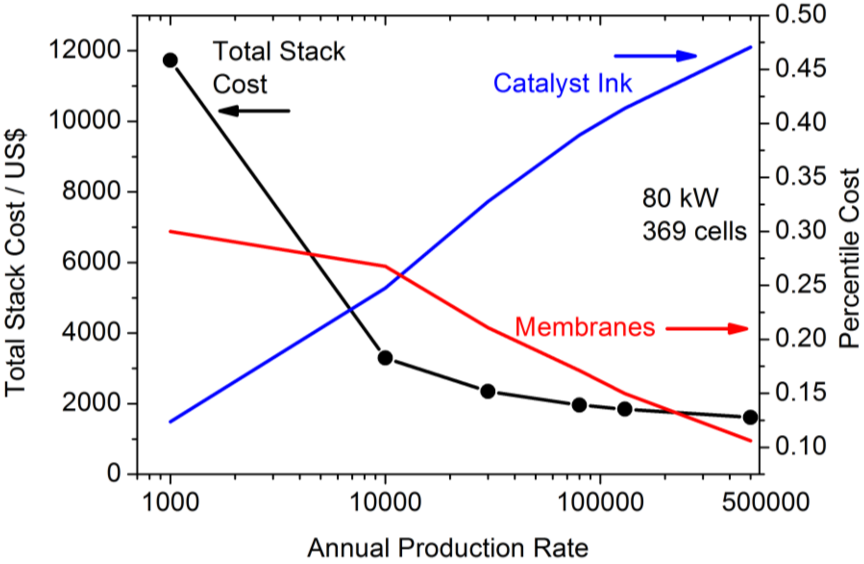
Slow kinetics

- Low power;
- High cost.

Increase Temperature.

Computational studies.

Model catalyst studies.

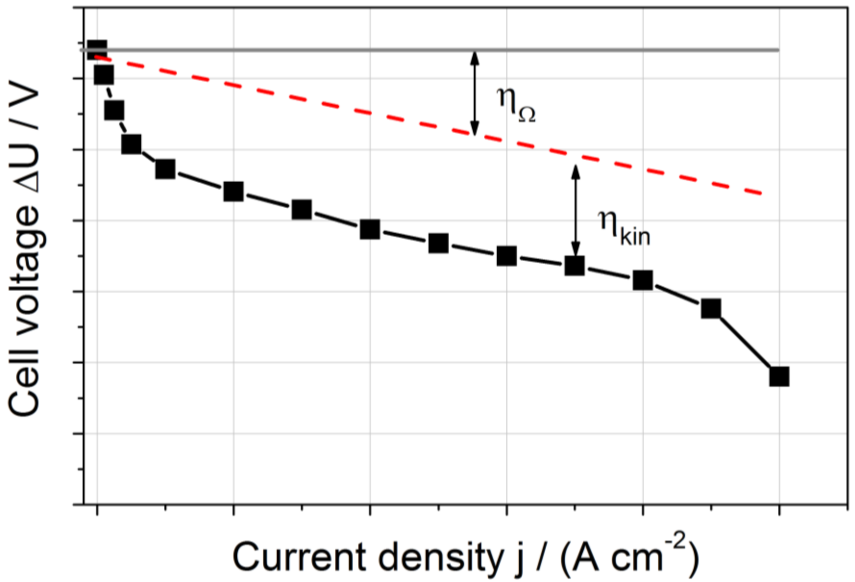


Values from: DOE Strategic Analysis: Mass Production Cost Estimation of Direct H_2 PEM Fuel Cell System for Transportation Applications (2012)

Friedl J, Stimming U. Electrochim. Acta 2013;101:41–58.

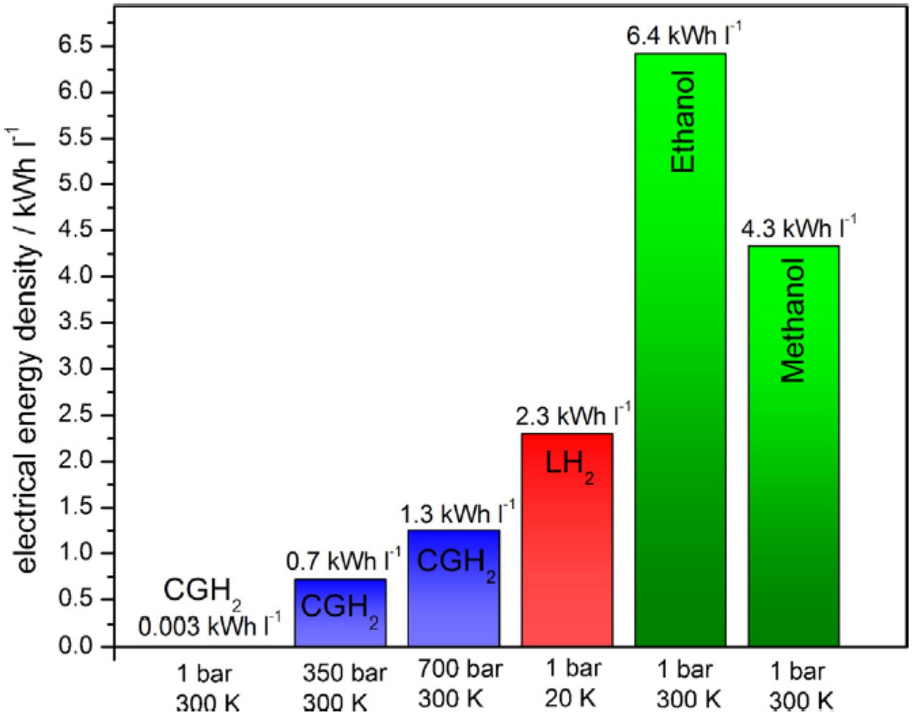
Fuel Cells

Characteristic Curve PEM



kinetic losses evident

Many possible fuels – high energy

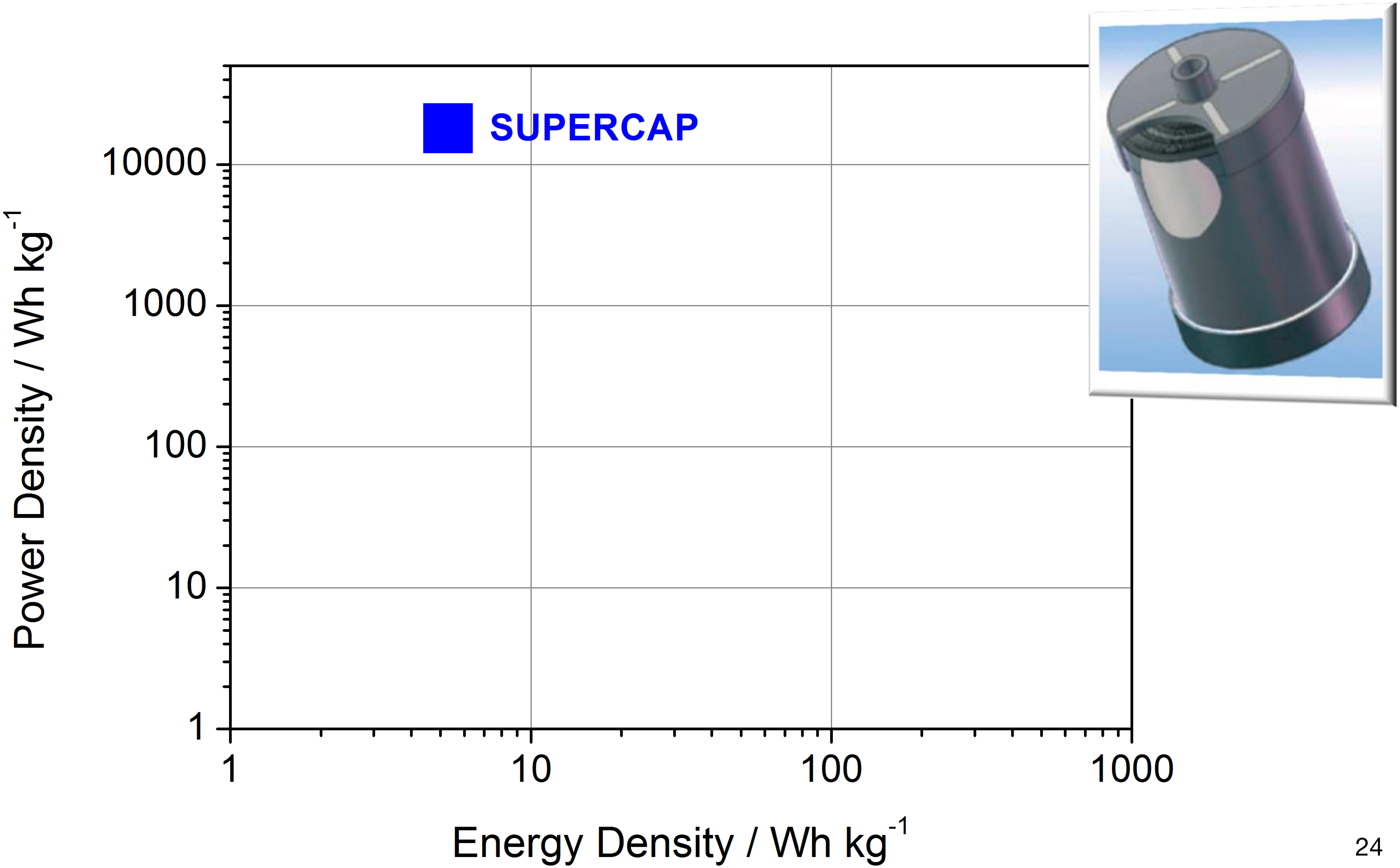


Friedl J, Stimming U. Electrochim. Acta 2013;101:41–58.

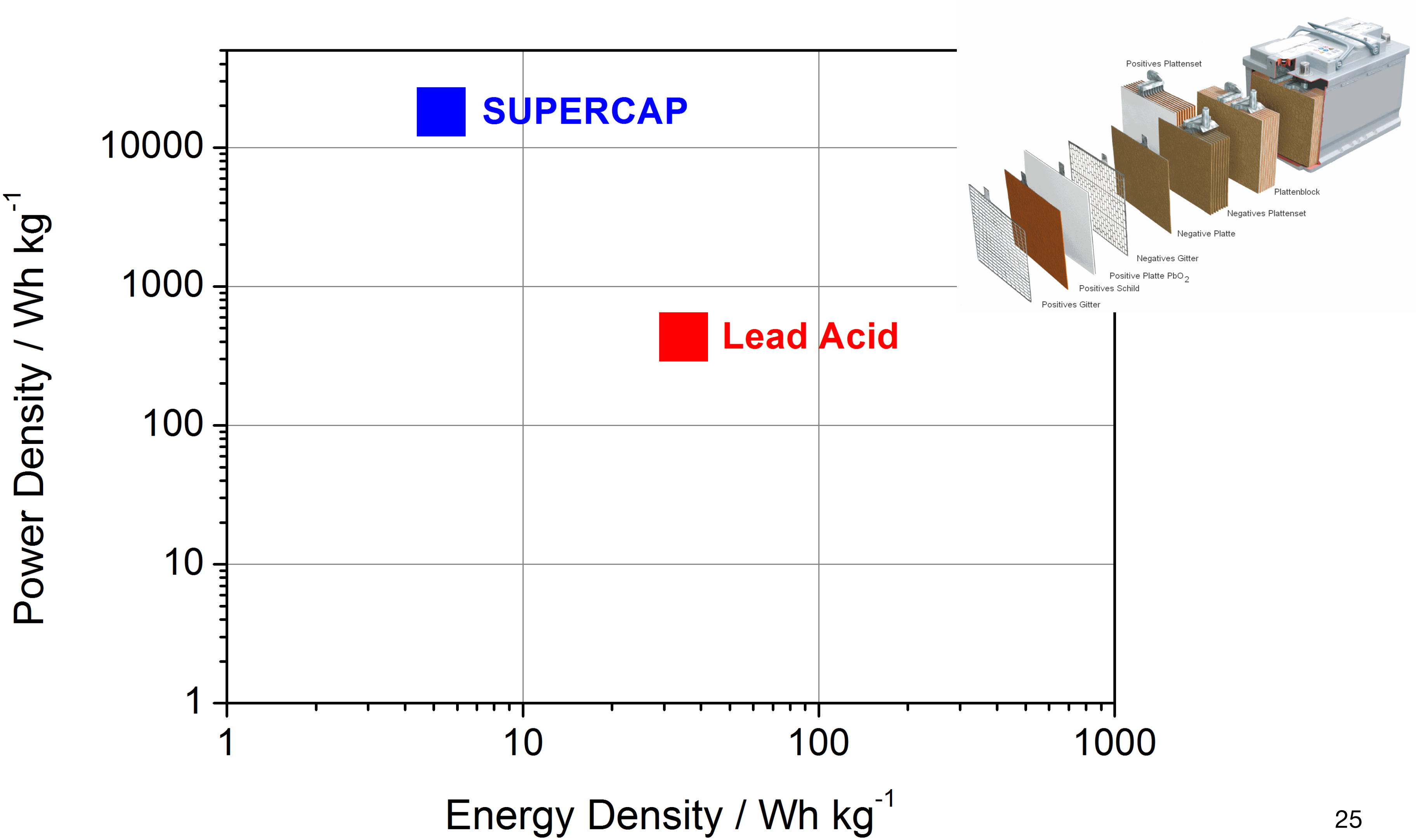
POWER: No faradaic reactions

ENERGY: Double layer only

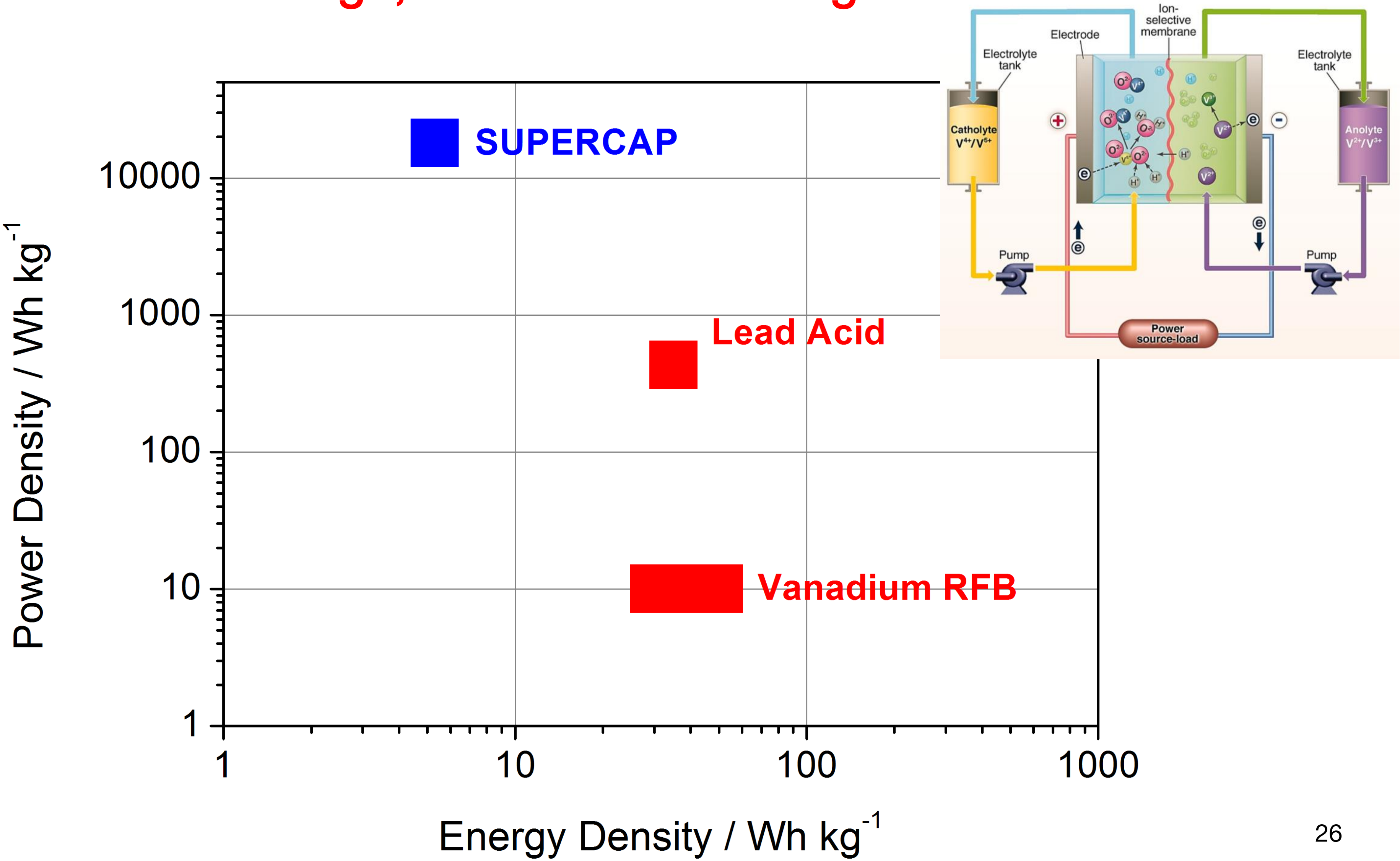
CYCLE LIFE: Very high, no faradaic reaction



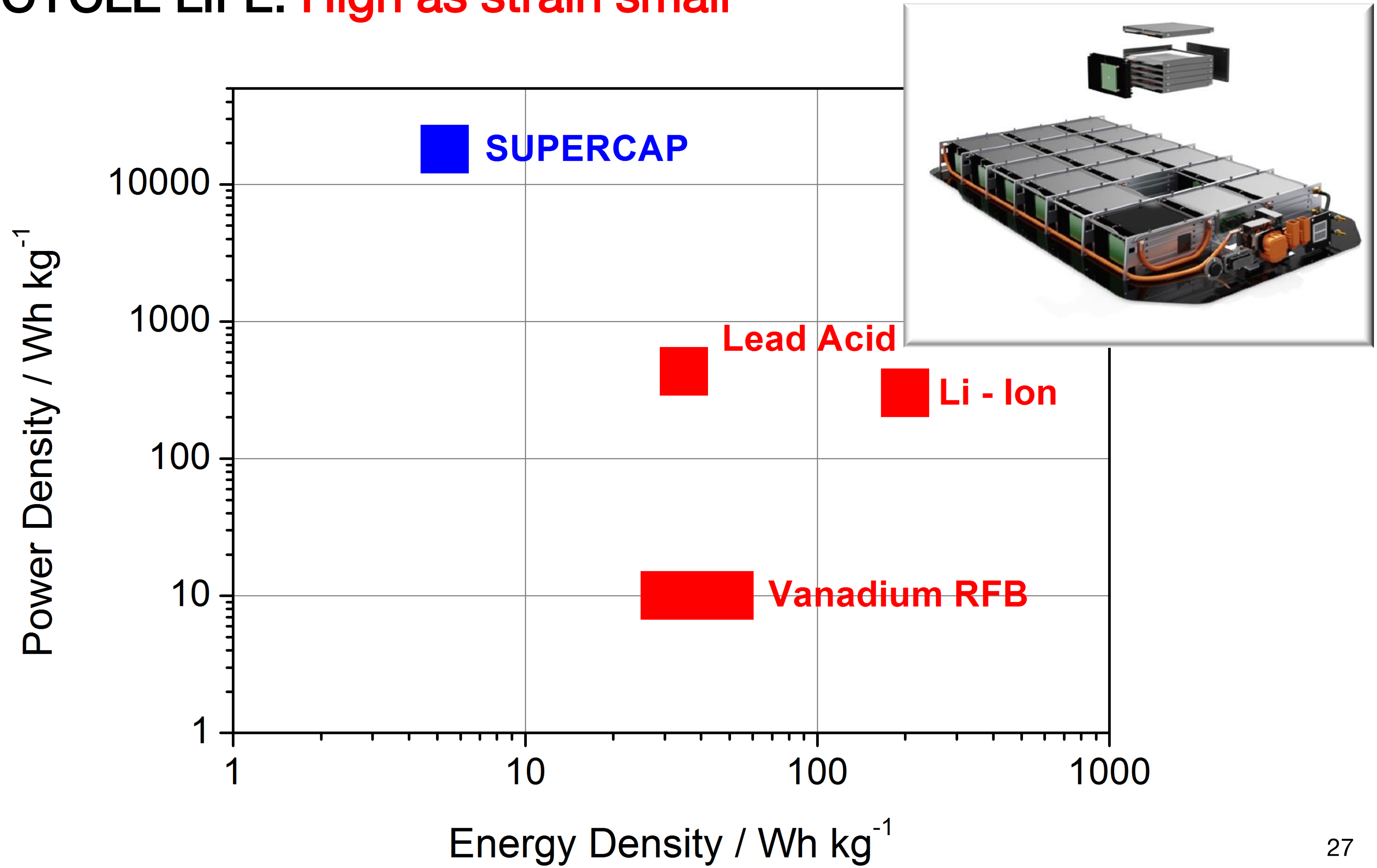
POWER: Facile Charge transfer
ENERGY: Stored in electrodes
CYCLE LIFE: Low, electrode conversion



POWER: Sluggish Charge Transfer
ENERGY: Stored in electrolyte
CYCLE LIFE: High, electrodes for charge transfer

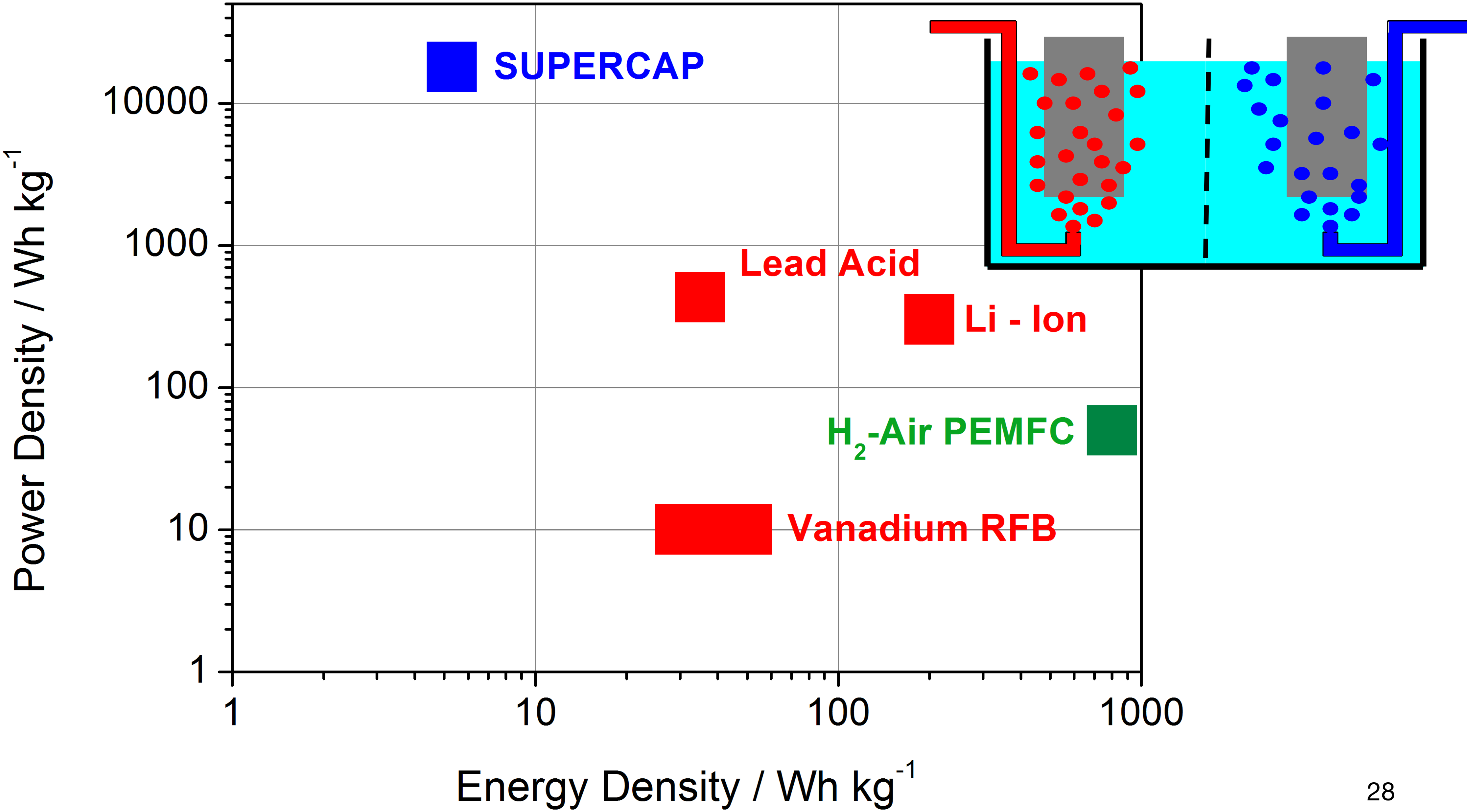


POWER: Intercalation reaction
ENERGY: No conversion but intercalation
CYCLE LIFE: High as strain small



POWER: Very sluggish O_2 reduction

ENERGY: High energy density fuels



Thank you for your attention!