Batteries and Supercapacitors for electrochemical energy storage: state-of-the art and next challenges

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Capacitors: Power
- high power density (>50 kW/kg)
- low energy density: <0,1 Wh/kg
- time constant: ~ 1 ms

Batteries:
- high energy (100-200 Wh/kg)
- low power: < 1kW/kg
- time constant: ~ 1h

Supercapacitors:
- high power (10-20 kW/kg)
- medium energy: 5 Wh/kg
- time constant: ~ 5 s

1. Batteries
   - Basics
   - Li-ion batteries
   - Perspectives

2. Supercapacitors
   - Basic principle
   - Applications
   - Microporous carbons

3. The French Network on Batteries
1.1 Batteries: basic principle

$$\Delta E_{cell} = E^+ - E^- \text{ (V)}$$  
$$Q_{cell} \text{ (mAh)} \quad \text{and} \quad \text{Energy} = \Delta E \times Q \text{ (Wh)}$$

Rechargeable cells $\rightarrow$ Accumulators (Batteries)
1.2 Li-ion Batteries: starting point (1990, Sony)

**Characteristics:**
- Li⁺ intercalation
- no Li metal
- Non aqueous Electrolyte

**Anode:** C graphite

\[
\text{LiC}_6 \rightleftharpoons \text{C}_6 + \text{Li}^+ + \text{e}; \quad E = 0.5 \text{ V vs Li}, \quad C = 372 \text{ mAh/g}
\]

→ Lithium ion intercalated (Li⁺) : **Li-ion batterie**

**Cathode:** LiCoO₂

\[
\text{Li}_{0.5}\text{CoO}_2 + 0.5 \text{ Li}^+ + 0.5 \text{ e} \rightleftharpoons \text{LiCoO}_2; \quad 177 \text{ mAh/g}
\]

Li – ion intercalation at both electrodes

\[\Delta E = 3.7\text{ V}; \quad C = 60 \text{ Ah/kg}; \quad W = 150 \text{ Wh/kg}\]
1.2 Li-ion batteries: a large family...
1.2 Current Li-ion batteries: the cathode chemistries

Cathode chemistry defines the name of the batteries (LFP, NMC, NCA...)

From M. Winter, AABA Conference 2011, Mainz
1.2 2D LiCoO$_2$-based cathodes: NMC chemistry

Li$_{1-x}$CoO$_2$ + xLi$^+$ + x e$^-$ $\leftrightarrow$ LiCoO$_2$

LiCoO$_2$: E=3.8 V, energy $\uparrow$
- C limited to 150 mAh/g
- Thermal stability issue (Co-O)

$\rightarrow$ LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (1/3): NMC chemistry

Co$^{3+}$: Active redox

Only Ni$^{2+}$ (active)
Mn$^{4+}$: no Ni$^{4+}$ (Mn un-active)
Cathode 3D: [LiFePO$_4$ nano + C]

LiFePO$_4$ (LFP); 1 Li$^+$ per mole

$$\text{FePO}_4 + x\text{Li}^+ + xe^- \leftrightarrow x\text{LiFePO}_4 + (1-x)\text{FePO}_4$$

- $E=3.45$ V vs Li
- $C=170$ mAh.g$^{-1}$

$\rightarrow$ no thermal runaway (P-O stable)

LiFePO$_4$
- high power (charge and discharge)
- thermal stability (no runaway)

**BUT**
- lower energy density (120 Wh/kg)
- Fe solubility issue for $T>50°C$
- needs for carbon coatings (conductivity)

www.saftbatteries.com

From M. Winter, AABA Conference 2011, Mainz
Lithium-Manganese Oxide (LMO)

\( \text{LiMn}_2\text{O}_4 \) (spinel structure \( \text{AB}_2\text{O}_4 \))

\[
x\text{Li}^+ + xe^- + \text{Li}_{(1-x)}\text{Mn}_2\text{O}_4 \leftrightarrow \text{LiMn}_2\text{O}_4
\]

0.8 Li per \( \text{Mn}_2\text{O}_4 \); \( C=120 \text{ mAh/g} \),

Pros :
- low cost,
- high cell voltage
- high power and thermal stability

Cons :
- -20% Capacity vs NMC
- \( T >50^\circ \text{C} \): \textbf{Mn}^{3+} \text{ dissolution}
  \[
  2\text{Mn}^{3+} \rightarrow \text{Mn}^{2+} \text{ (dissolution)} + \text{Mn}^{4+} \text{ (solid)}.
  \]
1.3 Advanced Li-ion batteries: Li alloys as anodes

**C**_{graphite} limited to 370 mAh/g $\rightarrow$ higher capacitve anodes?

### Li alloying reaction:

$$M^\circ + xLi + xe^- \iff Li_xM, \text{ with } x \leq 4.4$$

Sn, Si BUT

Huge volume change (+300%) leading to mechanical stress

No cyclability
1.3 Advanced Li-ion avancé: Si-based anodes

Ex of Silicium-based anodes: mechanical buffer

Nano-sizing helps in buffering mechanical stress → improved capacity (1,000 mAh/g)
Other strategies possible (ink formulation) ; commercialization in progress

G. Yushin et al., Nature Materials 2010
1.3 Advanced cathodes: Li-rich NMC phases

2007: Li-rich phase (M. Tackeray et al.)

Li[Li\textsubscript{0.2}Ni\textsubscript{0.14}Mn\textsubscript{0.54}Co\textsubscript{0.13}]O\textsubscript{2}

Classical cationic redox mechanism

Li[Li\textsubscript{0.2}Ni\textsuperscript{+2}_{0.14}Mn\textsuperscript{+4}_{0.54}Co\textsuperscript{+3}_{0.13}]O\textsubscript{2}

0.4 e⁻

Fundamental problem

→ Origin of this extra capacity

NiMnCo

2007: Li-rich phase (M. Tackeray et al.)

Why capacity > 280 mAh/g?

Charge/discharge at constant current

Capacity (mAh/g)

Potential (Volts vs. Li⁺/Li⁻)

Discharge

Charge

0.9 e⁻
Direct evidence of cumulative cationic ($M^{n+} \rightarrow M^{(n+1)+}$) and anionic ($O^2- \rightarrow O_2^{2-}$) redox processes!!

Feasibility of using previously disregarded heavy 4d-metals!!

→ Opens new paths for high capacity materials

JM Tarascon et al., *Nature (Materials 2014)*
1.4 Perspectives: what technology for the future?
1.4 Perspectives: Li-O₂ batteries

Few advantages and .... Lot of issues!!

E Theoretical: 2300 Wh/kg

Theoretically: 800-900 Wh/kg

\[
\begin{align*}
O_2(g) + 2Li^+ + 2e^- & \rightarrow Li_2O_2(s) \\
\Delta E & = 4V
\end{align*}
\]

- Instability vs Li° and high polarization
- low reaction kinetics
- reaction G + L \rightarrow S: low power
- Precipitation of Li₂O₂ (insulating)
- No cycle life
- Catalyst + porous material: key


Dominique Larcher, LRCS, Amiens
Use a redox mediator ($I_3^-/I^-$) to oxidize OH$^-$ in H$_2$O during charge and dissolve LiO$_2$ in discharge.

**Discharge Reactions**

1. Electrochemical: $4Li^+ + 4O_2 + 4e^- \rightarrow 4LiO_2$
2. Chemical: $4LiO_2 + 2H_2O \xrightarrow{via \text{the \ action \ of \ } Li} 4LiOH + 3O_2$

**Charge Reactions**

1. Electrochemical: $6I^- \rightarrow 2I_3^- + 4e^-$
2. Chemical: $4LiOH + 2I_3^- \rightarrow 4Li^+ + 6I^- + 2H_2O + O_2$

Important improvement in the Li-O$_2$ technology but does not solve all the issues.
• **Na⁺ to replace Li⁺: Na-ion**

  **Cost:**  
  \[ \text{Li}_2\text{CO}_3: 0.9 \text{ euro/kg} \]  
  \[ \text{Na}_2\text{CO}_3: 0.08 \text{ euro/kg} \]

  **Abundance:**  
  \[ \text{Na}^+ = \text{Li}^+ \times 10^5 ! \]

  **Potential:**  
  \[ \text{Li}^+/\text{Li}: -3.05 \text{ V} \]  
  \[ \text{Na}^+/\text{Na}: -2.71 \text{V} \]

  **Capacity:**  
  \[ \text{Li}^+/\text{Li}: 3860 \text{ mAh/g} \]  
  \[ \text{Na}^+/\text{Na}: 1166 \text{ mAh/g} \]

→ **Alternative to Li-ion at lower cost ; -30% energy density**

→ **Mass storage (renewable, grids...)**
1.4 Perspectives: Li-S batteries

Reactions at the cathode can be schematically described as follows:

1. \( \frac{3}{4} S_8 + 2 Li^+ + 2\bar{e} \rightarrow Li_2S_6 \)  
2. \( \frac{2}{3} Li_2S_6 + 2/3 Li^+ + 2/3 \bar{e} \rightarrow Li_2S_4 \)  
3. \( \frac{3}{4} Li_2S_4 + 1/2 Li^+ + 1/2 \bar{e} \rightarrow Li_2S_3 \)  
4. \( 2\frac{3}{3}Li_2S_3 + 2/3 Li^+ + 2/3 \bar{e} \rightarrow Li_2S_2 \)  
5. \( 1\frac{2}{2}Li_2S_2 + Li^+ + \bar{e} \rightarrow Li_2S \)  

(3) can be as well \( Li_2S_4 + 4e^- + 4Li \rightarrow Li_2S_2 + 2 Li_2S \)

One solution: sulfur confinement in porous carbon
1.4 Perspectives: Li-S batteries

From confinement to adsorption on polar solid electronic conductor

Ti$_4$O$_7$ / S composites (70% wt)

Li-S: old-fashion technology (50 years old) but
Recent advances in favor of a fast commercialization
.... well ahead Metal-Air systems!!!
The development of new rechargeable battery systems could fuel various energy applications, from personal electronics to grid storage. Rechargeable aluminium-based batteries offer the possibilities of low cost and low flammability, together with three-electron-redox properties leading to high capacity. However, research efforts over the past 30 years have encountered numerous problems, such as cathode material disintegration, low cell discharge voltage (about 0.55 volts; ref. 5), capacitive behaviour without discharge voltage plateaus (1.1–0.2 volts or 1.8–0.8 volts) and insufficient cycle life (less than 100 cycles) with rapid capacity decay (by 26–85 per cent over 100 cycles). Here we present a rechargeable aluminium battery with high-rate capability that uses an aluminium metal anode and a three-dimensional graphitic-foam cathode. The battery operates through the electrochemical deposition and dissolution of aluminium at the anode, and intercalation/de-intercalation of chloroaluminate anions in the graphite, using a non-flammable ionic liquid electrolyte. The cell exhibits well-defined discharge voltage plateaus near 2 volts, a specific capacity of about 70 mA h g⁻¹ and a Coulombic efficiency of approximately 98 per cent. The cathode was found to enable fast anion diffusion and intercalation, affording charging times of around one minute with a current density of ~4,000 mA g⁻¹ (equivalent to ~3,000 W kg⁻¹), and to withstand more than 7,500 cycles without capacity decay.
**Al-ion:**
- Cell voltage 2 V, C=60 mAh/g, ionic liquid,
- Negative electrode = Al foam, positive = Carbon foam → vol energy??
- One charge per Al complex!!!!

→ grav. Energy 5 to 10 times lower, low vol. energy...
→ Interesting concept but long and winding road to replace Li!!
ENVIA (http://enviasystems.com/) made a recent announcement on the 450 Wh/kg batteries using Si-based anode.

400 Wh/kg: very high energy density...

...but: thick electrodes, low rates and soft packaging
Outline

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   - Perspectives

2. Supercapacitors
   - Basic principe
   - Applications
   - Microporous carbons

3. The French Network on Batteries
Electrochemical Energy Storage devices

**Batteries:**
- high energy (250 Wh/kg)
- low P: up to kW/kg
- time constant: 10’s min

**Supercapacitors:**
- high power (15-20 kW/kg)
- medium energy: 5 Wh/kg
- time constant: ~ 10 s


**Batteries and Supercapacitors: complementary devices**
2.1 Charge storage mechanism in EDLCs

Charge storage: electrostatic (Double Layer Capacitance)

\[ C = \frac{(\varepsilon_0 \varepsilon_r S)}{d} \]

\[ C \approx 10 - 20 \text{ } \mu\text{F/cm}^2 \]

- **High Surface Area carbon**
  
  \[ \text{SSA} \approx 1500 \text{ m}^2\text{g}^{-1} \]
  
  \[ \Rightarrow > 100 \text{ F.g}^{-1} \text{ of carbon} \]

- **Non-aqueous electrolyte**
  
  \[ \Rightarrow \Delta E_{\text{max}} = 2.7 \text{ V} \]

**Characteristics:**

- Surface Storage: low E but high P
- \( V_{\text{charge}} = V_{\text{discharge}} \)
- low \( \Delta \text{vol.} \): cyclability > 1 million cycles
2.2 Applications: power delivery

- A380 door emergency opening

16 powered by 35 V / 28.5 F modules (Maxwell)
(14 series-connected of 4 SC 100F in parallel)

Advantages by using Ultracaps
- Low weight
- Excellent life time due to high cycle nun
- High reliability
- No maintenance
2.2 Applications: energy recovery

SC modules:
1) braking energy recovery
2) electric drive (100’s m)
Starter/Alternator and recovery micro-hybrid e-Hdi Citroen C3, C4, C5 diesel (2012)

- 15% gasoil
- CO$_2$ < 130g per km

Mazda: i-ELOOP concept

Peugeot: e-HDI 308 1.6 HDi 110 ch
http://www.turbo.fr/peugeot/peugeot-308/essai-auto/410344-essai-peugeot-308/
2.2 Applications: electric drive

Blue Tram de Blue Solutions (Bolloré)
- electric drive: supercapacitors
- 1.5 km autonomy

Key interest: charging rate (60 s), cyclability, cost (facteur 10)

Plant opened last February 2015
50 Blue Tram per year
2.3 Active Materials in EDLCs: porous carbons

Coconut Shell → Carbon powder → Activation (oxidation) → Activated Carbon = Porous carbons

Macropores: > 50 nm
Micropores: < 2 nm
Mesopores: 2 nm - 50 nm

→ high SSA > 1500 m²/g

BUT
Activated carbons

Pore Size Distribution

O. Barbieri et al. / Carbon 43 (2005) 1303–1310
Capacitance increase in carbon micropores (<1nm), electrolyte AN+1M \((\text{C}_2\text{H}_5)_4^+\text{BF}_4^-\)

- **Pores < size of solvated ions accessible to ions!**
- **Huge capacitance increase in nanopores: +100%!**

**Capacitance increase in nanopores < 1 nm:**
- paradigm change
- new concept to prepare carbons

2.3 CDCs in neat EMI,TFISI electrolyte

Ionic Liquids: no solvent (only molten salts) → no solvation shell

No solvent, cation size ≈ anion size:

Maximum C at ~ 0.72 nm → when ion size ~ pore size... WHY??

1. Electrolyte is inside pores even at $\Psi=0$V: not an electrosorption driven process
2.3 MD modeling of BMI\textsubscript{1},PF\textsubscript{6} in CDCs

1. Electrolyte is inside pores even at $\Psi=0$V
2. Ion exchange with the electrolyte bulk!
3. Coordination number of ions decreases inside the pores ("desolvation")

2.4 Perspectives for supercapacitors

Increase energy density \((E=1/2 \ C.V^2)\) from 5 to >10 Wh/kg
\[ \Rightarrow t_{\text{discharge}} > 10\text{s} \]

1. Increase carbon capacitance (EDLC)
   - design porous carbons to maximize capacitance
   - understand the ion size /carbon pore size relationship

2. Fast redox materials
   - design nanostructured materials for high capacitance and high power
   - Ex: Nano-structured \(\text{Nb}_2\text{O}_5\)


3. Increase the cell voltage
   - ionic liquids-based electrolytes
   - hybrid devices (Li-ion capacitor)
3. The French network on batteries (RS2E)

**GOALS**

- address scientific and technologic issues of current and future electrochemical storage systems for mobile and stationary applications
- improve knowledge and technology transfer from research to industry
- develop the French expertise in the field

**RS2E | Réseau sur le Stockage Electrochimique de l’Energie**

= Research network on Electrochemical Energy Storage

**FUTURE HEADQUARTERS IN AMIENS (12/2016)**

**WHEN?**

SINCE 2011

**Director:** J.-M. Tarascon

**Deputy Director:** P. Simon
3. The RS2E network: organization

**Academic Research Center**
- 15 National research labs
  - LRCS, LG (Amiens)
  - CIRIMAT (Toulouse)
  - ICG-AIME (Montpellier)
  - IPREM (Pau)
  - ICMCB (Bordeaux)
  - IMN (Nantes)
  - ICR & MADIREL (Marseille)
  - CEMHTI (Orléans)
  - LCMCP, PECSA (Paris)
  - IS2M (Mulhouse)
  - LEPMI (Grenoble)
  - IRCICA (Lille)

**Technological Transfer Center**
- INDUSTRIAL CLUB
3.1 The RS2E network: research topics

**Advanced Li-ion**
(materials, formulation, electrolytes...)

**Capacitive Storage**
(nanostructured materials, carbons, pseudocapacitivities...)

**Eco-compatible Storage**
(synthesis, biomineralization, organic redox, ACV-recycling...)

**New Chemistries**
(Li-S, Na-ion, redox-flow, solid-state batteries...)

**Smart Materials**
(faradic/photovoltaic, 3D microbatteries, micro SC...)

**Safety**
(ageing, additives, Thermal and electrochemical stability)

**Theory**
(combinatory approach, Transfer limitations, System modelling)

**Instrumentation**
(in-situ techniques (XRD, HRTEM, HREELS, Synchrotron access))
Focus on two recent achievements:

1. Advanced Li-ion batteries: improving the capacity (Ah)
   - high capacity Li-rich cathode

2. Supercapacitor
   → basic understanding of ion transfer in nanopores

3. Sodium-ion batteries: an alternative to Li-ion for grid storage?
   - Na-ion battery « Task Force »
3.2 The Li-rich NMC phases

Direct evidence of cumulative cationic \( (M^{n+} \rightarrow M^{(n+1)+}) \)
and anionic \( (O^{2-} \rightarrow O_2^{2-}) \) redox processes!!

Feasibility of using previously disregarded heavy 4d-metals!!

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3.2 Supercapacitor: In-situ NMR

Different storage mechanism with electrode polarity:
Positive electrode: anion in / cations out → ion exchange
Negative electrode: cation in (desolvated), anions constant → counter ion adsorption

Why? → Key concerns to address to design optimized carbon structures

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1.4 Perspectives: Na vs Li

- **Na⁺ to replace Li⁺: Na-ion**

  **Cost:**
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  → *Alternative to Li-ion at lower cost; -30% energy density*

  → *Mass storage (renewable, grids...)*
3. RS2E: Na-ion from Lab...to battery prototypes

- Na-ion battery prototypes
  i) 90 Wh/kg
  ii) 140 Wh/l
  (not optimized)
  6 patents + several under progress

Next steps:
- tests (rates, cyclability, ageing with T...)
- improving the performance (material optimization, move to Sb...)
- cost model
Some members of the RS2E team

www.energie-rs2e.com/en
Merci pour votre attention