Rechargeable batteries bridging the gap between the smart grid and electrical vehicles

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Present-day Energy Chain

Power plant
Future Sustainable Energy Chain

- **Wind**
- **Solar**
- **μ-Heat-Power**
- **Heat pumps**

Power plant
Residential Storage

Fluctuating sources Require ~20% storage…!
Residential Storage

Fluctuating sources Require ~20% storage...!
“Electrical vehicles”: The dream

Réplique de la "jamais Contente"

La jamais Contente, 1ère voiture électrique construite en 1899 par Jenatzy
Smart Grid

“Residential storage” in Electrical Vehicles

Eureka…!
Electricity storage

Physical
- Super-capacitors
- Pseudo-capacitors

Electrochemical
- Batteries
- Redox-flow cells
- Metal-air systems
Physical storage in (Super)capacitors

Based on Electrochemical double layers

\[ C = \frac{\varepsilon \varepsilon_0 A}{d} \]
Electricity storage

Physical
- Super-capacitors
- Pseudo-capacitors

Electrochemical
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- Redox-flow cells
- Metal-air systems
Electricity storage

- **Physical**
  - Super-capacitors
  - Pseudo-capacitors

- **Electrochemical**
  - Batteries
  - Redox-flow cells
  - Metal-air systems
Fuel cells

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]

\[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O} \]
# Rechargeable battery chemistries

<table>
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Two ways to form a hydride

1. Gas phase

H₂ gas  |  Solid

H₂ (ass) 2H₂ (ad) diffusion 2H₂ (abs) (Hydride)
Fuel cells

\[ H_2 \rightarrow 2H^+ + 2e^- \]

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]
Two ways to form a hydride

1. Gas phase

\[ \text{H}_2 \text{ gas} \xrightarrow{\text{dis}} \text{H}_2 \text{ gas} \quad \xrightarrow{\text{ass}} 2\text{H}^{\text{ad}} \]

\[ \text{Solid} \quad \text{diffusion} \quad 2\text{H}^{\text{abs}} (\text{Hydride}) \]

2. Electrochemically

\[ \text{Electrolyte} \]

\[ \text{Electrode} \]

\[ \text{H}_2\text{O} + e^{-} \xrightarrow{\text{red}} \text{OH}^{-} + \text{H}^{\text{ad}} \]

\[ \text{H}^{\text{abs}} (\text{Hydride}) \]
NiMH battery concept

**Nickel electrode**

\[ \text{NiOOH} \]

\[ \text{Ni(OH)}_2 \]

\[ \text{OH}^- \]

\[ \text{H}_2\text{O} \]

\[ \text{e}^- \]

**Hydride electrode**

\[ \text{xOH}^- \]

\[ \text{MH}_x \]

\[ \text{M} \]

\[ \text{xH}_2\text{O} \]

\[ \text{xe}^- \]

Separator impregnated with KOH solution
NiMH battery concept

Overcharge

\[
4 \text{OH}^- \xrightarrow{\text{Ni}} \text{MH} \quad 2\text{H}_2\text{O} + \text{O}_2 + 4e^- 
\]

Nickel electrode

\[
e^- \quad \text{H}_2\text{O} \quad \text{NiOOH} 
\]

\[
\text{Ni(OH)}_2 \quad \text{OH}^- 
\]

Hydride electrode

\[
x\text{OH}^- \quad \text{MH}_x 
\]

\[
\text{M} \quad x\text{H}_2\text{O} \quad xe^- 
\]

Separator impregnated with KOH solution

Overdischarge

\[
2e^- + 2\text{H}_2\text{O} \xrightarrow{\text{Ni}} \text{MH} \quad 2\text{OH}^- + \text{H}_2 
\]
Simple CC-charging NiMH batteries

![Graph showing state-of-charge, voltage, temperature, and pressure](Graph.png)
Li-ion battery concept

lithium electrode

storage capacity

C

LiC

Li⁺

e⁻

cobalt oxide electrode

e⁻

Li⁺

CoO₂

charge

d

LiCoO₂

discharge

Li⁺
Li-ion battery concept

Lithium electrode

C
Li^+ e^-

LiC

C
Li^+ e^-

Cobalt oxide electrode

\( \text{LiCoO}_2 \)

\( \text{Li}^{\text{i}} \)

\( \text{e}^- \)

Charge

Discharge

Storage capacity
More complex CCCV charging Li-ion

![Graph showing voltage, current, and time characteristics of Li-ion charging. The graph includes a maximum voltage ($V_{\text{max}}$), maximum current ($I_{\text{s max}}$), minimum current ($I_{\text{s min}}$), and time (in minutes) axis.]
Efficiency rechargeable batteries excellent

Not affected by an inefficient Carnot cycle

\[ \eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \]

Discharge voltage curves as f(I)

New generation LiTiO₂ + LiMn₂O₄ batteries
Efficiency rechargeable batteries

Not affected by an inefficient Carnot cycle

Discharge voltage curves as f(I)

Discharge Efficiency as f(I)
Well-to-wheel efficiency
Internal Combustion Engine (ICE)

\[ \eta_{\text{ICE}} \approx 17\% \]

*In accordance with IEA WTW report 2007*
Efficiency battery-powered vehicles

ICE vs Conventional electricity generation

ICE efficiency $\eta_{ICE} \approx 17\%$

PHEV overall efficiency $\eta_{PHEV} \approx 34\%$

*In accordance with JRC WTW report 2007

**Figure 22.** WTW analysis of FCEVs and PHEVs based on primary energy efficiencies, assuming PHEV use only grid-supplied electricity which implies limited range.
Efficiency battery-powered vehicles

Conventional electricity generation

- Power Plants: 50%
- Power Lines: 92%
- Battery Charger: 89%
- Li-ion Batteries: 94%
- Electric Drive: 89%

PHEV overall efficiency = 34%

“Renewable” electricity generation

- Renewable: 100%
- Power Lines: 92%
- Battery Charger: 89%
- Li-ion Batteries: 94%
- Electric Drive: 89%

PHEV overall efficiency = 69%
Plug-in (Hybrid) Electrical Vehicles

Advantages:
• Much more efficient than ICE (> 2x)
• Significant reduction in CO$_2$ emissions (< 2x)
• Zero emission with sustainable energy sources…!
• Environmental friendly, no urban pollution…!
• Cost effective during life-time already now…!
• Grid stabilization *versus* electricity trading
• Silent driving…!

Disadvantages:
• High initial investment
• Limited driving range
• Recharging time not “instantaneous”
• Silent driving…!
Plug-in (Hybrid) Electrical Vehicles

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“The kWh feeling”

1 kWh = 3.6 MJ electricity
1 kWh storage in water (mgh) = pumping 360,000 liter 1 m high

1 kWh Li-ion battery weighs ~ 5-10 kg
1 kWh Li-ion battery you can drive about 7 km

If you want a driving range of 140 km that corresponds to a 20 kWh pack which weighs 100 - 200 kg and costs ~10,000 €…!
Plug-in (Hybrid) Electrical Vehicles

**Figure 17.** Half of all personal automobiles in the US travel 25 miles (40 km) or less each day, while eighty percent travel a maximum of 50 miles (80 km).

Source: EPRI Journal, Fall 2005

Limited driving range solutions:

(i) Range Extender (ICE, Fuel Cells)

(ii) Exchanging packs
Hyundai announcement Paris
Fuel cell-Battery Hybrid in production

Hyundai press release, September 2012
Limited driving range solutions:

(i) Range Extender (ICE, Fuel Cells)

(ii) Exchanging packs “Better Place” concept
Recharging time not “instantaneous”
New rapid charging strategies (Epyon/ABB)

Electric vehicle 15-30 min. charging solutions

Small vehicle chargers
- 4 & 8 kW (20–60 VDC)

Large vehicle chargers
- 20 kW (20–90 VDC)

Electric fuel stations
- 50 kW (200-460 VDC)
- 100 kW (100- 600 VDC)

http://www.epyonpower.com
Battery challenges to be met to enable electrical transportation

- Energy density
- Power density
- Cycle life
- Safety
- Cost
New Materials for Li-ion Batteries

New chemistries and Nano-structuring

**Anode materials**
- Si-based
- Sn-based
- Ti-based

**Cathode materials**
- LiCoO$_2$
  - LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$
  - LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$AlO$_2$
  - LiFePO$_4$ (-30% + safer)
  - LiMn$_2$O$_4$ (-30% + very safe)
New Materials for Li-ion Batteries

Anode materials
Graphite
Ti-based

Cathode materials
LiCoO$_2$
LiMn$_2$O$_4$
New Materials for Li-ion Batteries

Anode materials

Cathode materials

50Ah cells 100% DOD cycling test at 25°C in 2.0 – 2.8 V voltage window (EIS battery voltage range) and 2C charge/discharge rate
- 90% capacity retention after 9,000 cycles observed.
- Suggest at least 18,000 cycles at 80% capacity retention

9000 cycles x 6.2 kWh x 7 km/kWh
~ 400,000 km…!
New Materials for Li-ion Batteries

Anode materials

- Si-based

Graphite

Phase diagram LiSi
Silicon: >3000 mAh/g
Graphite: 375 mAh/g!
Morphology after Li-intercalation crystalline-Si
Impact CV-charging on cycle-life

Capacity [mAh]

Cycle number

Standard-CCCV

CV=4.3 V

CV=4.2 V
Surface protection

Improving the performance of Li-batteries by surface coating of positive electrode materials with AlF$_3$

TEM Images of the Pristine and AlF$_3$-coated LiNi$_{0.8}$Co$_{0.15}$Al$_{0.05}$O$_2$

ALD process under development...!
Changing bulk and surface properties

High energy gradient concentration cathode material

Y. K. Sun and K. Amine
Energy densities of various (battery) systems

http://mm.seas.upenn.edu/ql/www/reference/Li_air_battery/Girishkumar10.pdf
New Li-based Systems

- Specific energy (Wh kg\(^{-1}\))
  - Pb-acid: 50 km
  - Ni-Cd: 80 km
  - Ni-MH: 100 km
  - Li-ion: 160 km
  - Future Li-ion: >200 km
  - Zn-air: >225 km
  - Li-S: >400 km
  - Li-air: >550 km

- Price (US$ kW h\(^{-1}\))
  - Available: 200
  - Under development: 600
  - R&D: <150

http://www.nature.com/nmat/journal/v11/n1/pdf/nmat3191.pdf
New Li-based Systems

Smart Grid

Eureka…!

“Residential storage” in Electrical Vehicles
Electrification of our society offers fantastic new opportunities for both our research and industry...!

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