

Dag Noréus
Kemi - Stockholms universitet

Sammanfattning:



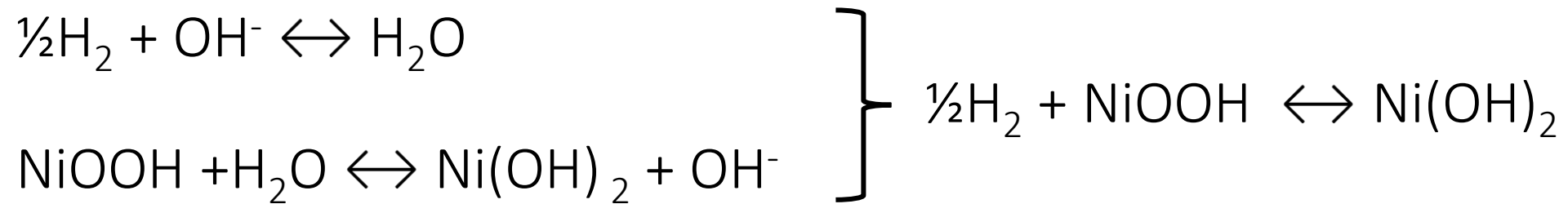
- Laddbara batterier bildar kaotiska system vid upp- och urladdning
- Det gör dem svåra och dyra att tillverka eftersom det krävs hög noggrannhet vid tillverkningen
- Dock blir det snabbt överproduktion med fallande priser.
Cellproduktionen är den länk i batterikedjan som är svårast att få lönsam
- Sällsynta jordartsmetaller används i NiMH celler pga deras korrosionsegenskaper

H	Jordartsmetaller																He						
Li	Be	Sällsynta jordartsmetaller (REE)																B	C	N	O	F	Ne
Na	Mg																	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr						
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe						
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn						
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt															

La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
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Lantanoider - Yttre elektroner $6s^2 5p^6 \rightarrow$ kemiskt lika
 Inre $4f^{2-14} \rightarrow$ intressanta magnet- och färg fenomen

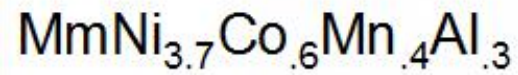
The NiH₂ battery has the longest cycle life and the simplest chemistry



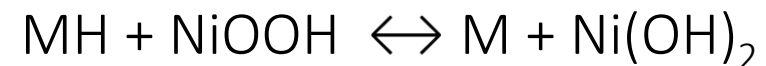
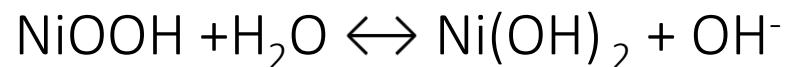
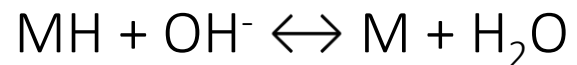
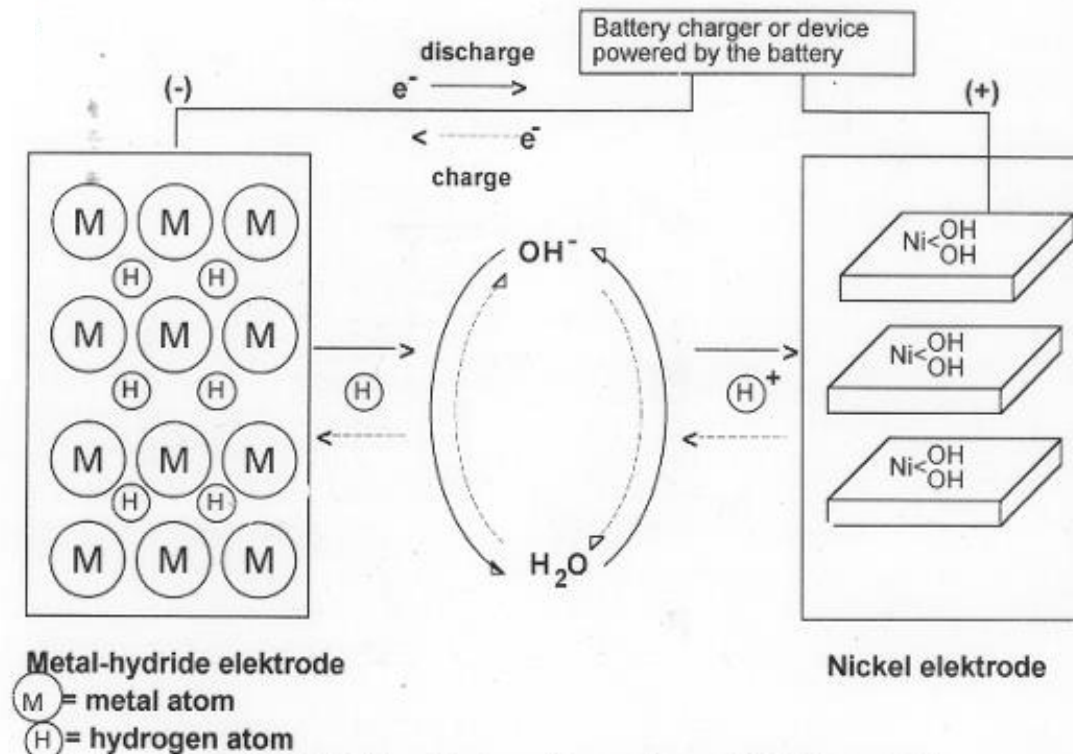
Used in space applications such as:

Comsat (1970), ISS,
Mercury Messenger,
Mars Odyssey, Hubble

THE METAL-HYDRIDE BATTERY



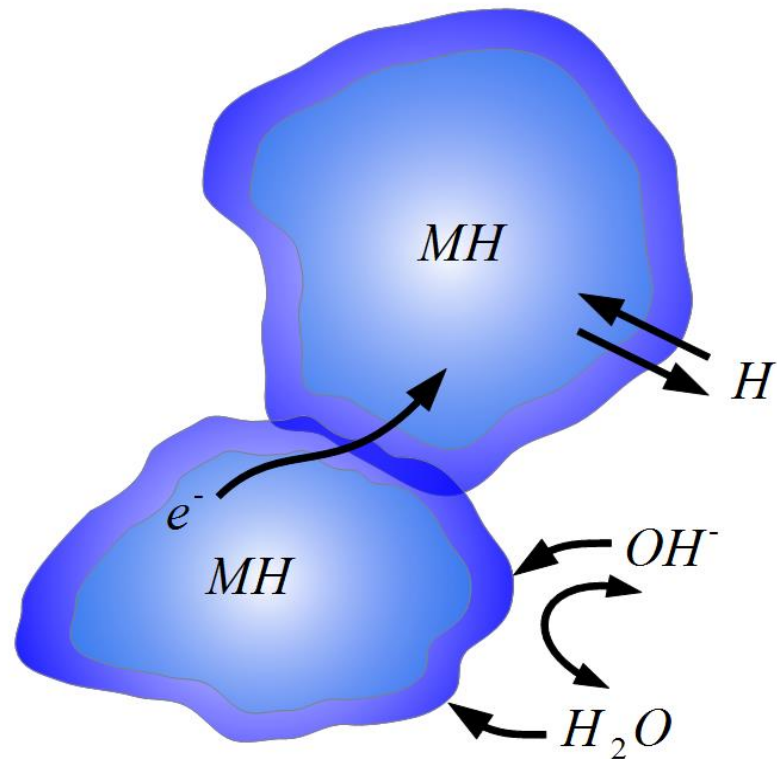
(H-battery Li-battery)



Surface reactions on metal hydride (MH) particles in the MH-electrode

The surface must:

- 1) protect the metal hydride from corrosion by the electrolyte
- 2) be electrically conductive
- 3) transport hydrogen between the surface and the interior of the metal hydride particle
- 4) be catalytically active in breaking and forming O-H bonds in the water molecules transporting hydrogen



- Corrosion Protection
- Electric Conductivity
- Transport Hydrogen
- Break and Form O-H Bonds

- This restricts the selection of alloy candidates
- NiMH battery alloys come from the magnet SmCo_5
- Philips found that SmCo_5 lost magnetization in moisture as it formed a metal hydride SmCo_5H_x $(\text{Sm} + 3 \text{H}_2\text{O} \rightarrow \text{Sm}(\text{OH})_3 + 3\text{H})$
- A trial-and-error search led to LaNi_5H_6
- $\text{MmNi}_{3.7}\text{Co}_{0.6}\text{Mn}_{0.4}\text{Al}_{0.3} \rightarrow$
 - Mm = Mischmetal
 - Co to increase ductility and reduce corrosion
 - Mn to optimize crystal size after hydrogenation
 - Al to reduce H-release pressure. Surprisingly this made it possible to create a corrosion protective surface!

Batteripack- Radio - Arlanda - Sanyo

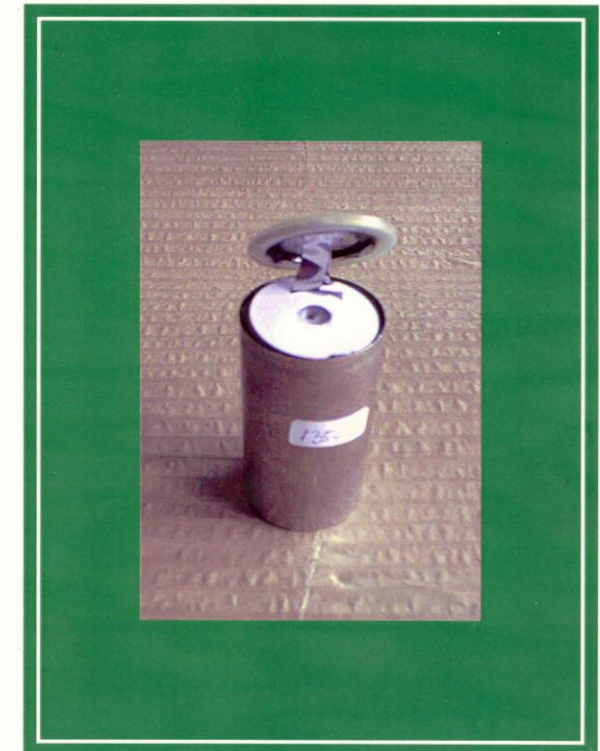
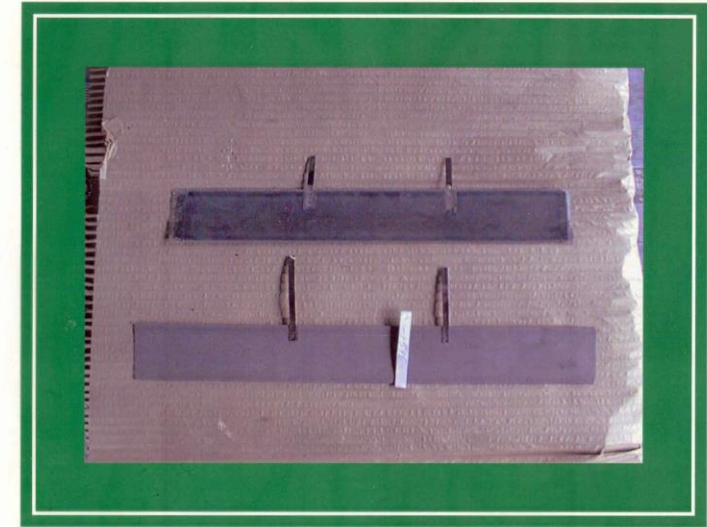
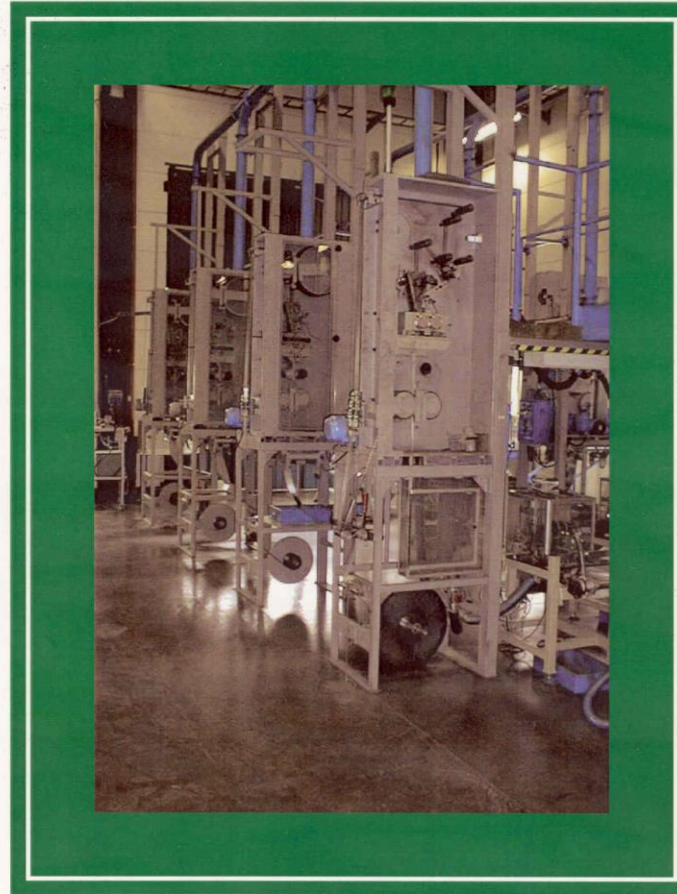
Första NiMH i Sverige 1992





Ni-Me

THE FLEXIBLE NIMH BATTERY MANUFACTURER OF SWEDEN



Equipment:
SAB NiFe Jungner

Unfortunately, at this time rechargeable NiMH batteries became strategic components in Japan for their portable electronics

Sanyo – Sanyo Batteries

Matsushita – Matsushita Batteries

Toshiba – Toshiba Batteries

Gates – Varta – Saft and we more or less gave up!

Rechargeable battery cells form chaotic systems when cycled!

If all electrode and parasitic reactions are not reversible the battery will derail upon cycling.

High conductivity in water-based batteries helps.

Main electrode reactions and parasitic side reactions must be fully reversible upon cycling else the battery will derail!

Reversibility is of outmost importance.

This is promoted by high production quality!

This leads to high production costs!

The best way to limit the chaotic development resulting from cycling the battery is never to cycle it!

The lead acid starter battery is a good example.

Second best is to have the electrodes work under as ideal conditions as possible.

This means homogeneous materials, no impurities, no gradients – high quality and high costs! High conductivity helps to smooth out critical gradients.

Einstein lär ha sagt: Galenskap är att göra samma sak om och om igen och vänta sig **olika** resultat.

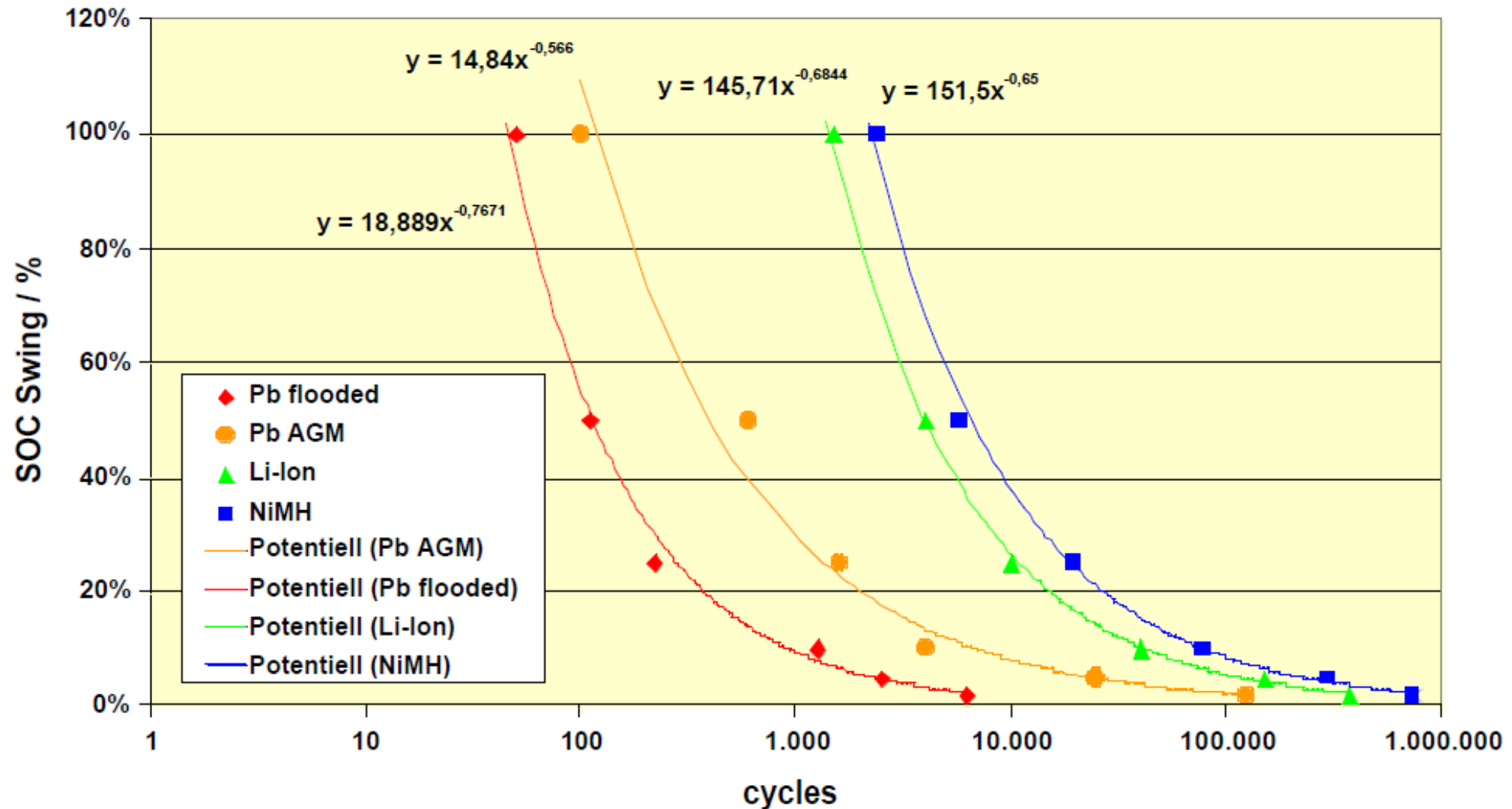
Inom batteriforskning prövar vi att göra samma sak om och om igen och hoppas få **samma** resultat.

Ändå blir det olika resultat. Sedan försöker vi klura ut vilken störning som ställde till det.

Det tar ofta lång tid!

Pb-, Li- and NiMH, cycles at different SOC

Best is to never cycle the battery



Source: VARTA GmbH

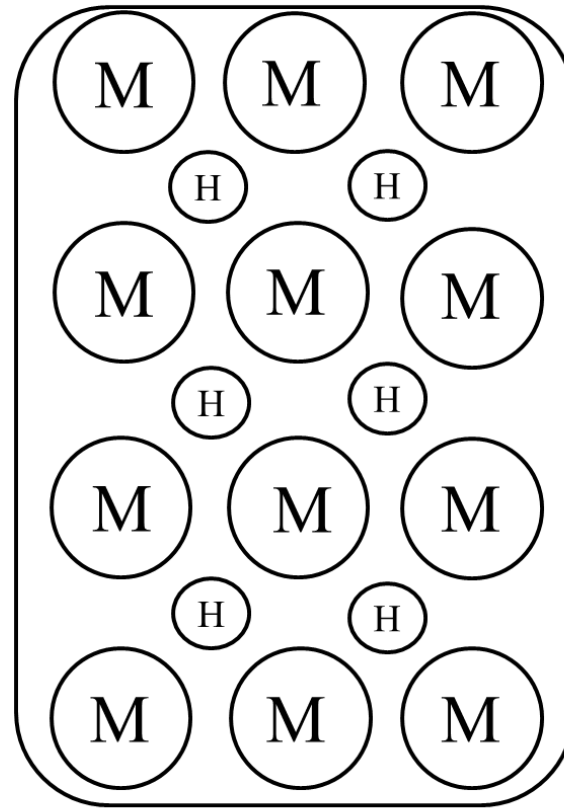
Example: A 1 kWh NiMH battery

Cycling 100 % SOC	→	2262 cycles	→	2262 kWh
Cycling 50 % SOC	→	6570 cycles	→	3285 kWh
Cycling 25 % SOC	→	19070 cycles	→	4770 kWh
Cycling 10 % SOC	→	78150 cycles	→	7815 kWh
Cycling 5 % SOC	→	227000 cycles	→	11350 kWh
Cycling 2 % SOC	→	$9.3 \cdot 10^5$ cycles	→	18590 kWh
Cycling 1 % SOC	→	$2.7 \cdot 10^7$ cycles	→	27000 kWh

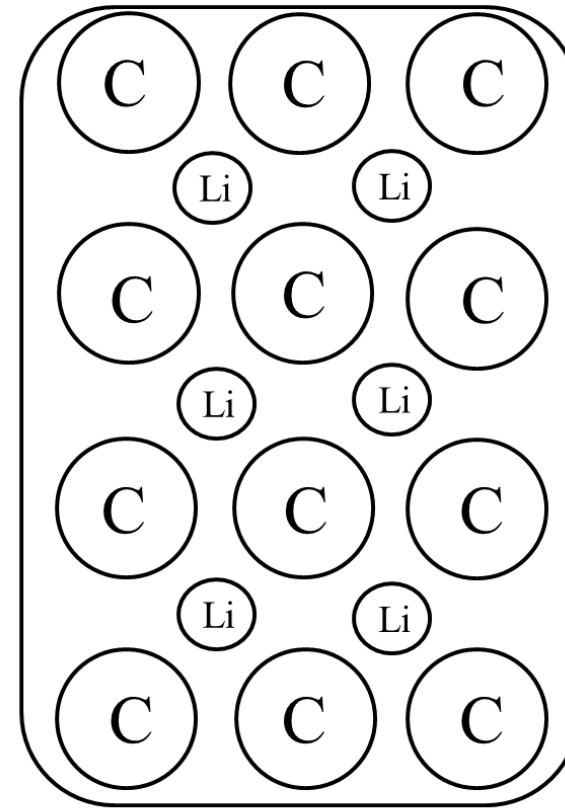
This explains why lead acid starter batteries and HEV batteries have long life expectancy

Li-batteries are even more difficult to make

Anodes



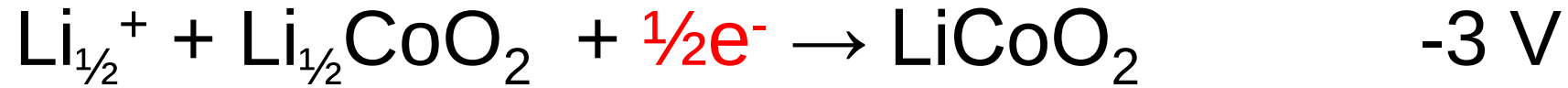
MH AB_5H_6
 $M \approx 72 \text{ g}$



LiC_6
 $C = 72 \text{ g}$

Anodes are similar. When charged they are filled with H- and Li-atoms, respectively, to about the same capacity.

Cathodes more different but based on similar transition metal oxides



Stronger Li-bond gives higher voltage and higher Wh capacity:

Li-battery - 4 Volt

H-battery - 1.3 Volt

Higher voltage leads to more instability problems, and water based electrolytes can not be used in Li-batteries.

2-orders of magnitude lower conductivity than water demands very thin electrodes and separators.

Japansk batteriteknologi dominerar marknaden (2021)

• CATL	33 %	Kina
• LG Energy	22 %	Syd Korea
• Panasonic	14 %	Japan
• BYD	7 %	Kina
• Samsung	5 %	Syd Korea
• SK Innovation	5 %	Syd Korea
• CALB	3 %	Kina
• AESC	2 %	Kina
• Guoxuan	2 %	Kina
• PEVE	1.3 %	Japan
• Resten av världen	5.7 %	

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