Dag Noréus

General problems with rechargeable batteries

Innovative Iron-Air Battery
High power hydrides for HEV batteries
Recycling of NiMH batteries

Cobalt free batteries

Rechargable batteries are not so ”rechargeable”

- An electrochemical cell can be made by almost any redox couple
- But non infinitesimal currents create gradients in current, voltage, temperature, electrolyte concentrations, composition. They fall over complicated surfaces and start, entangled and still unknown side reactions.
- When the cell is recharged all reactions must proceed in the exactly opposite direction, otherwise the cell will derail upon cycling.
- Rechargeable batteries are chaotic systems

Making and controlling rechargeable batteries is similar to forecasting weather

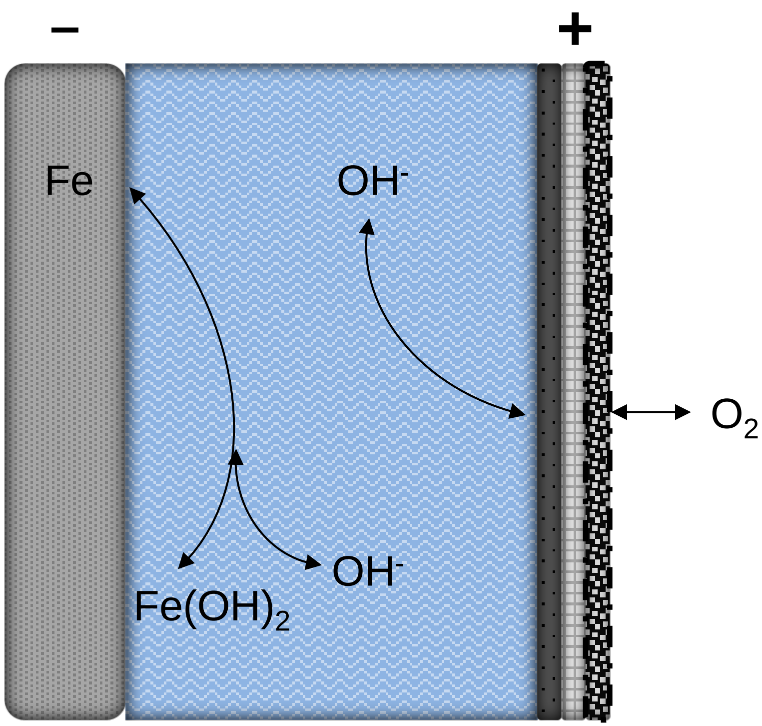
To underestimate this fact will lead to unpleasant ”surprices”

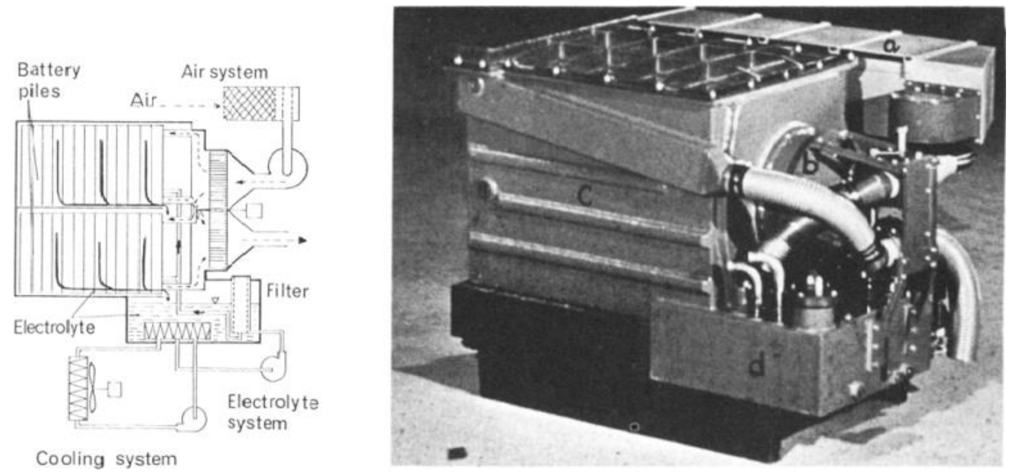
Higher cell voltage improves capacity but aggravates stability problems

Problems in 2012

Ener1	filed for protection under Chapter 11
A123	filed for protection under Chapter 11
Valence	filed for protection under Chapter 11

The Iron-Air Battery





L. Öjefors, L. Carlsson, *J.Power Sources* **1978**

Air (+) electrode: $\frac{1}{2}O_2 + H_2O + 2e^- \leftrightarrow 2OH^-$

Iron (-) electrode: $Fe + 2OH^- \rightarrow Fe(OH)_2 + 2e^-$

Cell Reaction: $Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2$

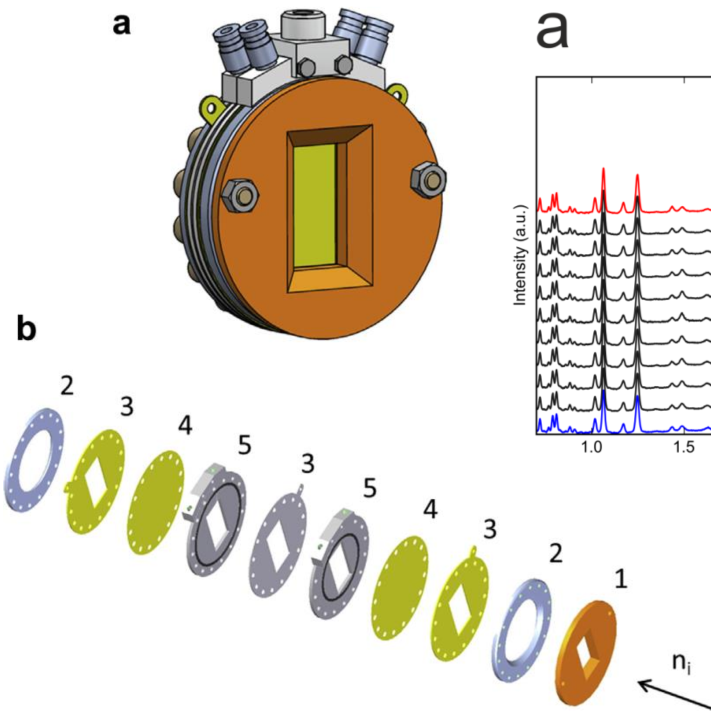
Theoretical Cell Voltage: 1.29 V

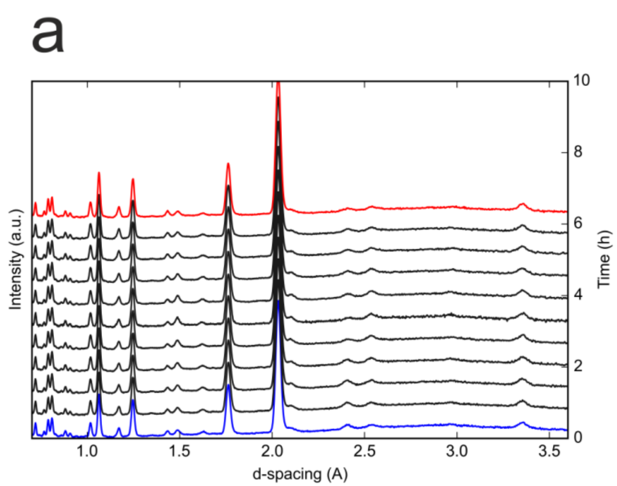
Theoretical Specific Energy: 780 Wh/kg

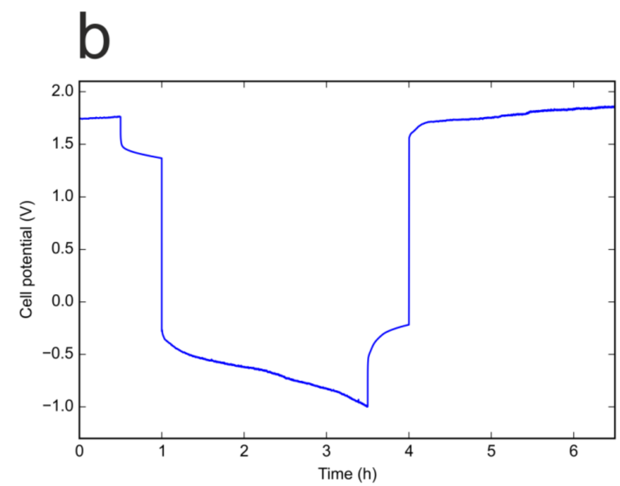
In-situ Neutron Diffraction

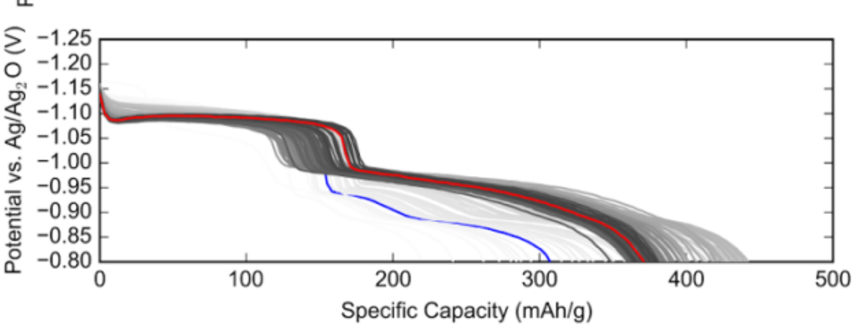
In-situ neutron diffraction of an Iron-Air cell at ISIS, UK

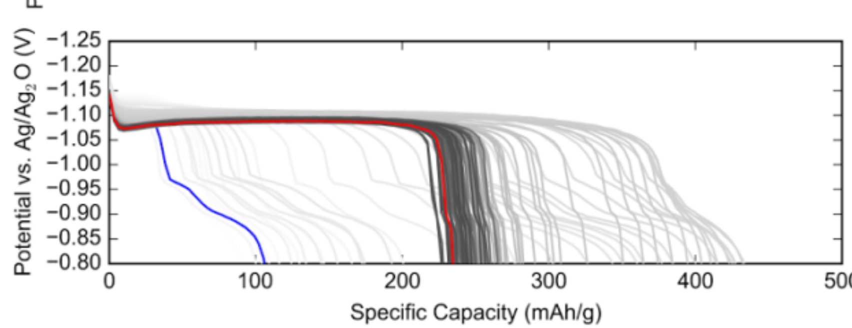
A new intermediate phase was detected whose intensity could be correlated to the charge discharge











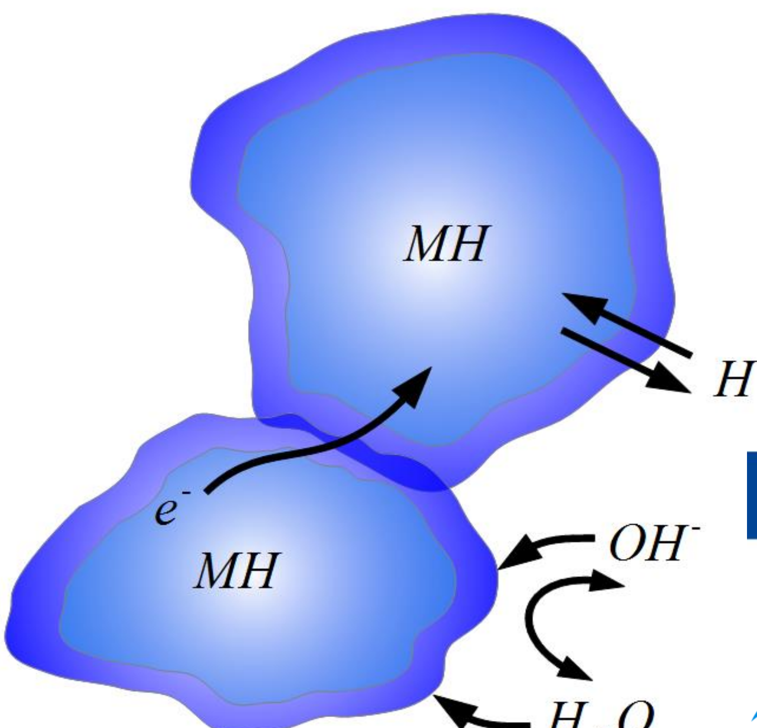
The new phase participates in the over all reaction leading to an increased 1st electron plataeu.

This increased capacity but so far reduced cycle life.

High power hydrides for HEV batteries: **Surface reactions are important.**

The surface must:

1) protect the metal hydride from corrosion by the electrolyte.
2) be electric conductive
3) transport hydrogen to the interior of the metal hydride particle
4) be catalytic 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

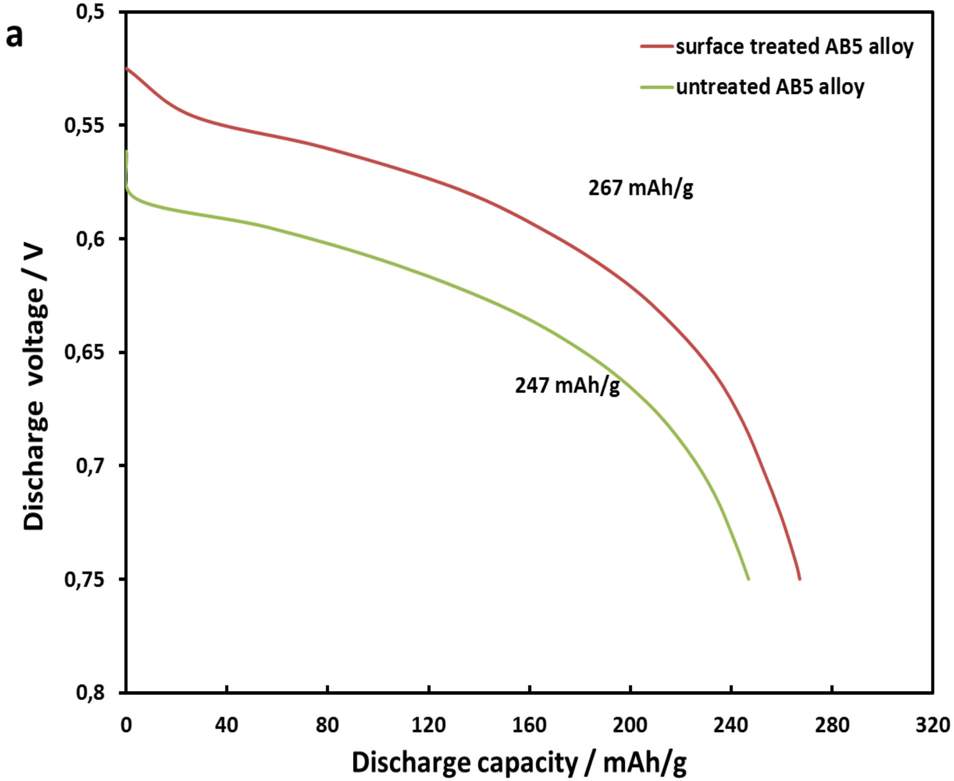
Höganäs

Stockholm University

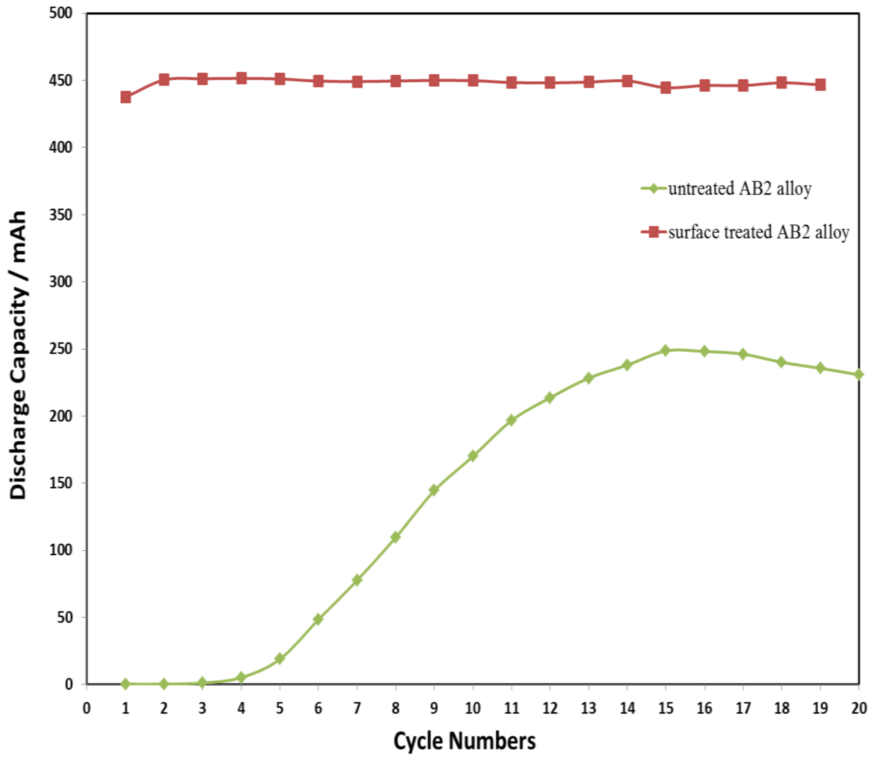
nilar

SCANIA

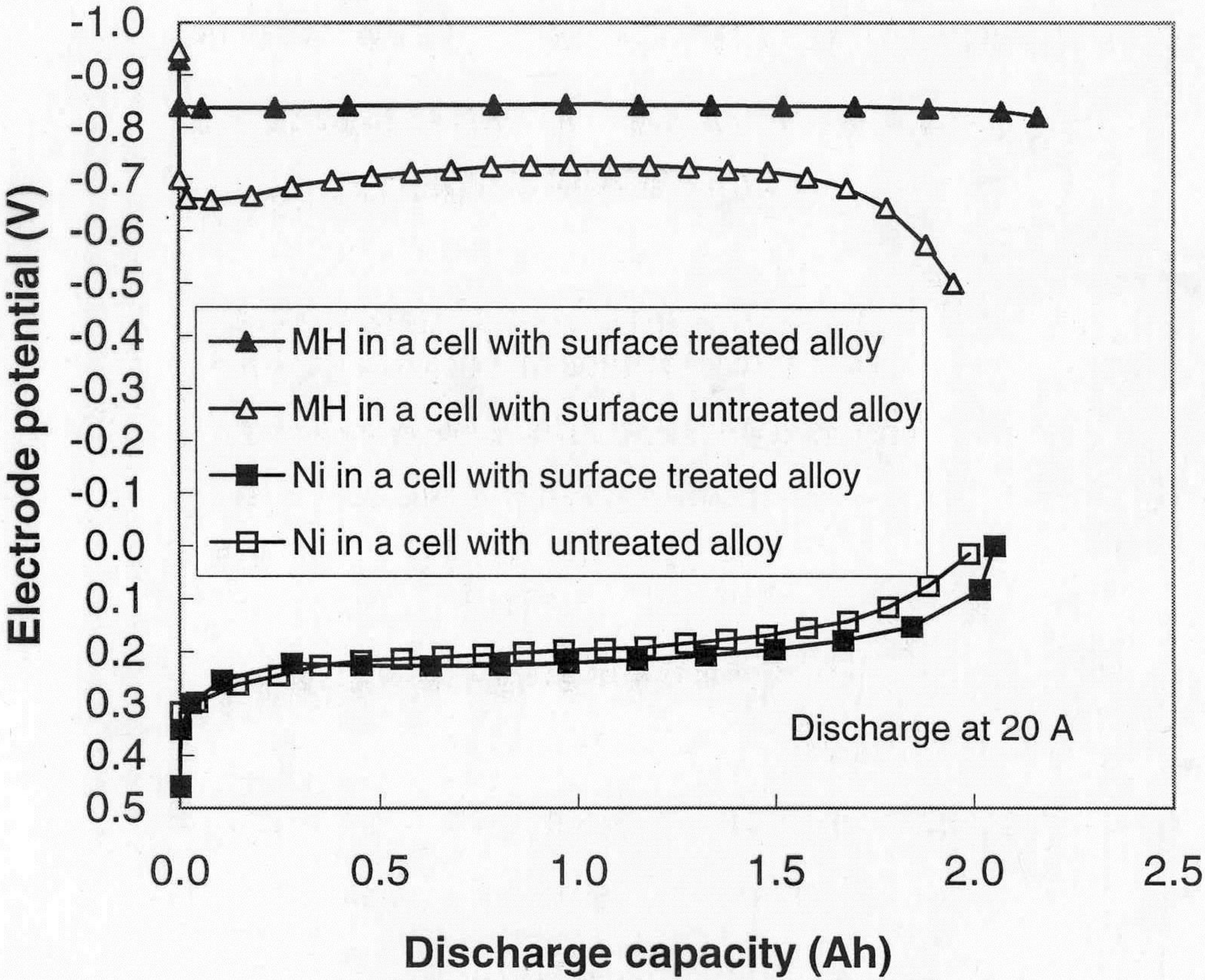
Results



High C-rate(640 mAh/g) discharge of surface treated and untreated AB_5 alloy.



Discharge capacity vs. cycle numbers for a surface treated and untreated AB_2 alloy.



Electrode potential (V)
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
-0.2
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
MH in a cell with surface treated alloy
MH in a cell with surface untreated alloy
Ni in a cell with surface treated alloy
Ni in a cell with untreated alloy
Discharge at 20 A
0.0
0.5
1.0
1.5
2.0
2.5
Discharge capacity (Ah)

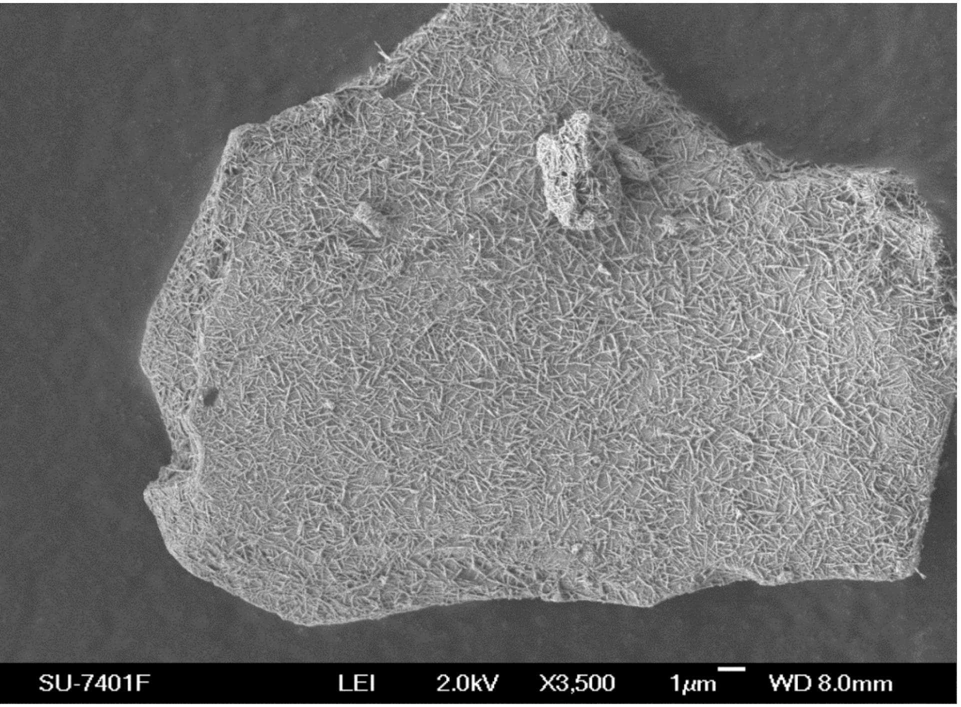
The disadvantage with the surface treated powder is that it becomes difficult to handle in large quantities.

We are now optimizing handleability with performance.

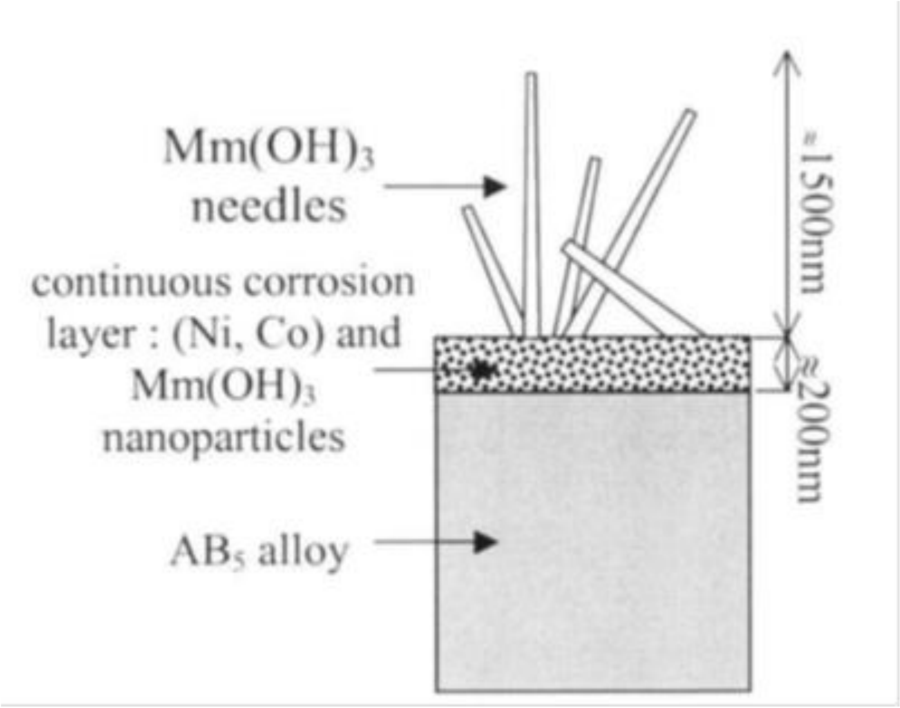
Recycling of NiMH batteries

During cycling he surface will corrode and form a very active surface by creating catalitic nickel containing clusters.

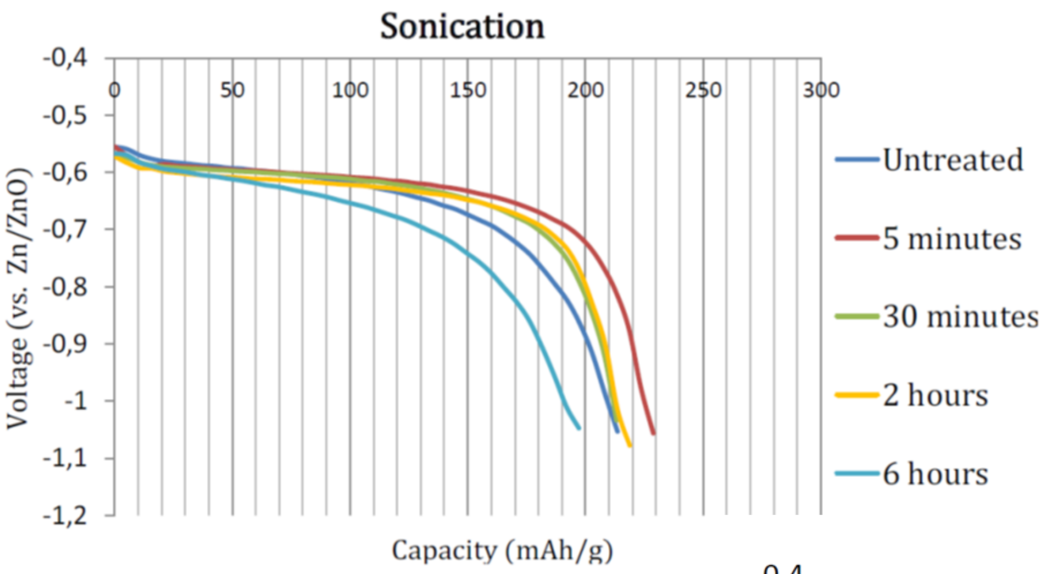
Eventually the battery will fail as the corrosion consumes the electrolyte. But most of the alloy will remain intact in the interior of the particles.

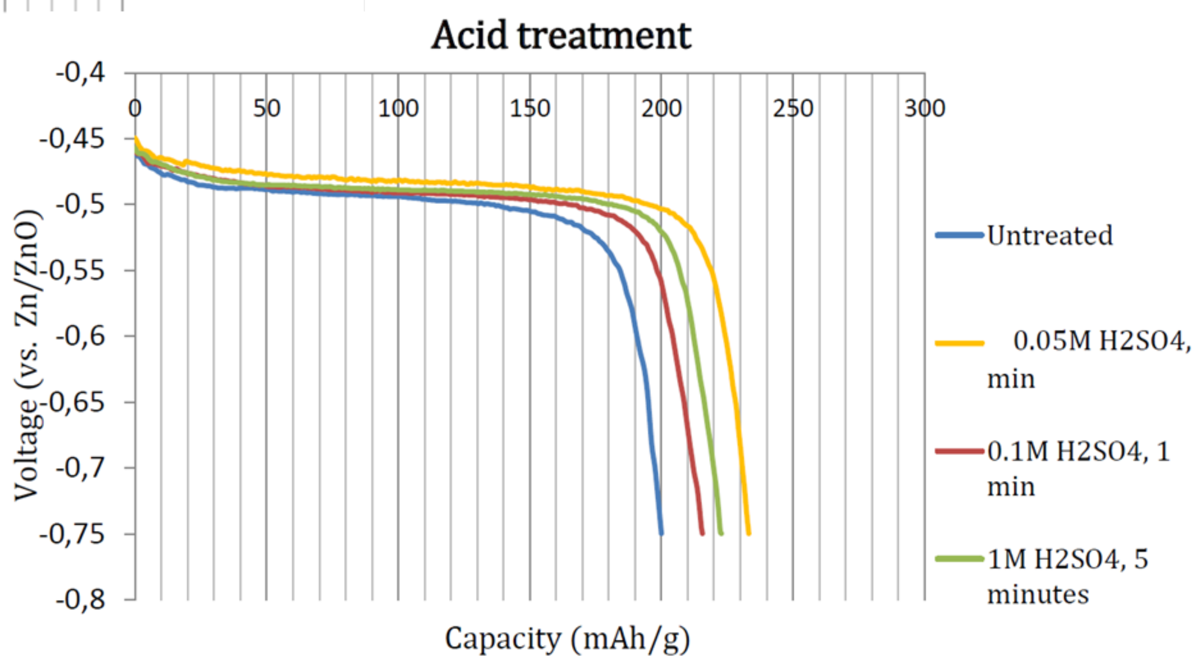


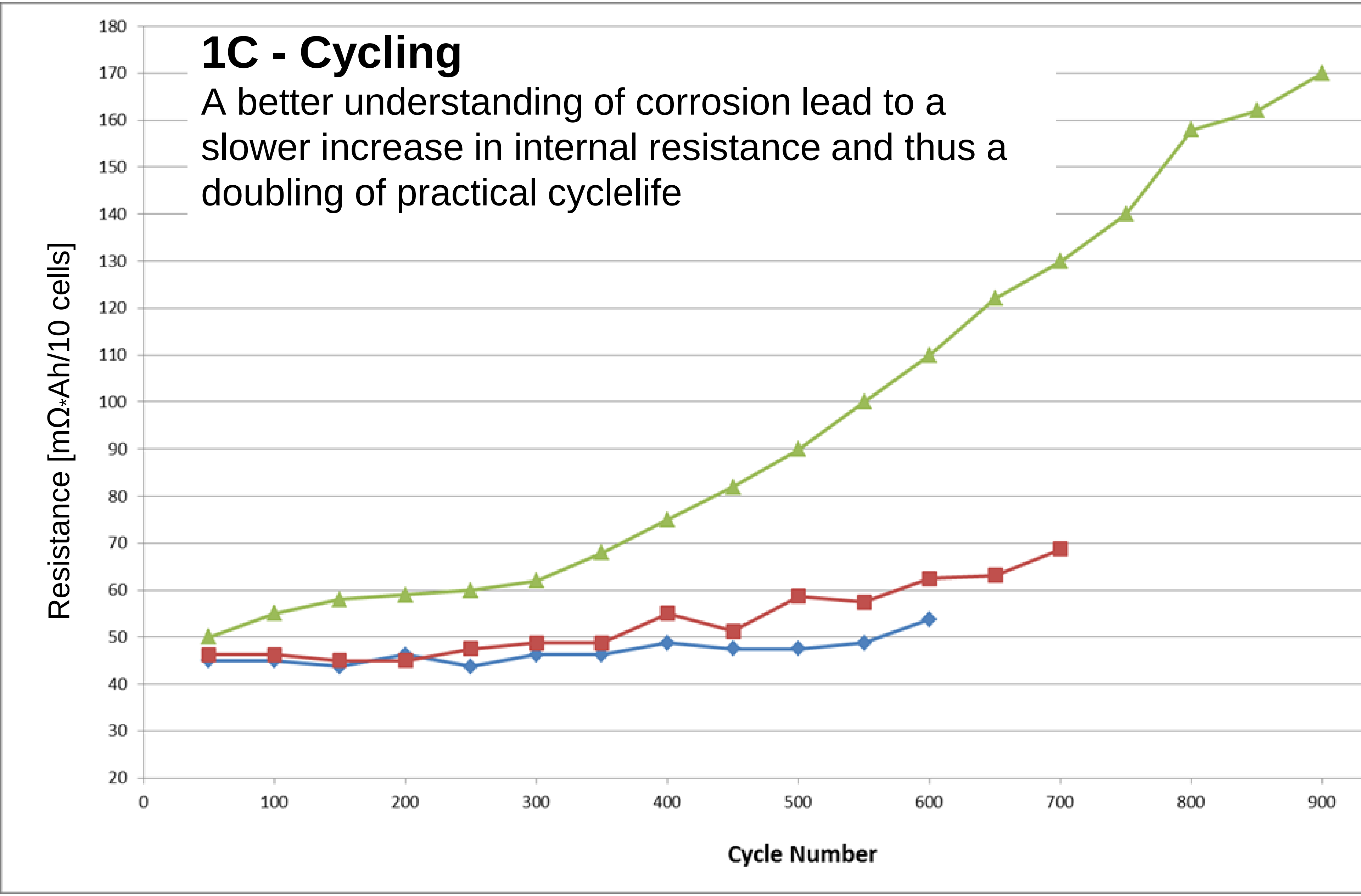
Corroded MH particle



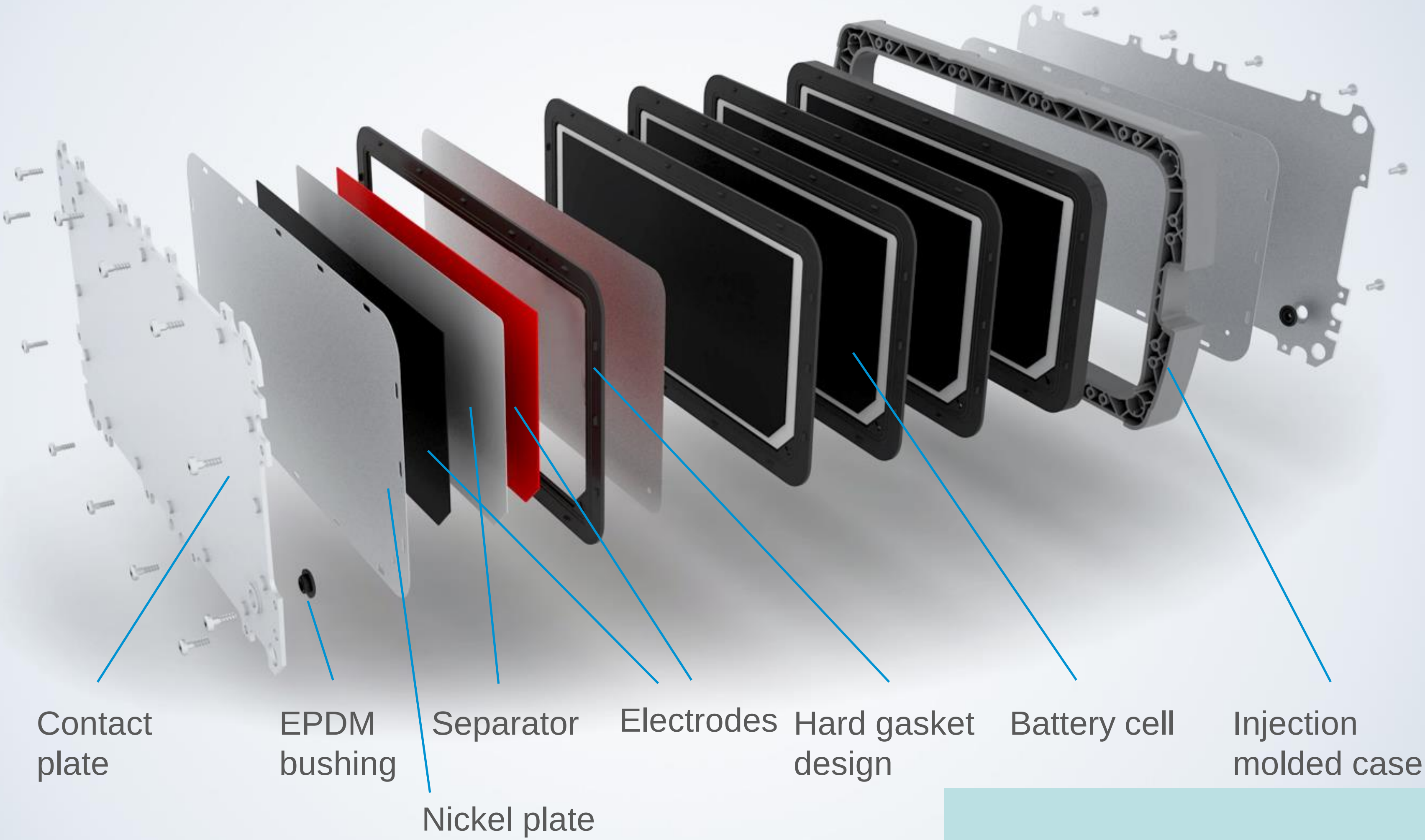
By combing mechanical and chemical cleaning methods we can recover the internal active parts of the alloy






1C - Cycling
A better understanding of corrosion lead to a slower increase in internal resistance and thus a doubling of practical cyclelife
Resistance [mΩ*Ah/10 cells]
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
0
100
200
300
400
500
600
700
800
900
Cycle Number

12 volt modules are built into a new bipolar concept



A system for marine applications consisting of 12 strings in parallel. Each string consists of three series connected 125 Volt battery packs

What NiMH cells can learn from Li-cells

NiCd and NiMH batteries used to have simple chargers. Cell chemistry should be capable to withstand 50 % overcharge.

This made it difficult to reach long cycle life

Li-cells can not cope with overcharge or overdischarge. They have sofisticated battery management units (BMU).

Protection circuits prevents overcharge and overdischarge

Overcharge and overdischarge states have to be avoided for Li-batteries with the help of BMUs.

This has started to be applied for NiMH to increase cycle life.

Advantages:

Flooded cell design prevents early dryout.

Carbon can be used in the cathode to enhance conductivity instead of nickel and cobalt.

Cobalt free batteries can be made to mitigate a coming cobalt price increase.

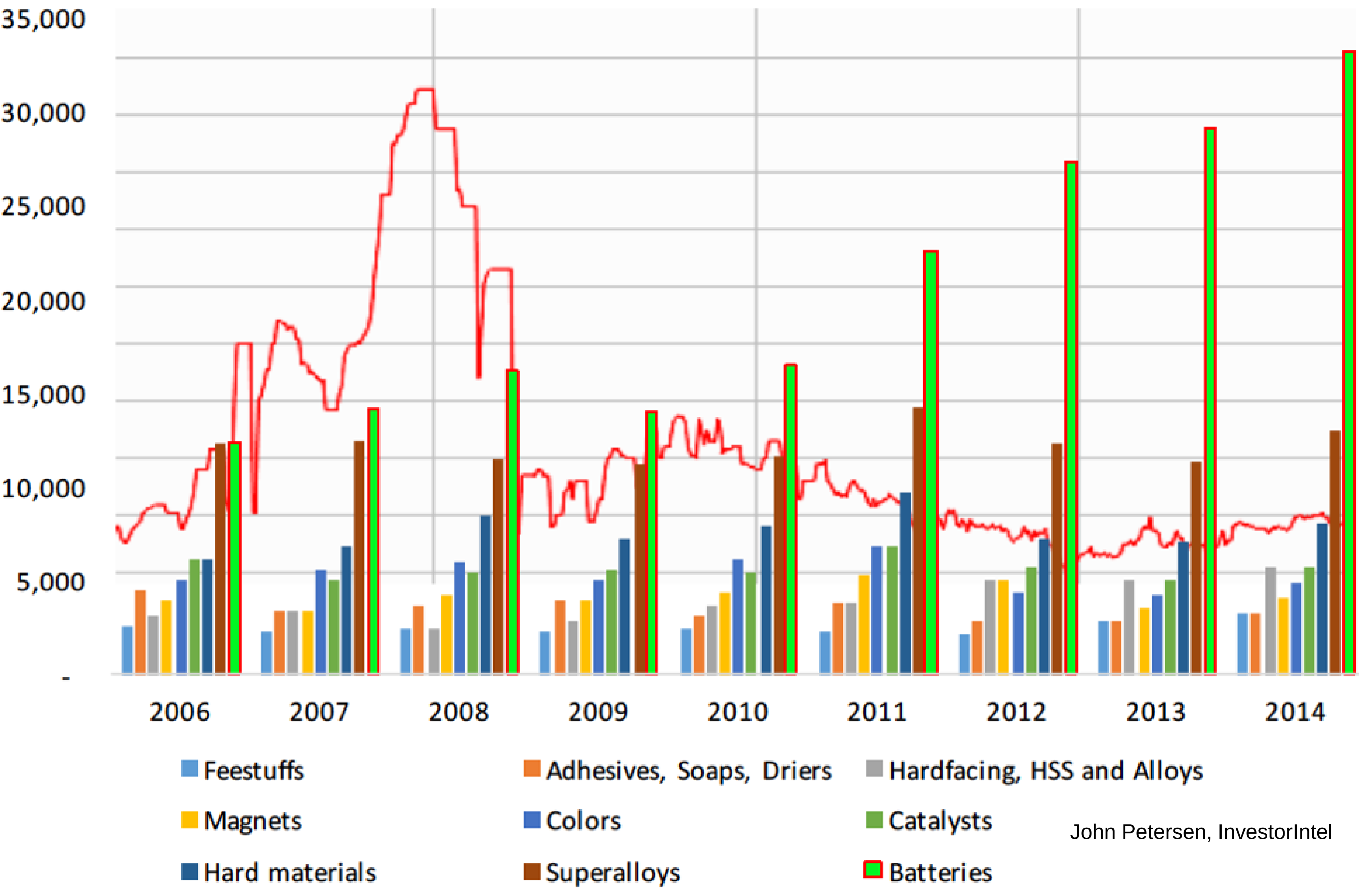
Refined Cobalt Supply and Demand Statistics from Cobalt Development Instute

Cobalt Supplies	2006 (tonnes)	2014 (tonnes)	Change (tonnes)	Change (percentage)
Total refined cobalt production	53,450	92,000	38,550	72%
Nickel by-product	25,656	46,000	20,344	79%
Copper by-product	19,777	40,480	20,704	105%
Primary cobalt operations	8,018	5,520	(2,498)	-31%

Cobalt Demand	2006 (tonnes)	2014 (tonnes)	Change (tonnes)	Change (% of Change)
Superalloys	11,759	14,720	2,961	8%
Hardfacing, High speed steel and Other alloys	2,940	6,440	3,500	9%
Magnets	3,742	4,600	859	2%
Hard materials – Carbides, Diamond tooling	5,880	9,200	3,321	8%
Catalysts	5,880	6,440	561	1%
Colors – Glass, Enamels, Plastics, Ceramics, Artists Colors and Fabrics	4,811	5,520	710	2%
Feestuffs, Biotech, Anodizing, Recording media, Electrolysis, Cu Electrowinning	2,405	3,680	1,275	8%
Batteries	11,759	37,720	25,961	67%
Tire Adhesives, Soaps, Driers (paint/ink)	4,276	3,680	(596)	-2%
World total	53,450	92,000	38,550	

John Petersen, InvestorIntel

Apparent Cobalt Demand By Application Class (with price history background $10 to $52)



Cobalt Ore Production Statistics from US Geological Survey

	2006 (tonnes)	2015 (tonnes)	Change (tonnes)	(% of Change)
United States		700	700	1%
Australia	6,000	6,000	-	0%
Brazil	1,000	2,600	1,600	2%
Canada	5,600	6,300	700	1%
China	1,400	7,200	5,800	9%
Congo (Kinshasa)	22,000	63,000	41,000	63%
Cuba	4,000	4,200	200	0%
Morocco	1,500		(1,500)	-2%
Madagascar		3,600	3,600	5%
New Caledonia6	1,100	3,300	2,200	3%
Phillipines		4,600	4,600	7%
Russia	5,100	6,300	1,200	2%
South Africa		2,800	2,800	4%
Zambia	8,600	5,500	(3,100)	-5%
Other countries	1,200	7,700	6,500	10%
World total	57,500	123,800	65,600	

John Petersen, InvestorIntel