



# **Electrically Rechargeable Metal-air Batteries Compared to Advanced Lithium-ion Batteries**

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**There are no fundamental scientific obstacles to creating batteries with ten times the energy content - for a given weight - of the best current batteries.**

**From the program of the Almaden Institute**

**But should this really be the focus of our efforts?**



**Hymotion 5kWh  
LiFePO<sub>4</sub>-based  
Li-ion pack**

**About 30 km all-  
electric range**

**It's a pretty big  
battery pack!**



# “Lithium-ion cells have high energy density”

## Where has it gone?

System	Cell	V	A-hr	Volume (mL)	Mass (g)	Wh/L
A123 LiFePO <sub>4</sub>	26650	3.3	2.3	35.5	70	215
Panasonic Ni-MH	18670	1.2	3.2	17.0	60	225
E-One Moli LiMn <sub>2</sub> O <sub>4</sub>	26700	3.8	2.9	37.2	101	232
Panasonic LiCoO <sub>2</sub>	18650	3.7	2.55	16.5	46.5	570

Material	Crystallographic density (g/cm <sup>3</sup> )	Average potential (V) (vs Li)	Reversible specific capacity (Ah/g)	Volumetric energy density (Wh/cm <sup>3</sup> )
LiCoO <sub>2</sub>	5.05	3.9	0.15 (to 4.2 V)	2.95
Li[Ni <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> ]O <sub>2</sub> <b>Called NMC</b>	4.77	3.7	0.163 (to 4.3 V)	2.87
Li <sub>1.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	4.18	4.1	0.120	2.06
LiFePO <sub>4</sub>	3.60	3.44	0.160	1.98

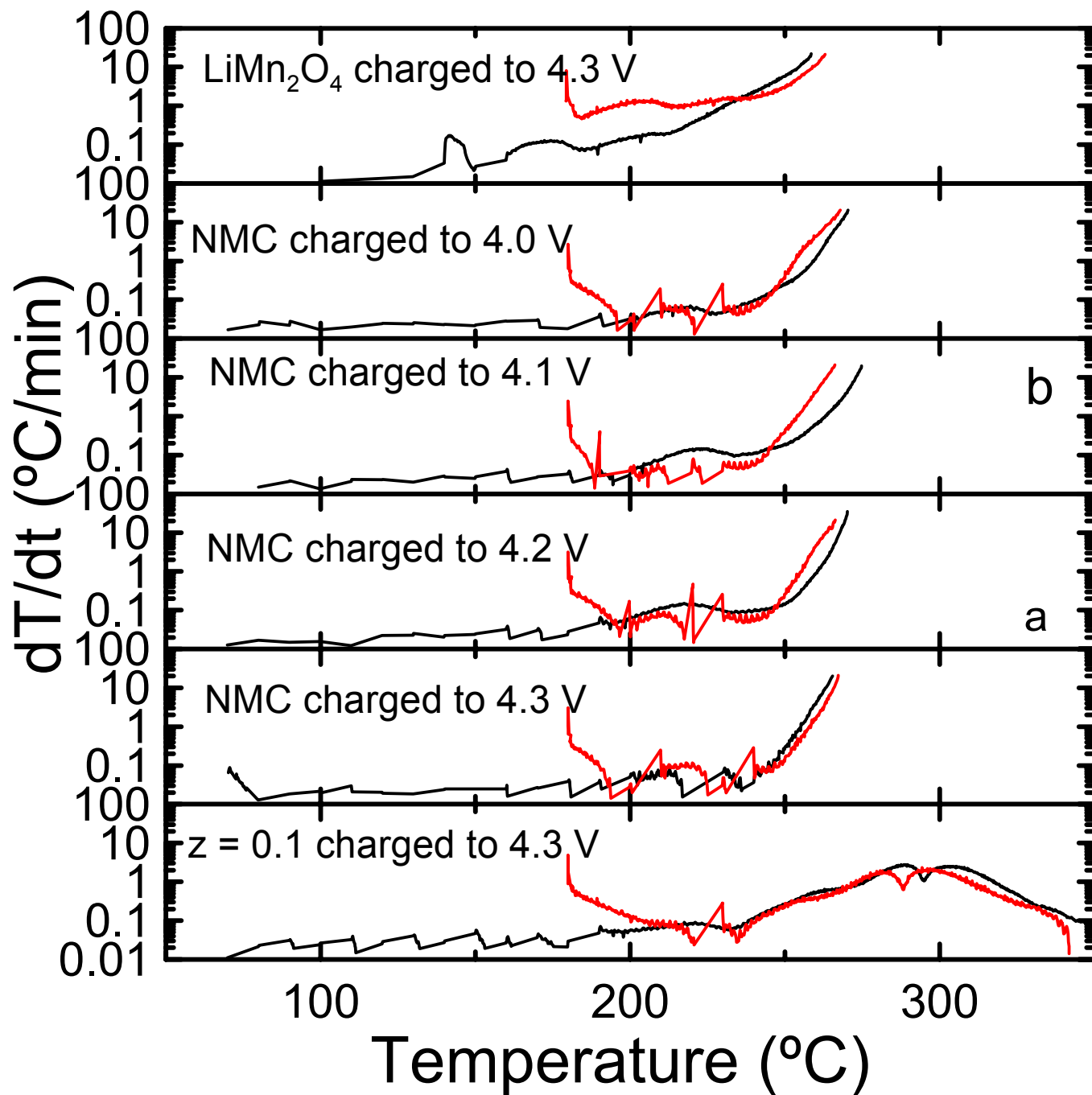
**LiFePO<sub>4</sub> will lead to the lowest energy density of any of the popular positive electrode choices!  
LiMn<sub>2</sub>O<sub>4</sub> is not much better.**

**Why are they being selected?**

“In our opinion, the cathode materials can be ranked from most safe to least safe in the following order **LiFePO<sub>4</sub>**,  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$ , **Li<sub>1+x</sub>Mn<sub>2-x</sub>O<sub>4</sub>**,  $\text{LiCoO}_2$ ,  $\text{Li}[\text{Ni}_{0.7}\text{Co}_{0.2}\text{Ti}_{0.05}\text{Mg}_{0.05}]\text{O}_2$ ,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ,  $\text{LiNiO}_2$ .”

D.D. MacNeil et al. - Journal of Power Sources  
**108**, 8–14, (2002).

**Adding Al to  $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3-z}\text{Al}_z]\text{O}_2$  improves the safety even more! See next slide.**



**z = 0.1 is a very good compromise between capacity and safety.**

**Safer than LiMn<sub>2</sub>O<sub>4</sub>!!!!**

# Where do we stand now?

Material	Density (g/cm <sup>3</sup> )	Average potential (V)	Reversible specific capacity (Ah/g)	Volumetric energy density (Wh/cm <sup>3</sup> )
LiCoO <sub>2</sub>	5.05	3.9	0.15 (to 4.2 V)	2.95
Li[Ni <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> ]O <sub>2</sub>	4.77	3.7	0.163 (to 4.3 V)	2.87
Li <sub>1.1</sub> Mn <sub>1.9</sub> O <sub>4</sub>	4.18	4.1	0.120	2.06
LiFePO <sub>4</sub>	3.60	3.44	0.160	1.98
Li[Ni <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>0.233</sub> Al <sub>0.1</sub> ]O <sub>2</sub>	4.60	3.75	0.140 (to 4.3 V)	2.42

## Summary:

**$\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{0.233}\text{Al}_{0.1}]\text{O}_2$  stores almost as much energy as  $\text{LiCoO}_2$ . It appears to be safer than  $\text{Li}_{1.1}\text{Mn}_{1.9}\text{O}_4$  and rivals  $\text{LiFePO}_4$ .**

**Lots of scientists are working on SAFE materials that are better than  $\text{LiFePO}_4$ .**

**I am confident that energy density of computer cells can be realized in SAFE Li-ion cells for vehicles. TESLA USES SUCH CELLS NOW.**

**Therefore –  $\text{LiCoO}_2$ /graphite numbers are valid for comparison to new technologies.**

# Air-fueled Battery Could Last Up to 10 Times Longer

by Engineering and Physical Sciences Research Council

Swindon, UK [RenewableEnergyWorld.com]

A new type of air-fueled battery could give up to ten times the energy storage of designs currently available.

"The key is to use oxygen in the air as a re-agent, rather than carry the necessary chemicals around inside the battery."

-- Peter Bruce, Chemistry Professor, University of St Andrews

This step-change in capacity could pave the way for a new generation of electric cars, mobile phones and laptops.

The research work, funded by the [Engineering and Physical Sciences Research Council \(EPSRC\)](#), is being led by researchers at the University of St Andrews with partners at Strathclyde and Newcastle.

## Lithium–Air Battery

SJ Visco, E Nimon, LC De Jonghe, PolyPlus Battery Company, Berkeley, CA, USA, and Lawrence Berkeley National Laboratory, Berkeley, USA

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### Introduction

The large free energy for the reaction of lithium with oxygen has attracted the interest of battery researchers for decades. At a nominal potential of about 3V, the theoretical specific energy for a lithium/air battery is over 5000 Wh kg<sup>-1</sup> for the reaction forming LiOH ( $\text{Li} + 1/4\text{O}_2 + 1/2 \text{H}_2\text{O} \leftrightarrow \text{LiOH}$ ) and **11,000 Wh kg<sup>-1</sup>** for the reaction forming **Li<sub>2</sub>O<sub>2</sub>** ( $2 \text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$ ) or for the reaction of lithium with dissolved oxygen in seawater, rivaling the energy density for hydrocarbon fuel cells and **far exceeding Li-ion battery chemistry that has a theoretical specific energy of about 400 Wh kg<sup>-1</sup>.**

**Where does 11,000 Wh/kg come from?**

**Start with Li - (6.9 g/mole)**

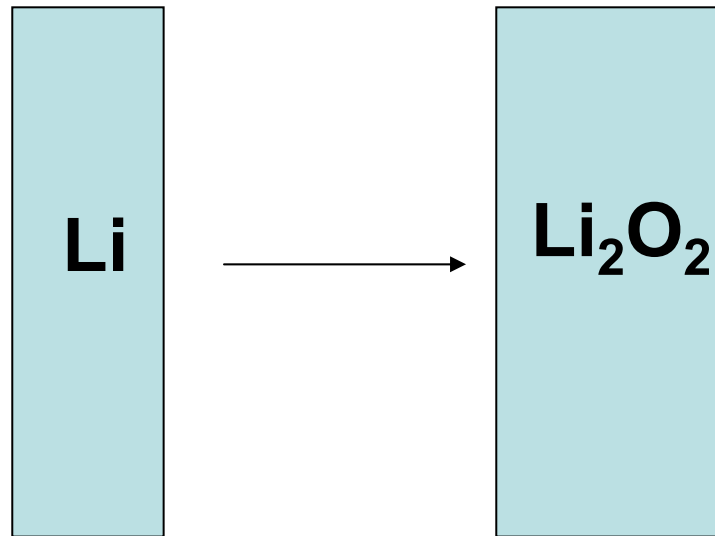
**Assume oxygen is “free” and we don’t need to worry about its mass.**

$$\text{Spec. E.} = \frac{3 \text{ V} \times 96500 \text{ C/mol}}{3600 \text{ C/Ah} \times 0.0069 \text{ kg/mol}}$$

$$\text{Spec. E.} = 11,500 \text{ Wh/kg}$$

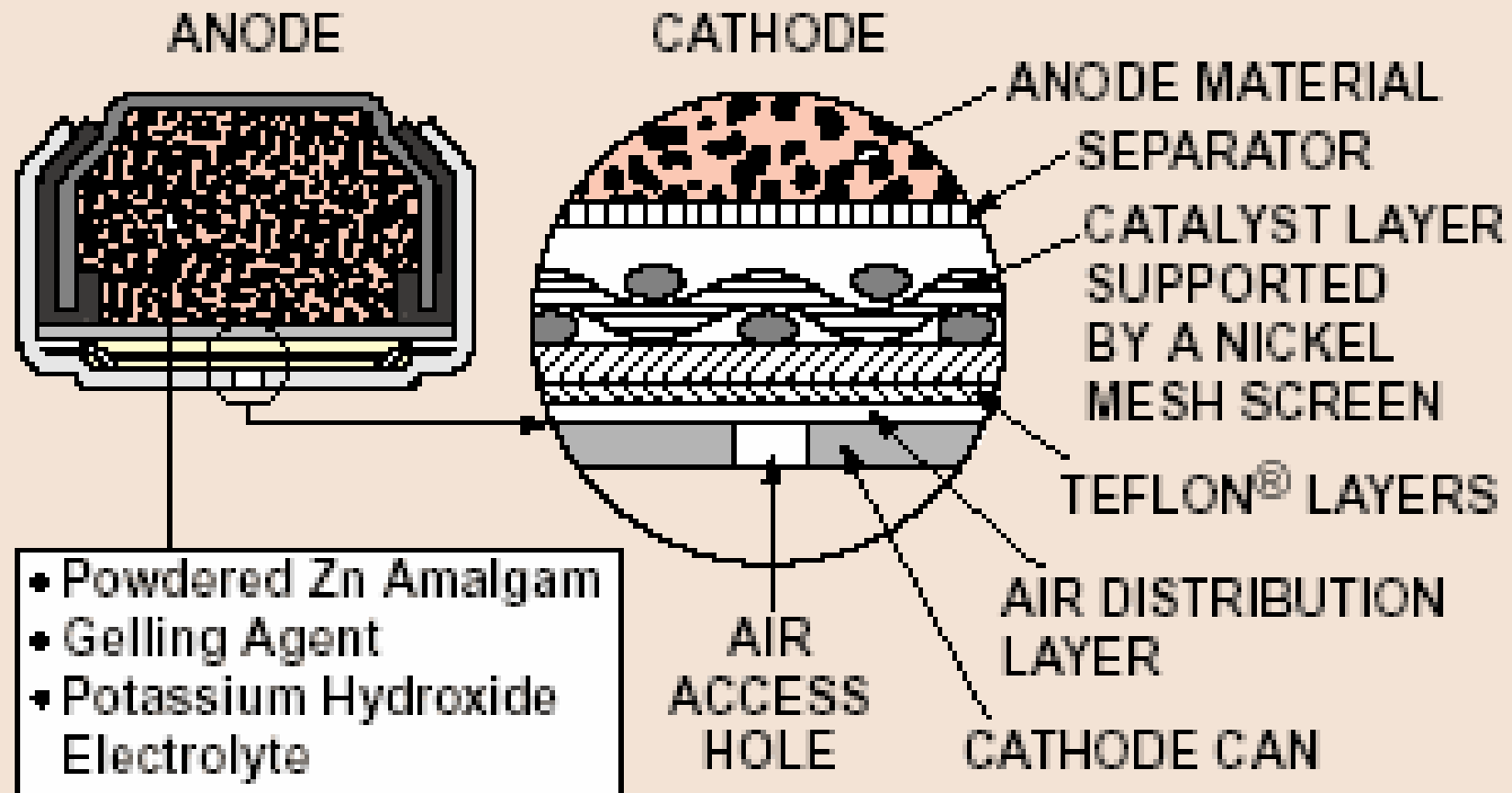
**OK – we understand the assumptions.**

**But surely this is unfair and we need to count the mass of the formed  $\text{Li}_2\text{O}_2$ , especially if we're talking about a rechargeable battery.**



**Vol. E. = 3500 Wh/kg (assuming only  $\text{Li}_2\text{O}_2$ )**

**FIGURE 3.4.1**



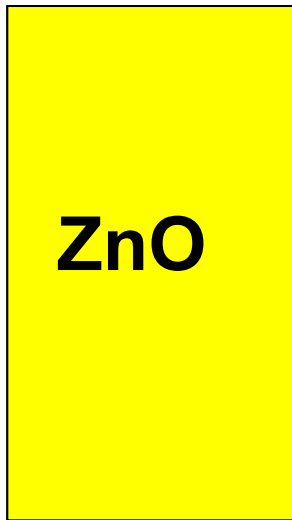
The electrodes for the DURACELL® zinc air cell are shown.

**Zn-air is fundamentally different to Li-air because  $\text{ZnO}_{14}$  forms in the same space as the Zn occupied.**

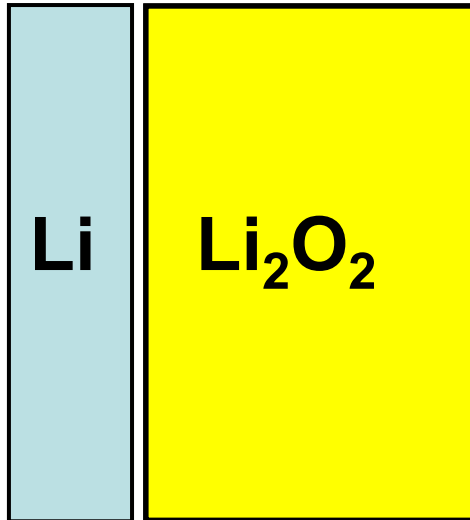
**Zn-air and Li-air are fundamentally different.**

**Zn-air is a “one compartment cell”**

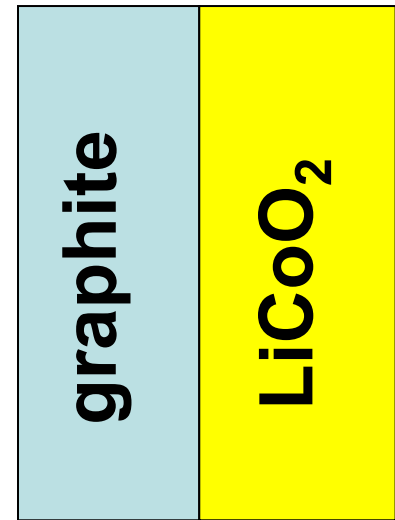
**Li-air is a “two compartment cell”**



**830 Wh/kg**



**“3500” Wh/kg**



**390 Wh/kg**

**Hard to compare based on mass, since don't know what mass the space for the  $\text{Li}_2\text{O}_2$  and the peripherals will have.**

**Instead, compare based on volume:**

**[N.B. – Volume matters for a vehicle and for energy storage applications.**

**This was well pointed out by Ted Miller yesterday]**

**Assumptions:**

**$\text{LiCoO}_2$  – 140 mAh/g, 5.05 g/cc, 3.8V Li-ion cell**

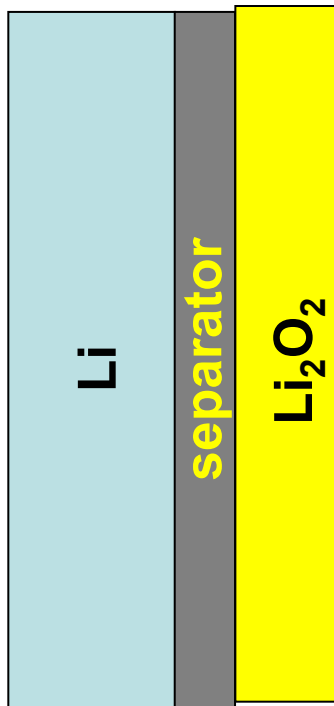
**$\text{Li}_2\text{O}_2$  – 1165 mAh/g, 2.3 g/cc, 3.0 V Li-air cell**

**Li – 3860 mAh/g, 0.51 g/cc**

**Graphite – 350 mAh/g, 2.2 g/cc**

**Use Feynman-style approach!**

## Bulk Li-Air



**Assume no porosity required**

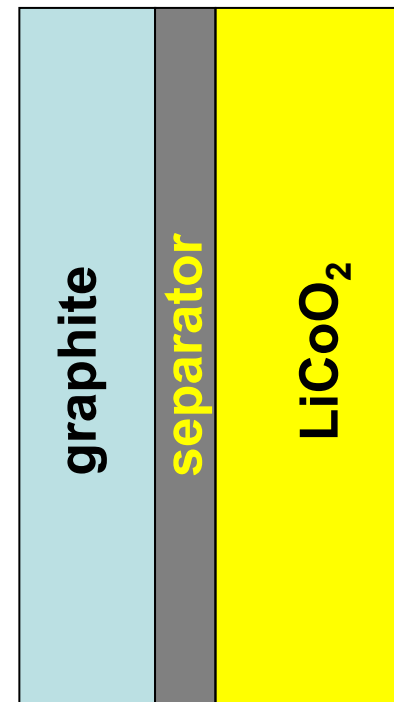
**Assume perfect, zero thickness separator**

**Assume 3.0 V**

**Assume Li thickness =  $x$**

**$\text{Li}_2\text{O}_2$  needs to be =  $.74x$**

## Bulk Li-ion



**Assume no porosity required**

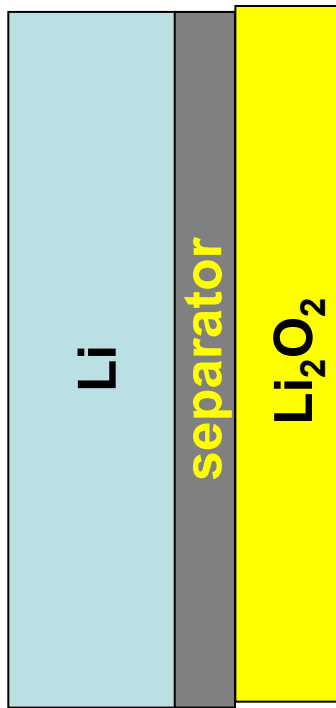
**Assume perfect, zero thickness separator**

**Assume 3.8 V**

**Assume graphite thickness =  $x$**

**$\text{LiCoO}_2$  needs to be  $1.15x$**

## Bulk Li-Air



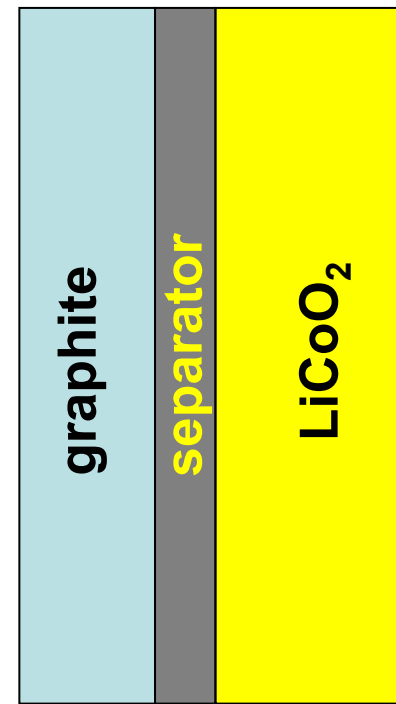
**Assume no porosity required**

**Assume perfect, zero thickness separator**

**Assume 3.0 V**

**Get 3400 Wh/L**

## Bulk Li-ion



**Assume no porosity required**

**Assume perfect, zero thickness separator**

**Assume 3.8 V**

**Get 1450 Wh/L**

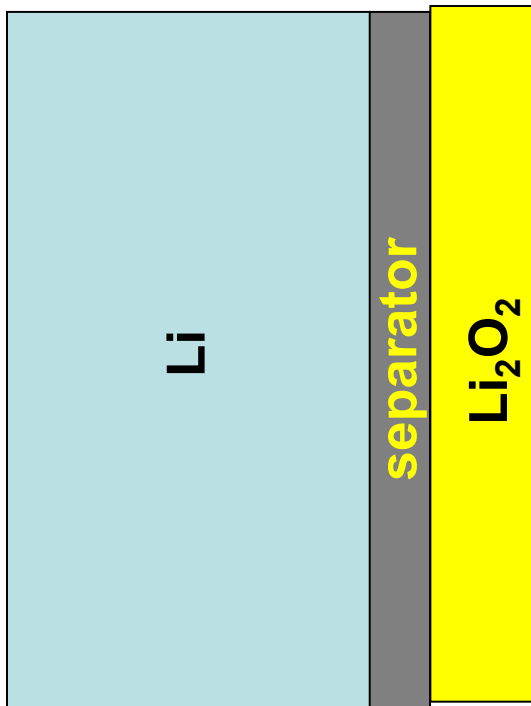
**But Li metal does not cycle efficiently. Need to have excess lithium. This amount is debatable but we will pick a three-fold excess.**

K. Brandt Solid State Ionics **69** (1994) 173-183.

“Through a combination of these measures, cells of the Canadian company Moli Energy achieved in the late 80's lithium cycling efficiencies of over 99% [ 19 ] translating into a life cycle of about 300 cycles with a lithium excess according to Eq. (2) of  $R= 3$ .”

**This means 4 times what is really used.**

## Bulk Li-Air



Assume no porosity required

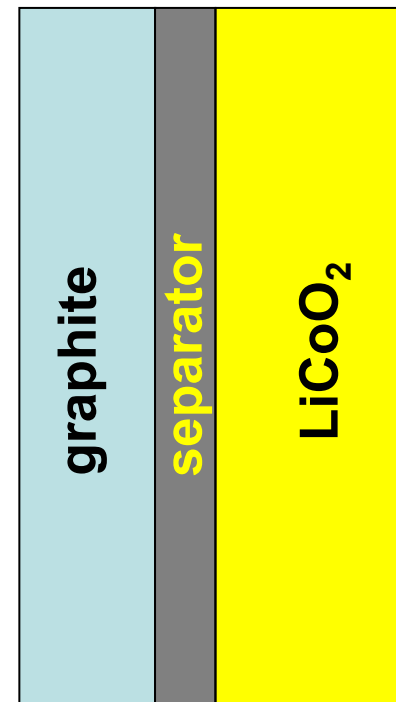
Assume perfect, zero thickness separator

Assume 3.0 V,

Assume 3-fold excess Li

**Get 1254 Wh/L**

## Bulk Li-ion

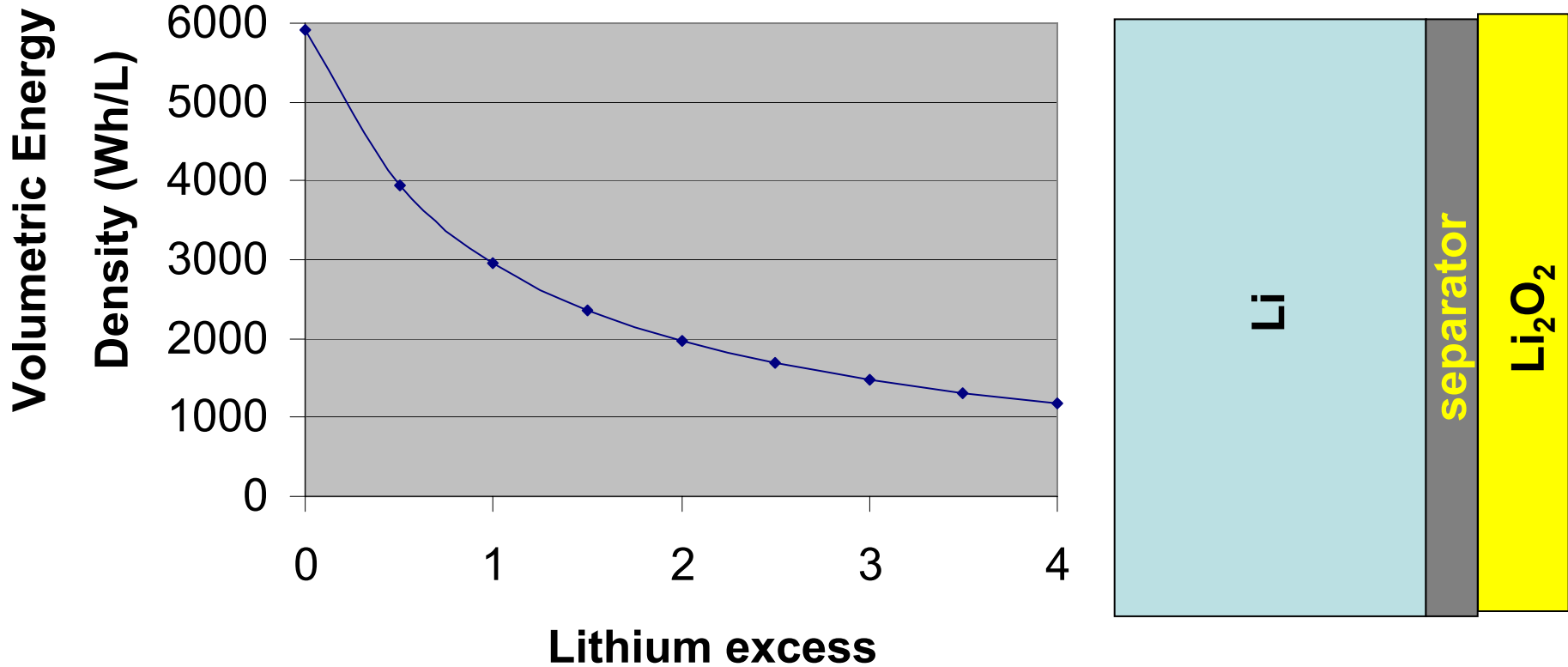


Assume no porosity required

Assume perfect, zero thickness separator

Assume 3.8 V

**Get 1450 Wh/L**

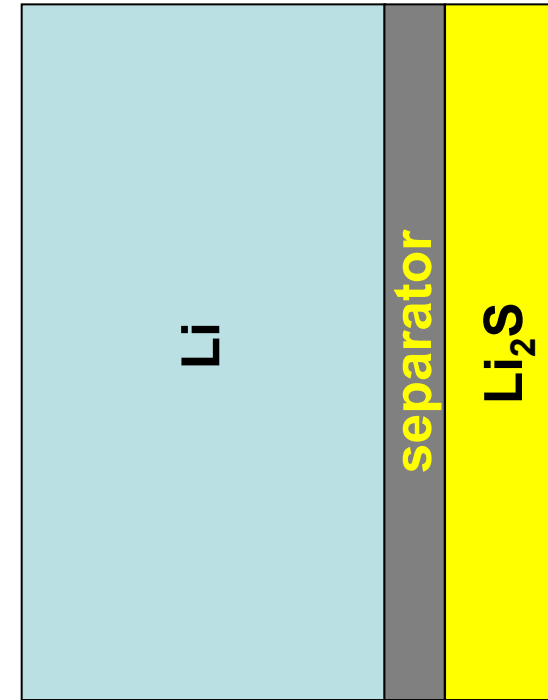
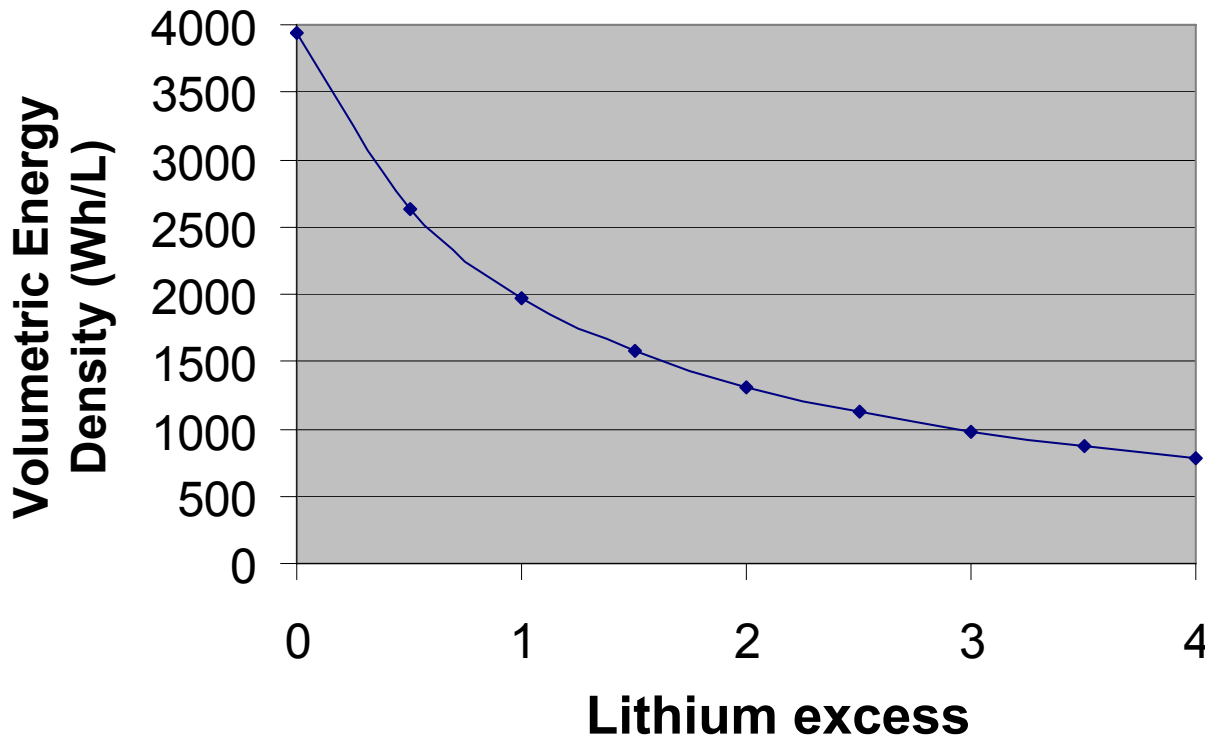


**Assume no porosity required**

**Assume perfect, zero thickness separator**

**Assume 3.0 V, ASSUME Li<sub>2</sub>O<sub>2</sub> is zero thickness (This accounts for possibility of Li<sub>2</sub>O).**

**Assume n-fold excess Li**



**Assume no porosity required**

**Assume perfect, zero thickness separator**

**Assume 2.0 V, ASSUME  $\text{Li}_2\text{S}$  is zero thickness.**

**Assume n-fold excess Li**

**This slide is  
for Linda**

**Therefore, the Li-air and Li-S batteries are all about Li.**

**In order for these batteries to be volumetrically useful, one needs to basically have a very small lithium excess.**

**This means learning how to strip and plate lithium effectively which was studied intensely in the 70's, 80's and early 90's. Maybe we're smarter now.**



**Li/MnO<sub>2</sub> rechargeable cell, Moli Energy about 1989**

**[Is this ancient history, irrelevant to the present day? Am I a dinosaur?]**

- Dec. 1988 - 2 Million Li/MoS<sub>2</sub> cells in the field (NEC laptop and NTT Cell phone)**
- Spring 1989 - Li/MnO<sub>2</sub> cell ready to go**
- Spring 1989 - Safety incidents in the field**
- Summer 1989 - We understand the problems**
- Summer 1989 - Complete recall of all phone packs and Moli goes into receivership.**
- Spring 1990 - NEC and Mitsui buy Moli.**

## The Safety Problem (Cells with Li metal anodes)

Li is not thermodynamically stable in non-aqueous electrolytes



As cells cycle, the surface area of the metallic Li increases without limit because the plated Li deposit is not compact **[This is Elton's Gray Layer]**. After about 25 to 50 cycles under certain conditions, cells cannot withstand temperatures above 120°C. The passivation mechanism breaks down and thermal runaway occurs

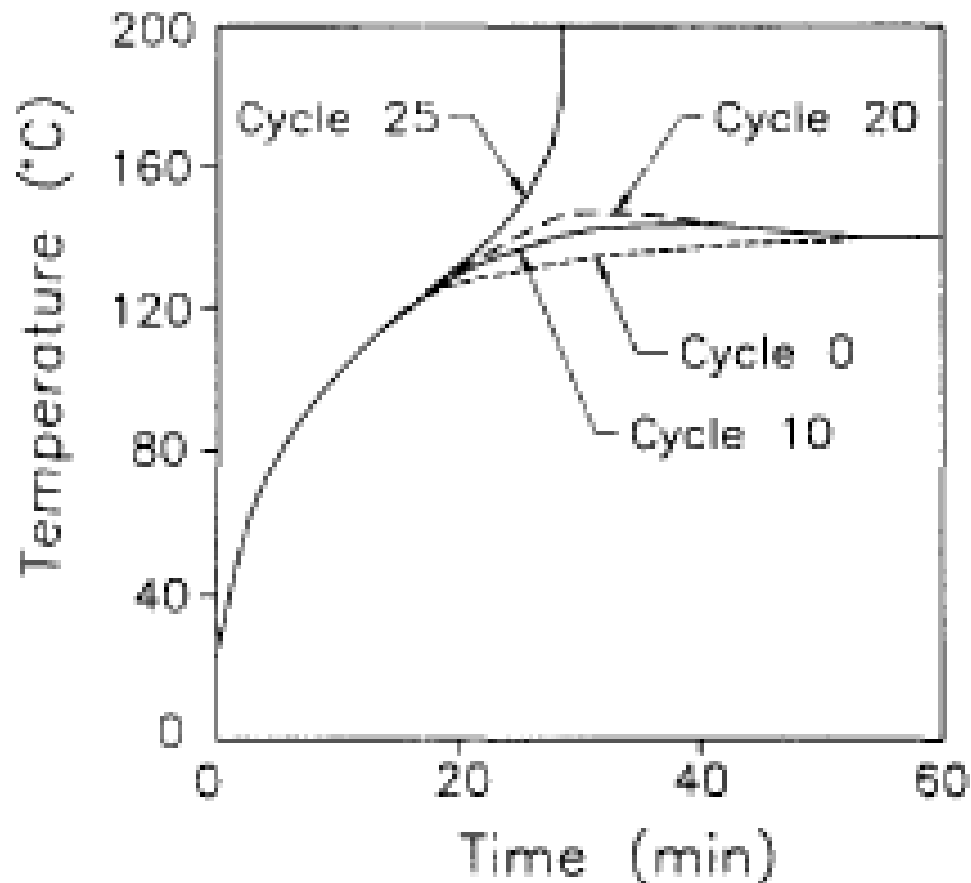


Fig. 1. Temperature response of cycled Li/MnO<sub>2</sub> AA-size cells subjected to 140 °C hot-box test. These cells had a nominal capacity of 600 mAh, contained 1 M LiAsF<sub>6</sub>/PC-EC electrolyte and were cycled at 21 °C at a low rate ( $\pm C/10$ ) to promote the formation of high surface area lithium. The number of cycles completed prior to the hot-box test is indicated on the graph; from Ref. [10].

Safety of metallic Li gets worse and worse with cycle number. Even though cells can pass oven test at the beginning of life, mossy cycled Li is very reactive.

This is why the whole industry switched to Li-ion in 1989-1990.

**Nevertheless, NEC and Mitsui insist on the "Confirmation Test" when they purchase Moli in 1990.**

**500,000 cells made, each individually x-rayed for manufacturing defects.**

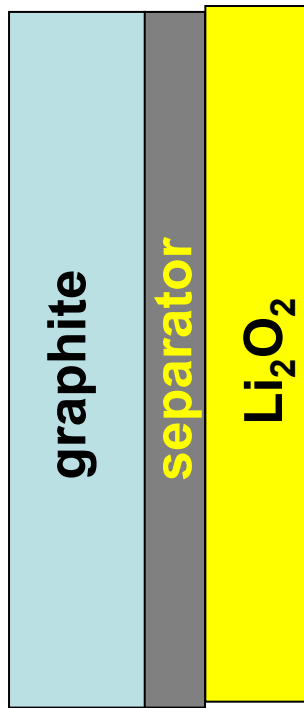
**50,000 cell phone battery packs built and cycled under low rate conditions. (Over 5000 chargers built for the task.)**

**After 1.5 years of assembly and testing many serious failures.**

**NEC and Mitsui decide to abandon Li metal cells FOREVER.**

**Even Hydro Quebec eventually abandoned Li metal cells with polymer electrolyte.**

## Bulk Li-Air with graphite negative



**Assume no porosity required**

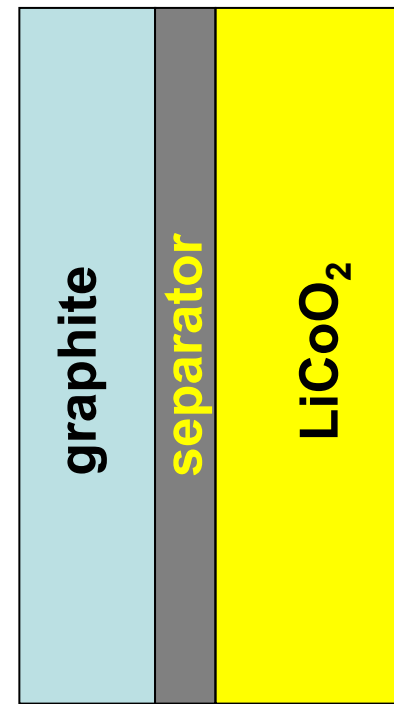
**Assume perfect, zero thickness separator**

**Assume 3.0 V**

**Assume 60 micron graphite**

**Li<sub>2</sub>O<sub>2</sub> needs to be 19 microns**

## Bulk Li-ion



**Assume no porosity required**

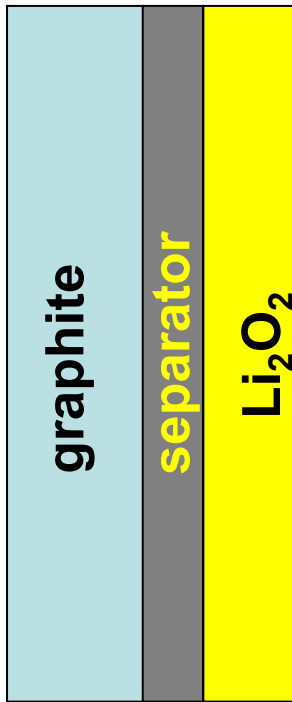
**Assume perfect, zero thickness separator**

**Assume 3.8 V**

**Assume 60 micron graphite**

**LiCoO<sub>2</sub> needs to be 69 microns<sub>29</sub>**

## Bulk Li-Air with graphite negative



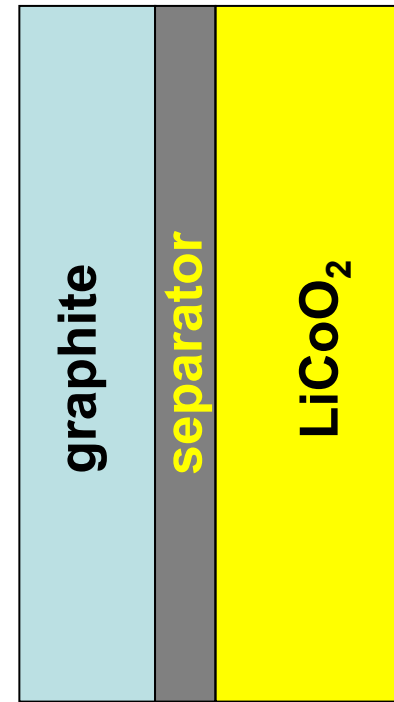
Total stack height = 79 micron

Voltage = 3 V

Same capacity since same graphite

**1880 Wh/L**

## Bulk Li-ion



Total stack height = 129 micron

Voltage = 3.8 V

Same capacity since same graphite

**1450 Wh/L**

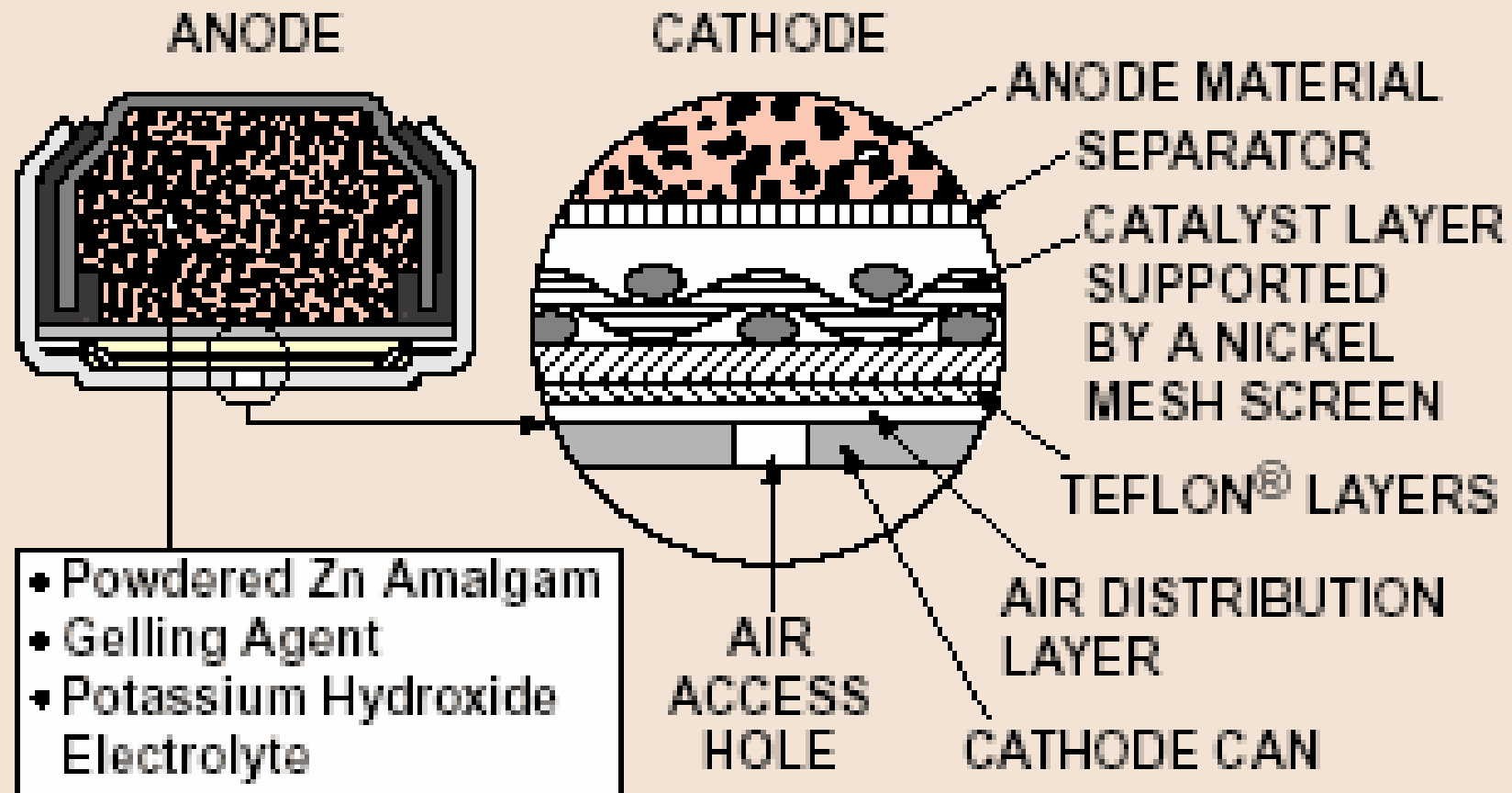
**18650 cells get 600 Wh/L now.**

## Comment:

Rechargeable Li-air and rechargeable Li-S will be very very challenging. Even if graphite (or Si) is used there are a whole host of problems. [Protecting the negative, Li excess, air handling, etc.] Don't bet the farm.

Simple Li-ion today – **without advanced electrodes**, can be as volumetrically efficient as Li-air in my opinion. With advanced electrodes, it can be better.

FIGURE 3.4.1



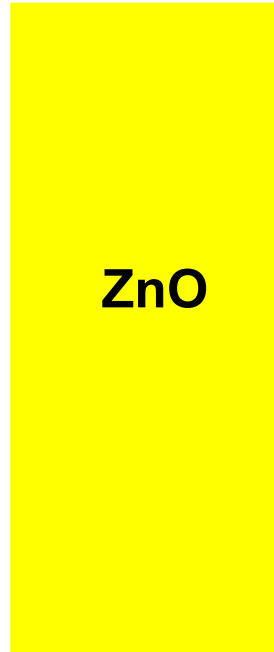
The electrodes for the DURACELL® zinc air cell are shown.

**Zn-air is fundamentally different to Li-air because  $ZnO_2$  forms in the same space as the Zn occupied.**

## Bulk Zn-air



1.2 V delivered



Assume:

Perfect separator (zero thickness)

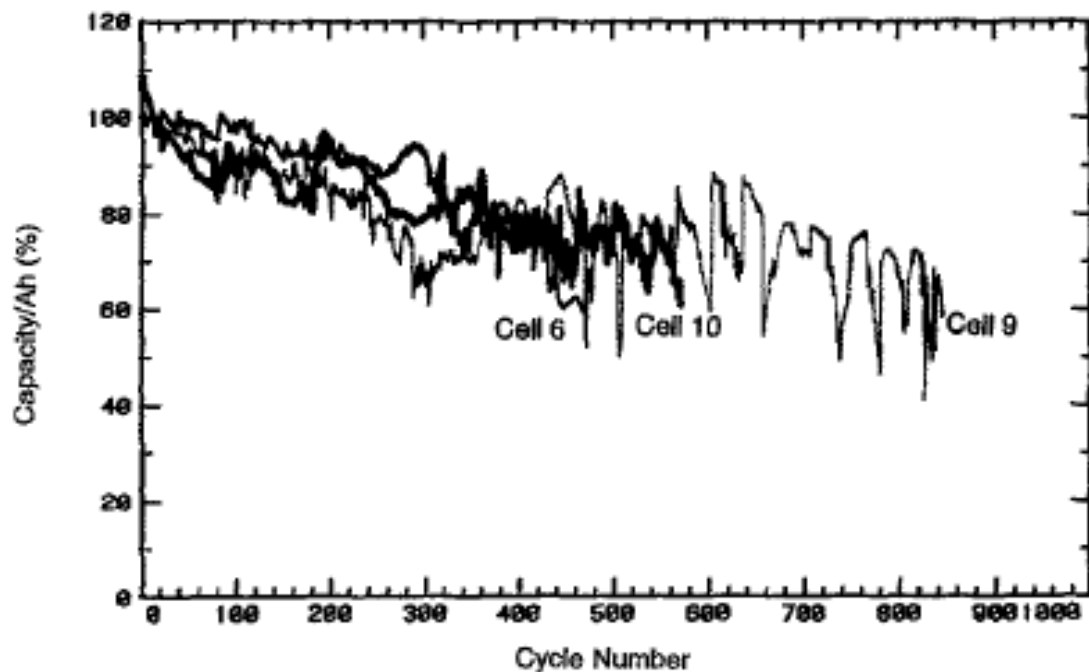
Perfect catalyst (zero thickness)

No current collectors

No porosity

$$\begin{aligned} \text{Vol. Energy Density} &= 0.661 \text{ Ah/g} * 5606 \text{ g/L} * 1.2 \text{ V} \\ &= \underline{\underline{4400 \text{ Wh/L}}} \end{aligned}$$

Even the tiny Duracell DA13 gets 1756 Wh/L !



**This looks pretty good for a typical Li-ion computer cell.**

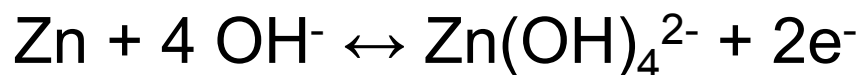
**But it's not a Li-ion cell. It is a Ni-Zn cell, with a Zn electrode.**

**T. C. Adler, F. R. McLarnon, and E. J. Cairns, J. Electrochem. Soc. 140, 293 (1993).**

**These 1.35 Ah cells used a novel electrolyte designed to give better stability to the Zn electrode.**

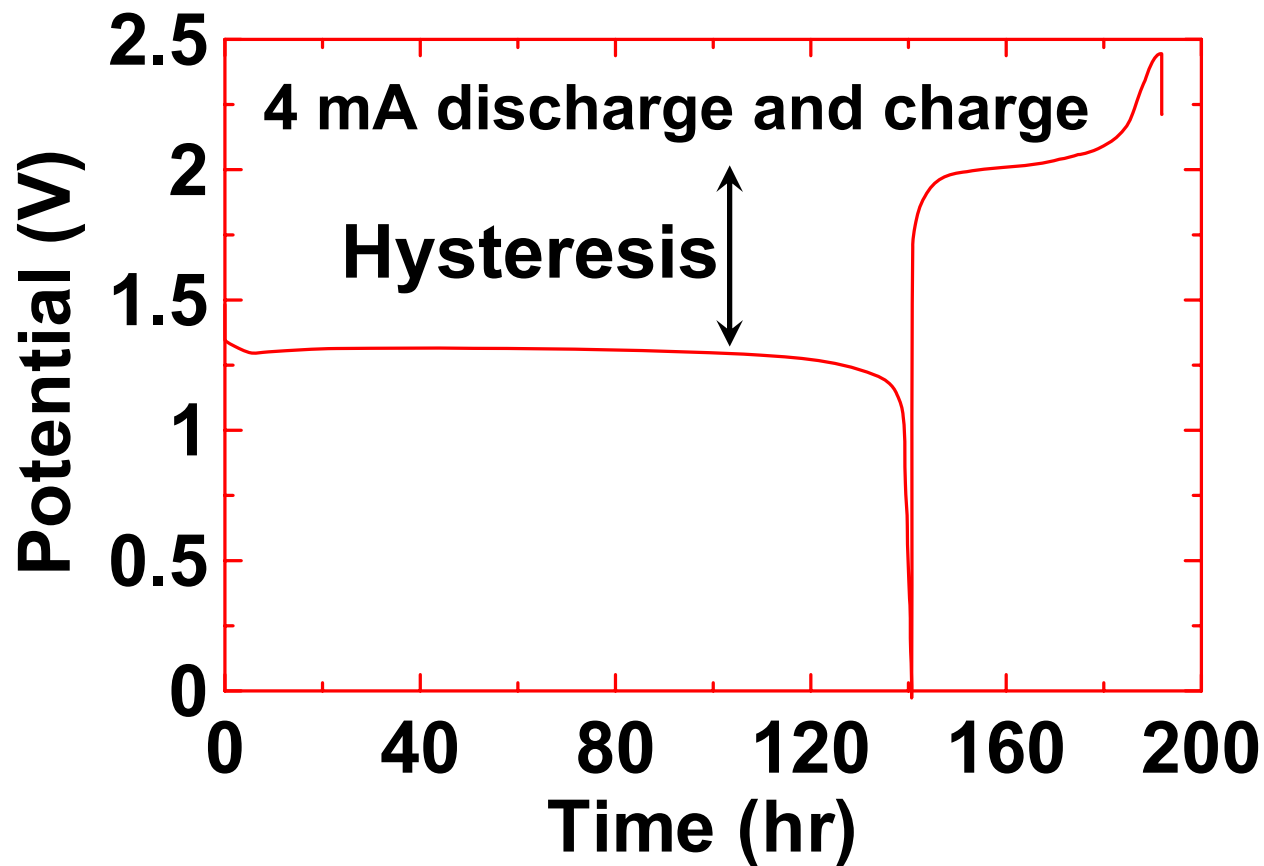
**Doesn't this prove that the Zn electrode can be cycled??**

*Zinc-nickel oxide battery.*--The Zn/KOH/NiOOH cell is based on dissolution-precipitation reactions at the Zn electrode:



This is the same reaction as happens in the Zn-Air cell.

**“Within the limits of our experimental parameters and experimental reproducibility and error, the optimum composition is 3.2-4.5 M KOH, 1.8 M each KF and K<sub>2</sub>CO<sub>3</sub>, and 0.5 M LiF in suspension, saturated with ZnO.” - From a 1998 paper by the Cairns group.**



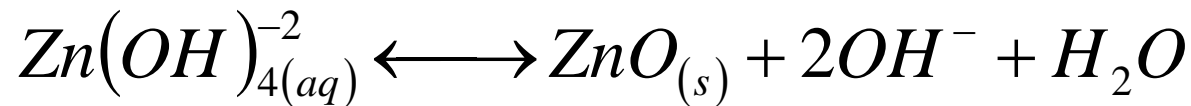
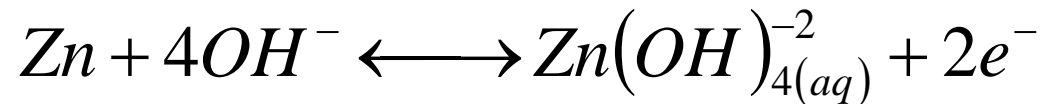
Discharge and charge of a commercial #675 size (non-rechargeable) Zn-air cell. 4 mA current. Cell weight = 1.8 grams.

Note that the cell is somewhat rechargeable

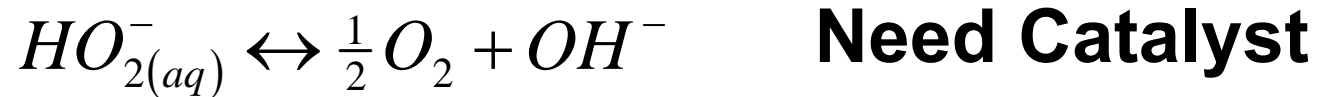
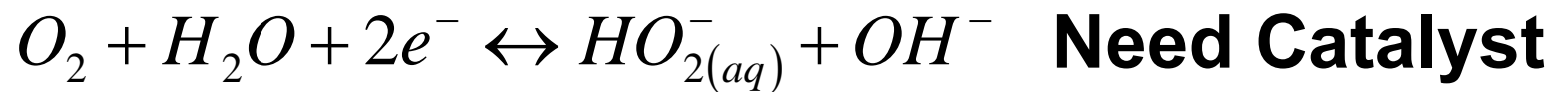
# How Zn-Air Works (Briefly)

The discharge reactions are as follows.

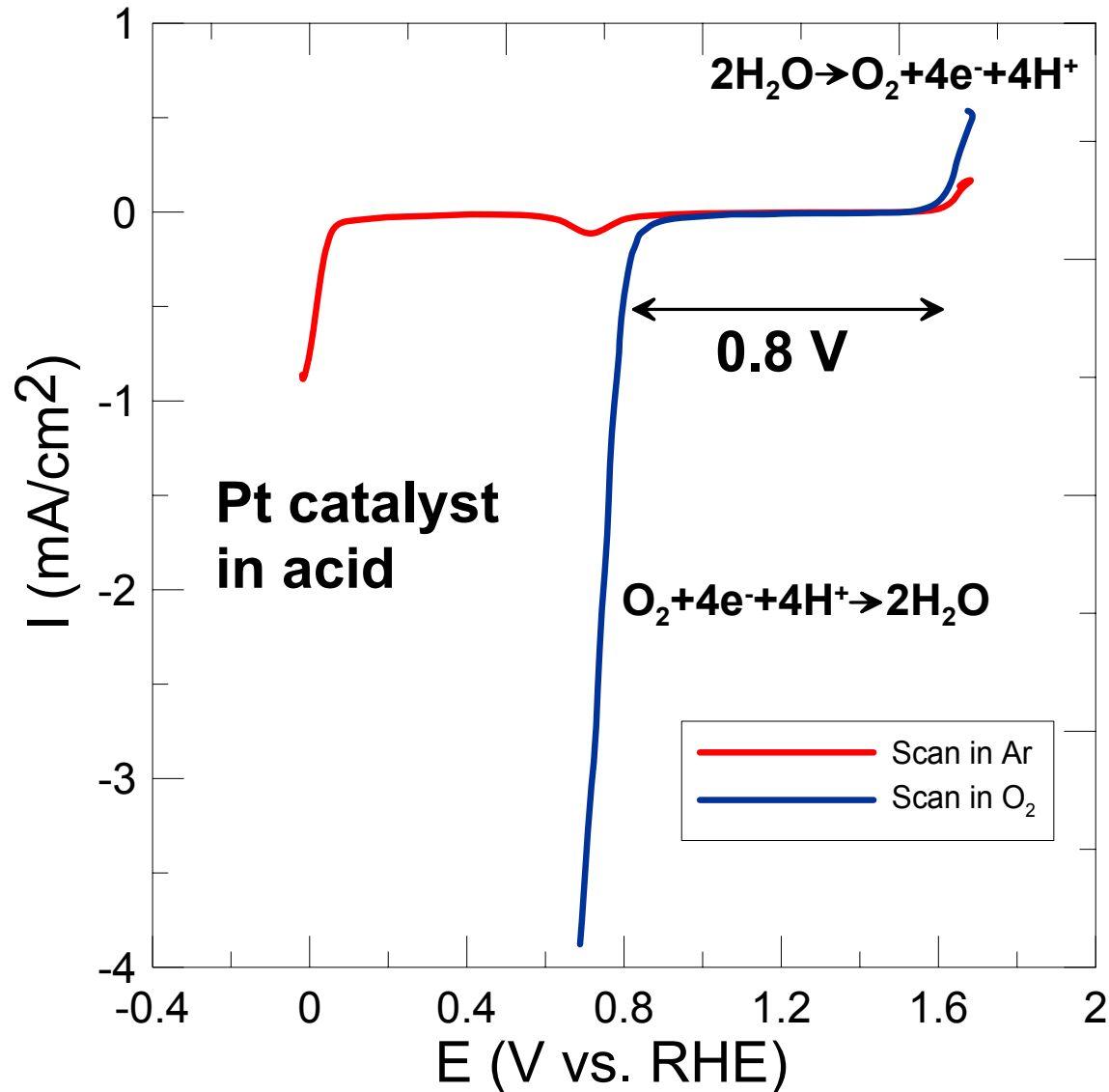
- At the Zn electrode:



- At the Carbon electrode:



# Cyclic Voltammetry Experiments



The hysteresis in the cell arises mostly at the air electrode side. The oxygen evolution reaction and the oxygen reduction reaction are separated by 0.7 to 0.8 V due to activation barriers.

**Let's talk about efficiencies:**

**Zn-air – Charge 2.0 V, Discharge 1.2 V 60%**

**Li-air – Charge 3.8 V, Discharge 3.0 V 79%**

**[I have given the Li/air guys the benefit of the doubt here as well]**

**Li-ion – No true hysteresis – 95% under real conditions**

**What really matters for automotive and energy storage?**

**Volumetric Energy Density – We discussed this.**

**Efficiency – cost of a charge, don't want to waste renewable energy. Can be addressed by Univ. and Govt. labs thru new materials.**

**Cost of batteries – can this be addressed by universities and govt. labs?**

**Safety – hard to address by universities and govt. labs.**

**Cycle life – at the automotive and energy storage level > 3000 cycles, need real cells - so hard for universities and govt. labs. (OR IS IT?)**

**Automotive and energy storage cells require excellent cycle life (> 3000 cycles)**

**There have been numerous papers and patents published on electrolyte additives, positive electrode material coatings, new electrode materials, etc. that lead to better cycle life.**

**e.g. SEI modifiers on the negative electrode side – vinylene carbonate, vinyl acetate**

**e.g. H<sub>2</sub>O and HF scavengers to reduce transition metal dissolution on positive electrode**

**e.g. AlF<sub>3</sub> and other coatings on NMC to improve cycle life to high potential, etc. etc. etc.**

The cycle life of rechargeable cells is not infinity because small fractions of cell components are consumed during each cycle. The amount of these components consumed can be measured using the “coulombic efficiency” (CE):

$$CE = Q_c/Q_d = [\text{Charge in}]/[\text{Charge out}]$$

It is of utmost importance to be able to **measure** the coulombic efficiency accurately, **but traditional battery charger systems cannot.**

10,000 cycles need at least 99.99% CE

e.g.  $0.9999^{10000} = 0.367$

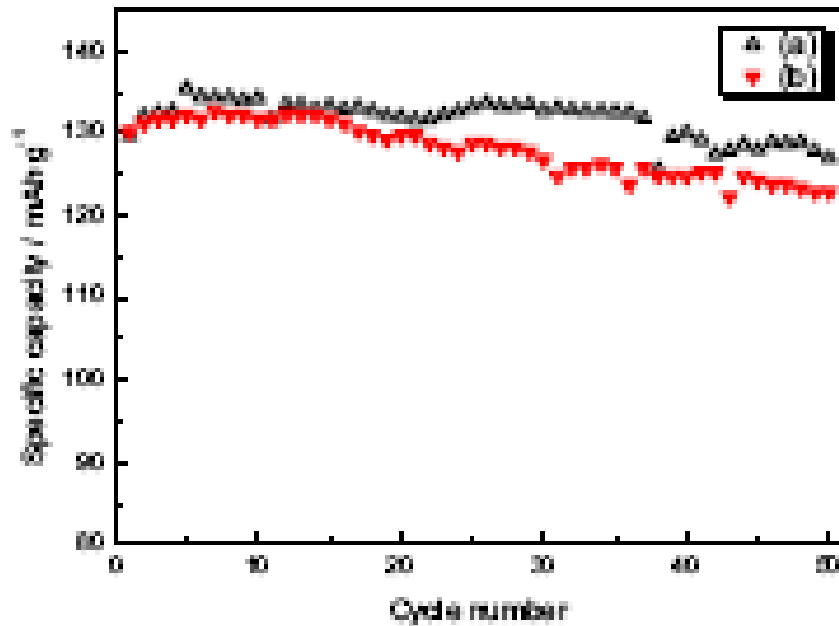


Fig. 4 Cycling performance of different cathode materials: a  $\text{LiMn}_{1-x}\text{Cr}_{2x}\text{Ni}_{1-x}\text{O}_4$  and b  $\text{LiNi}_{0.2}\text{Mn}_{0.2}\text{O}_4$

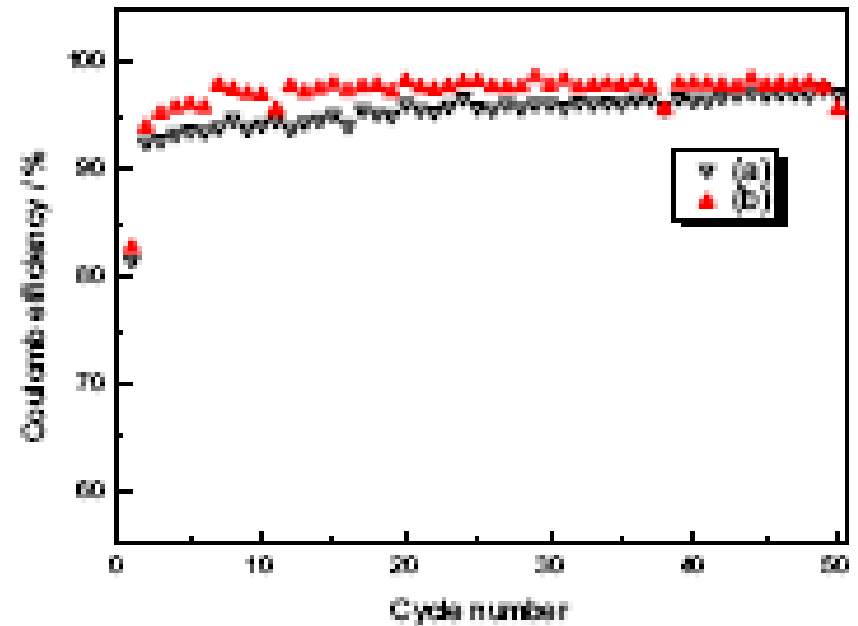


Fig. 5 Coulombic efficiency of  $\text{LiNi}_{0.2}\text{Mn}_{0.2}\text{O}_4$  (a) and  $\text{LiMn}_{1-x}\text{Cr}_{2x}\text{Ni}_{1-x}\text{O}_4$  (b) in 50 cycles

**Typical Literature Data**  
**Look at the scatter!**

## High Precision Charger (HPC)

Used to measure the columbic efficiency of different electrodes and electrolyte additives

Delivers current with an accuracy of 0.03%

### Apparatus

Keithley 220 current source

Keithley 2750 digital multimeter

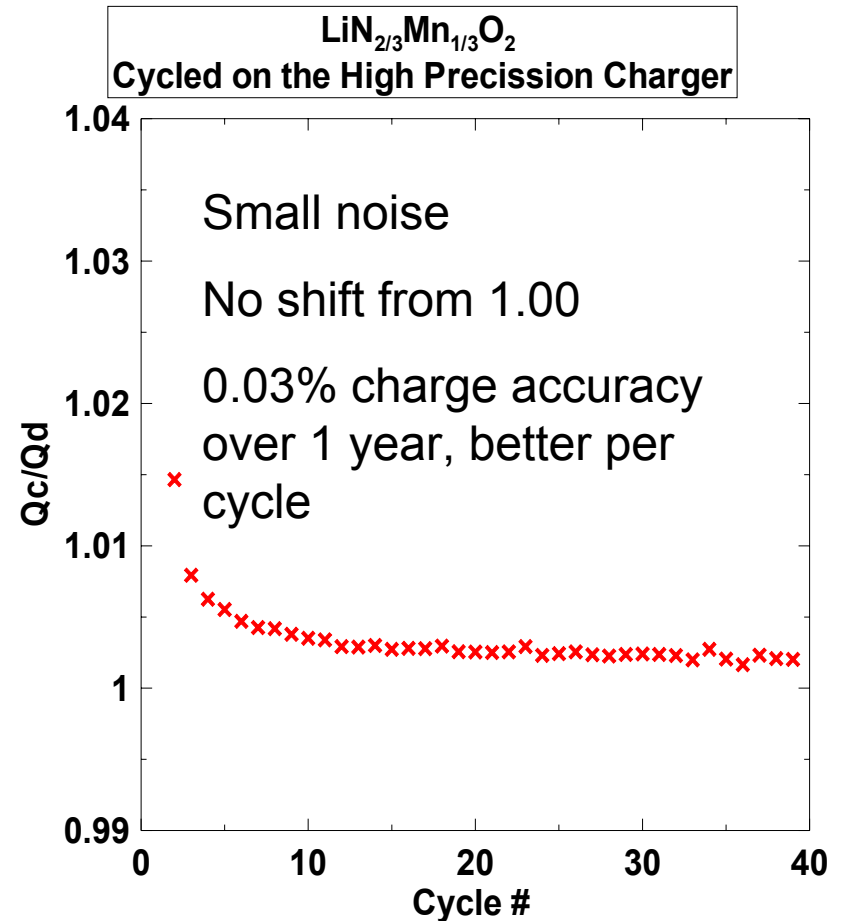
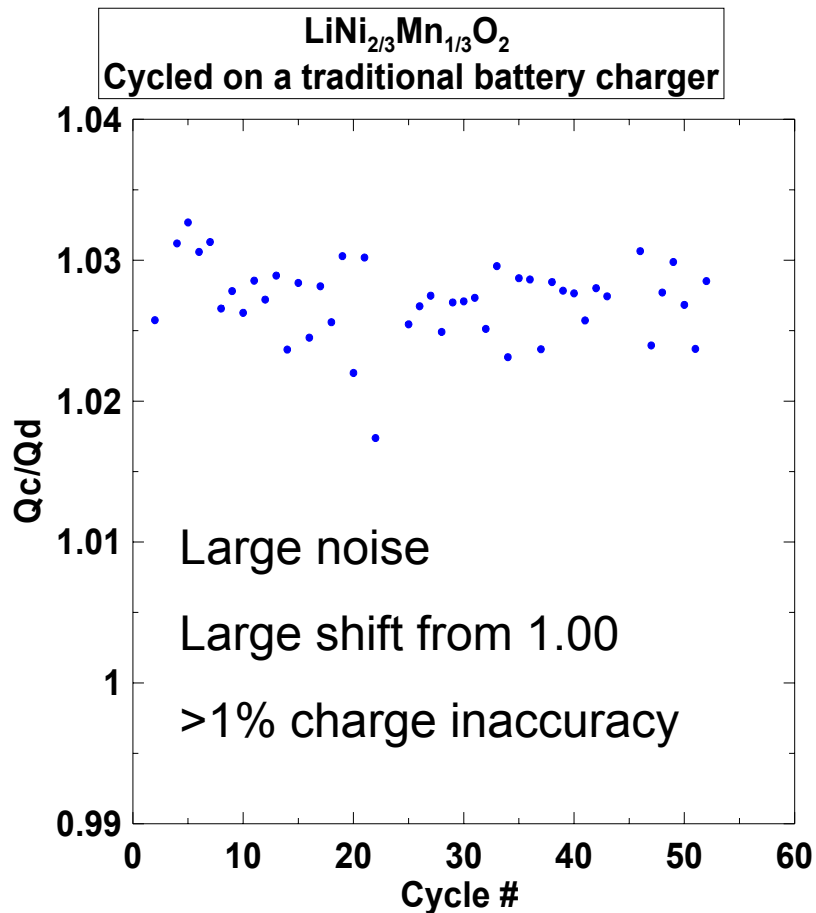
Omega temperature controller

Temperature controlled box

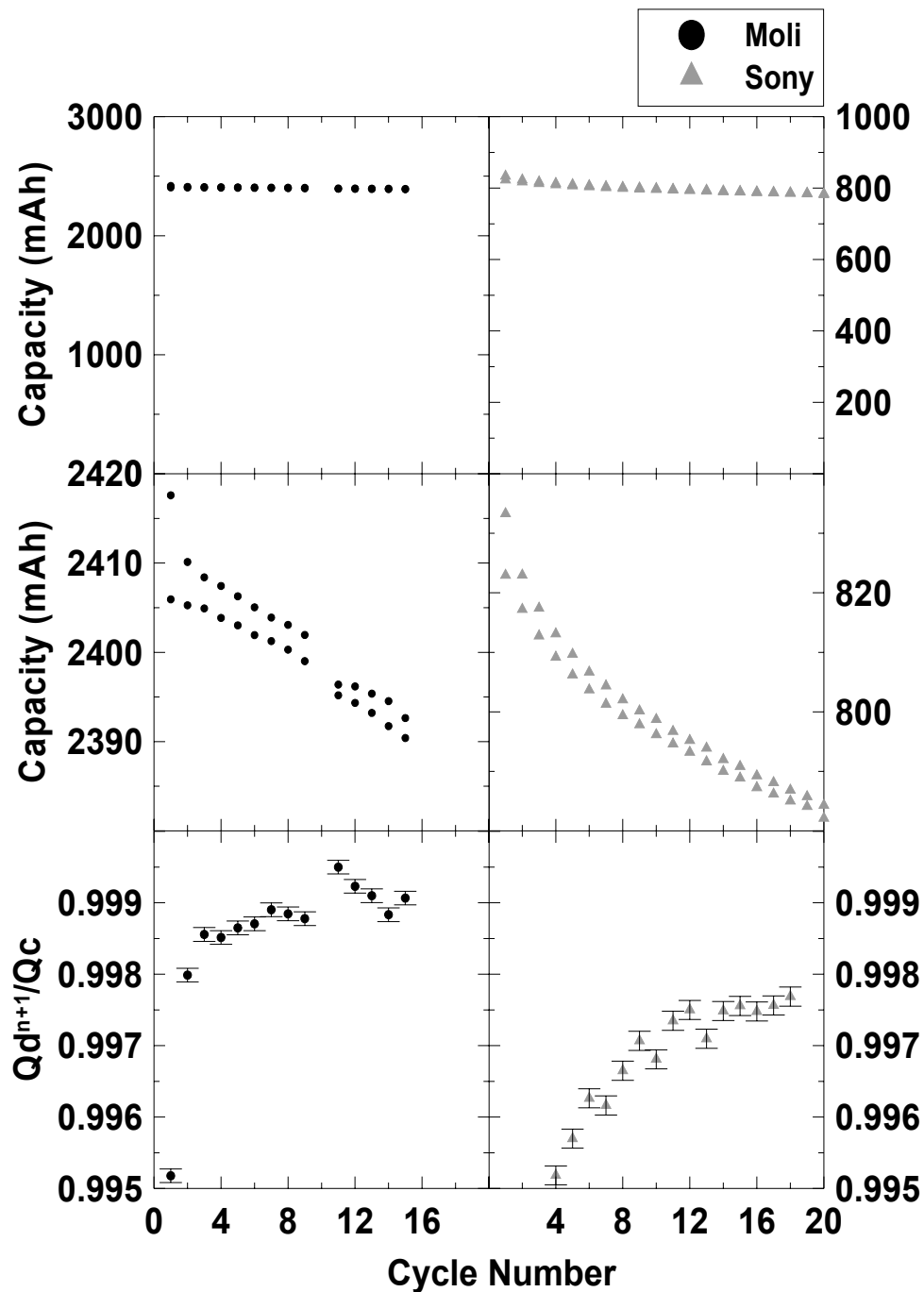
Custom labview software program

The HPC has many impressive characteristics!





**Our high precision charger is the best in the world, but still not what we ultimately need.**

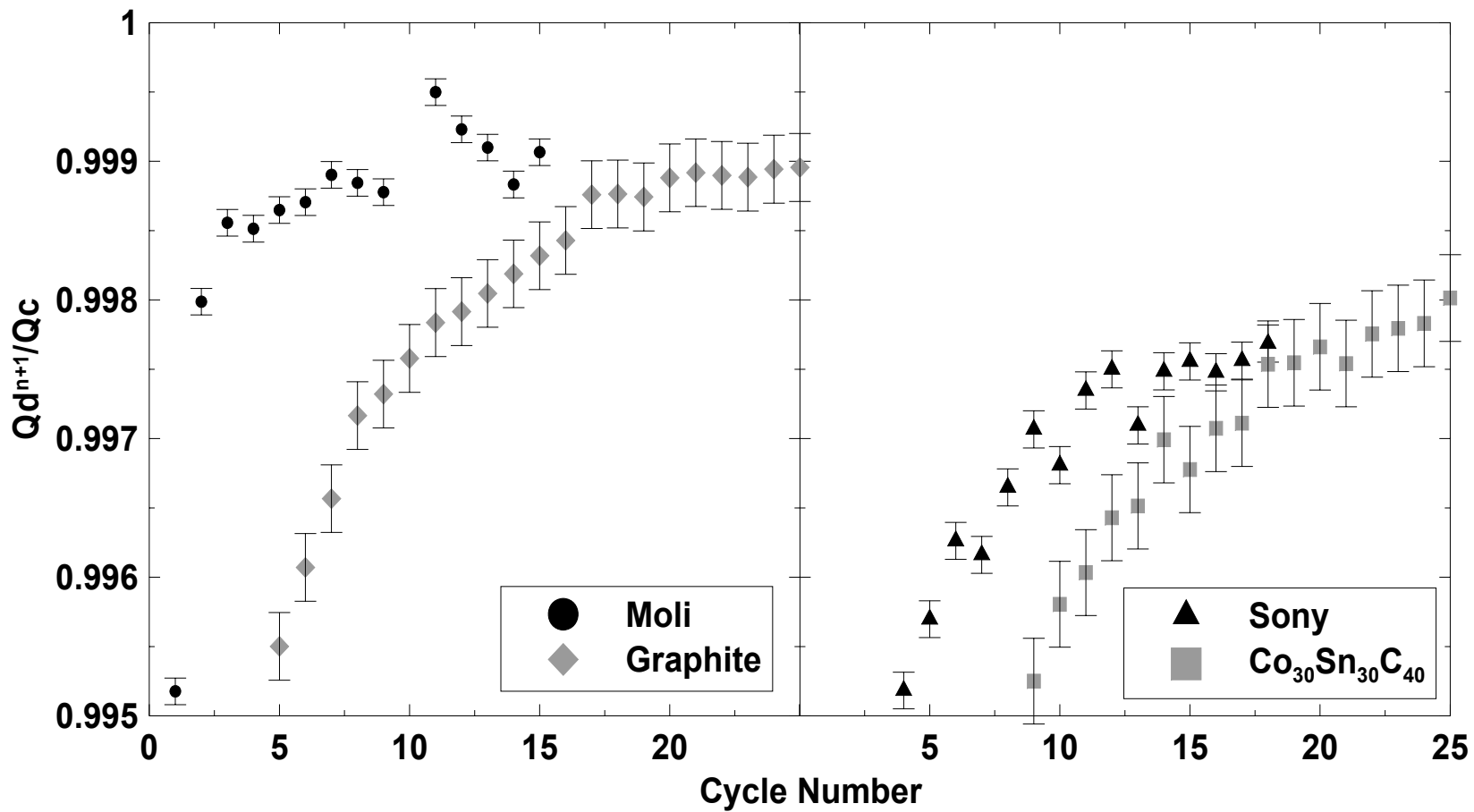


**Moli**  
**LiCoO<sub>2</sub>/graphite**

**compared to**

**Sony Nexelion**  
**LiCoO<sub>2</sub>-NMC/Sn-TM-C**

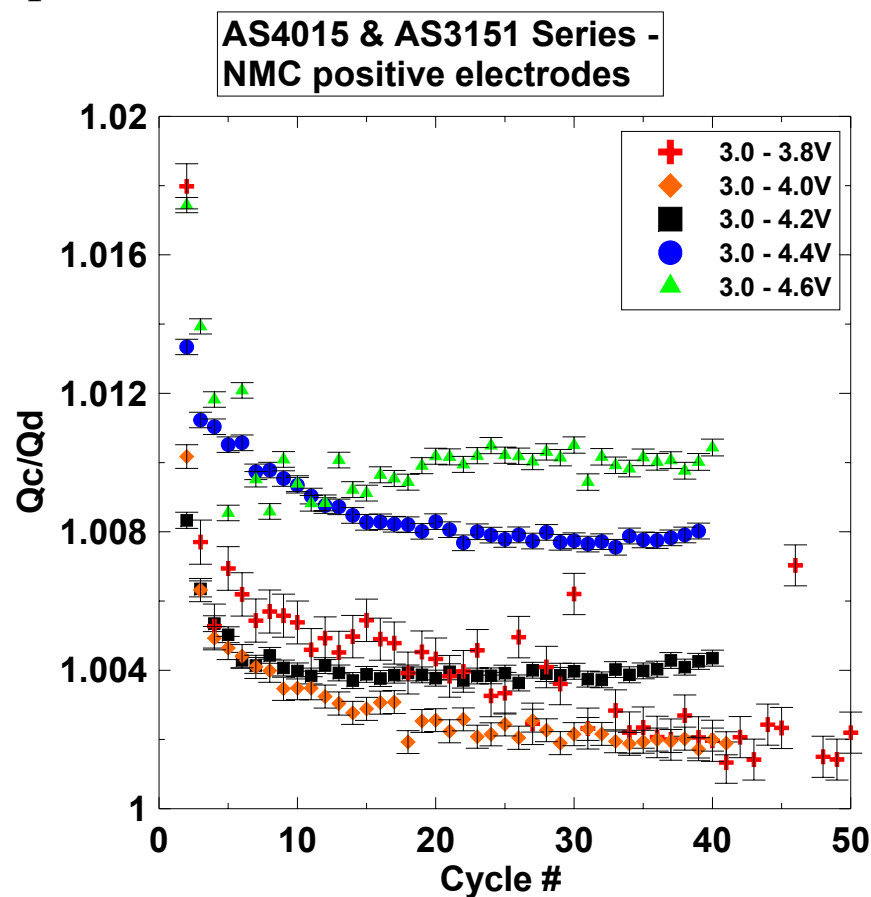
**All cycled at C/24**  
**rates**



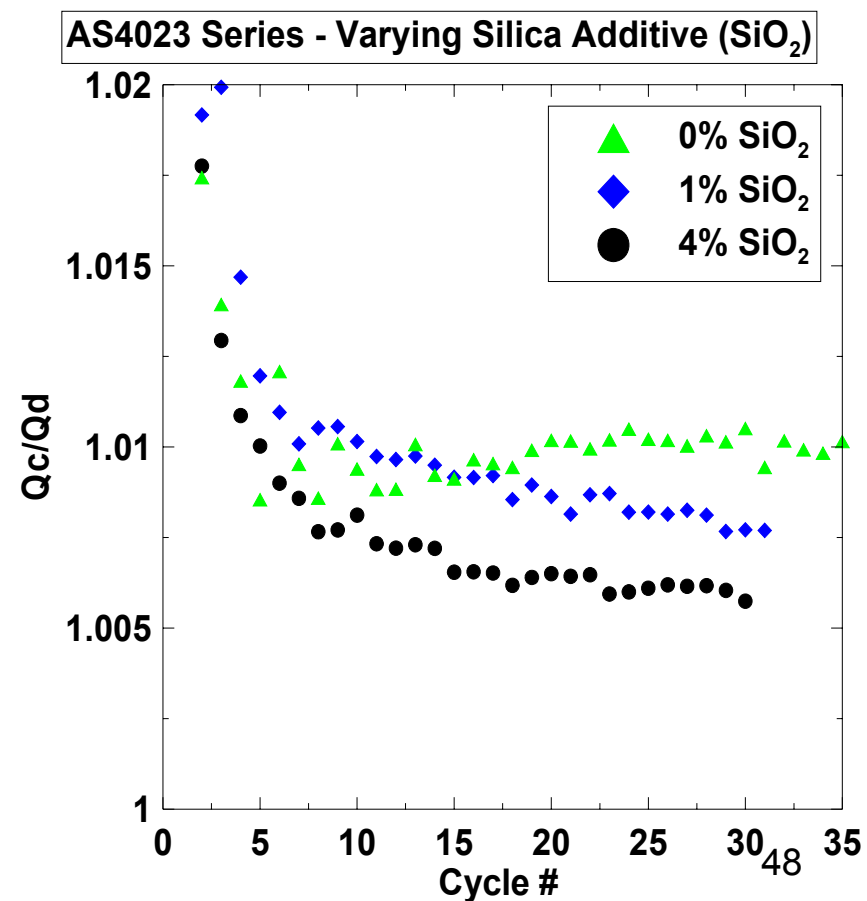
**Li-ion cells compared to corresponding  $\frac{1}{2}$  cells**

## Example: NMC positive electrode material

NMC Li-ion Cells cycled to  $> 4.2$  V sometimes show short life. Graph below predicts this.



Potential solution: additives improve the CE of NMC charged to 4.6 V





**40-channel high-precision charger operational at Dalhousie (taken August 22)**

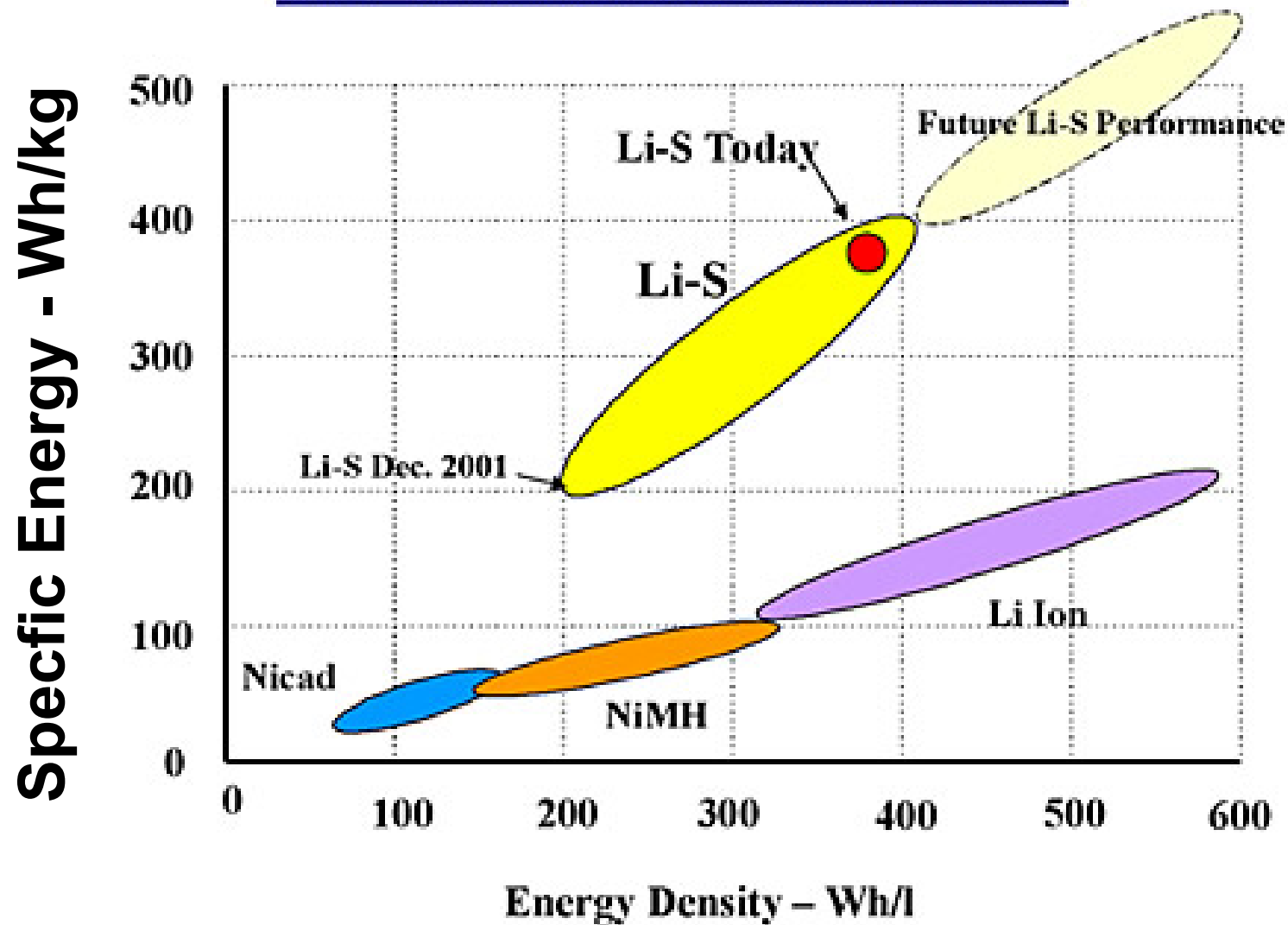
**You can't do the science without the tools**

**We need systems 10x better than this!! IBM (and Si Valley) can surely help here!**

## **Concluding remarks**

- 1. There is a lot do. Lithium-ion is pretty hard to beat volumetrically AND it will improve incrementally over time as well (See Talk by Mike Thackeray)**
- 2. University (and other) researchers need to “get relevant” to help with automotive batteries.**
- 3. Focus on what’s important and learn from the past. Do not use metallic lithium in rechargeable batteries (my **STRONG** opinion). Don’t bet the farm on air and S-systems.**
- 4. Hold more events like this.**

## Li-S vs. Other Cell Chemistries



Taken from the Sion Power website August 24, 2009

- Not more volumetrically efficient than Li-ion. What about safety? Why no products after decades?



**GM's Chevy Volt will be a plug-in hybrid using Li-ion batteries. The batteries considered were graphite/LiFePO<sub>4</sub> Li-ion batteries made by A123 Co. or graphite/LiMn<sub>2</sub>O<sub>4</sub> batteries made by LG Chem.**<sup>52</sup>