Electrochemical Approaches to Electrical Energy Storage

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outline

- the energy storage landscape
- an electrometallurgical approach to large-scale storage
- portable storage: beyond lithium

misconceptions about batteries

- not much has changed: not true!

electrical energy storage

	(Wh/kg)	(MJ/kg)
lead acid	35	0.13
NiCd	45	0.16
NaS	80	0.28
NiMH	90	0.32
Li ion	150	0.54
gasoline	12000	43

misconceptions about batteries

- not much has changed: not true!
- no Moore's Law (transistor count 2x every 2 years):
  - ✏ the battery is an electrochemical device
    - ☞ 2 interfacial reactions, each drawing upon reagents transported from contiguous volumes
    - ☞ mass and charge transport required
- all microelectronics are silicon-based:
  - ☞ device performance improvements come from better manufacturing capabilities
- all new batteries are based on entirely new chemistries
  - ☞ radical innovation

different approaches for different applications

- don’t pay for attributes you don’t need
- cell phone needs to be idiot-proof
- car needs to be crashworthy
- safety is a premium in both applications
- how about service temperature?
  - ☞ human contact?
- stationary batteries: more freedom in choice of chemistry but very low price point

market price points

APPLICATION	PRICE POINT
laptop computer	$2,000 - $3,000 / kWh
communications	$1,000 / kWh
automobile traction	$100 - 200 / kWh
stationary storage	$50 / kWh

severity of service conditions

price

storage is the key enabler

- for deployment of renewables: unless their intermittency can be addressed they cannot contribute to baseload
  - ☞ even if you had 100% conversion efficiency in photovoltaics they still wouldn't make it in much of the marketplace
- in grid-level storage we need to think about the problem differently when combustion is an option:
  - ☞ batteries invented for portable applications are not scalable at an acceptable price point
  - ☞ stringing together thousands of Li-ion batteries won't do: here the whole is less than the sum of its parts

storage is the key enabler

- smart grid requires rapid response capability
  - ☞ colossal electric cache

August 13, 2003
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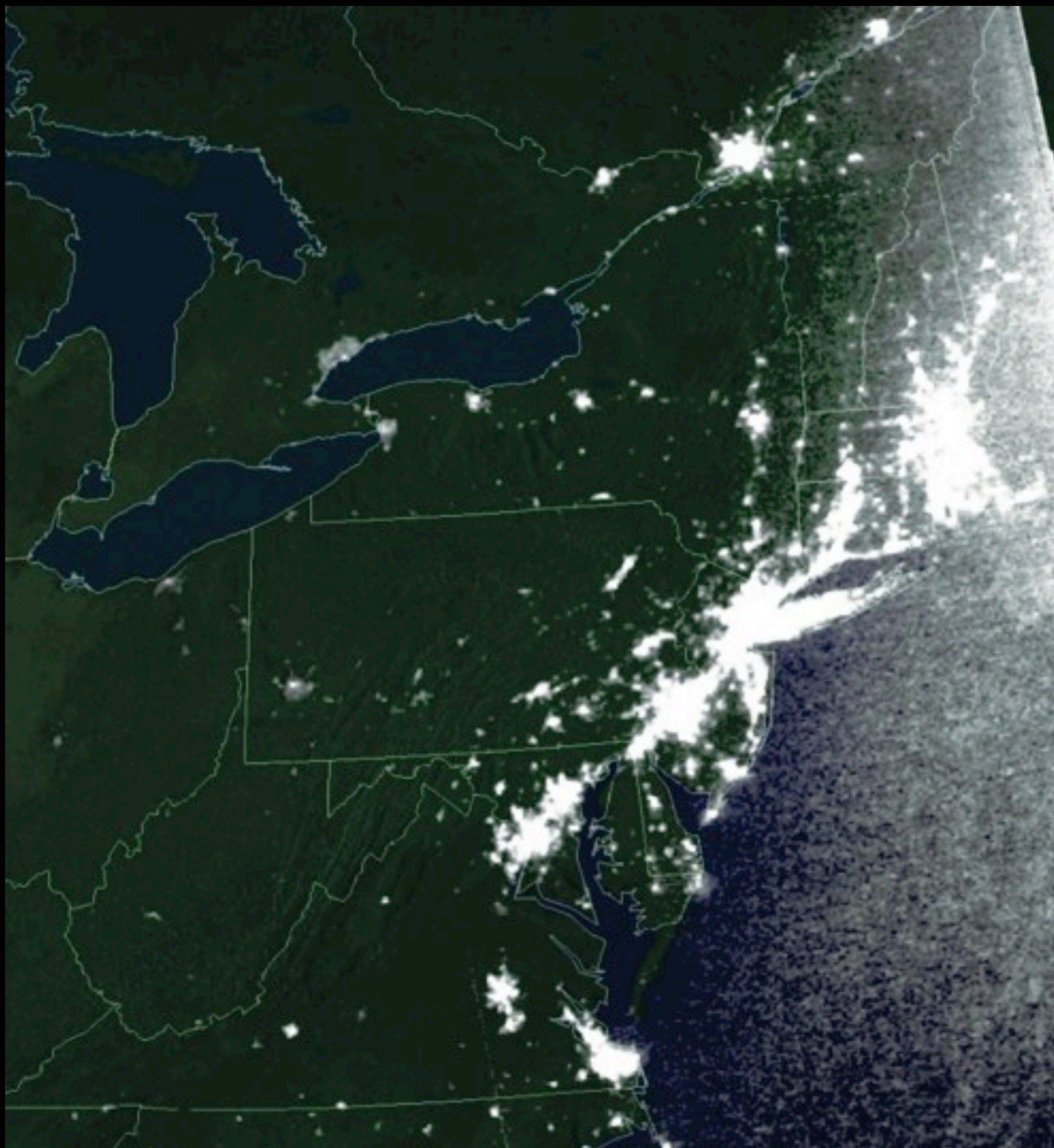

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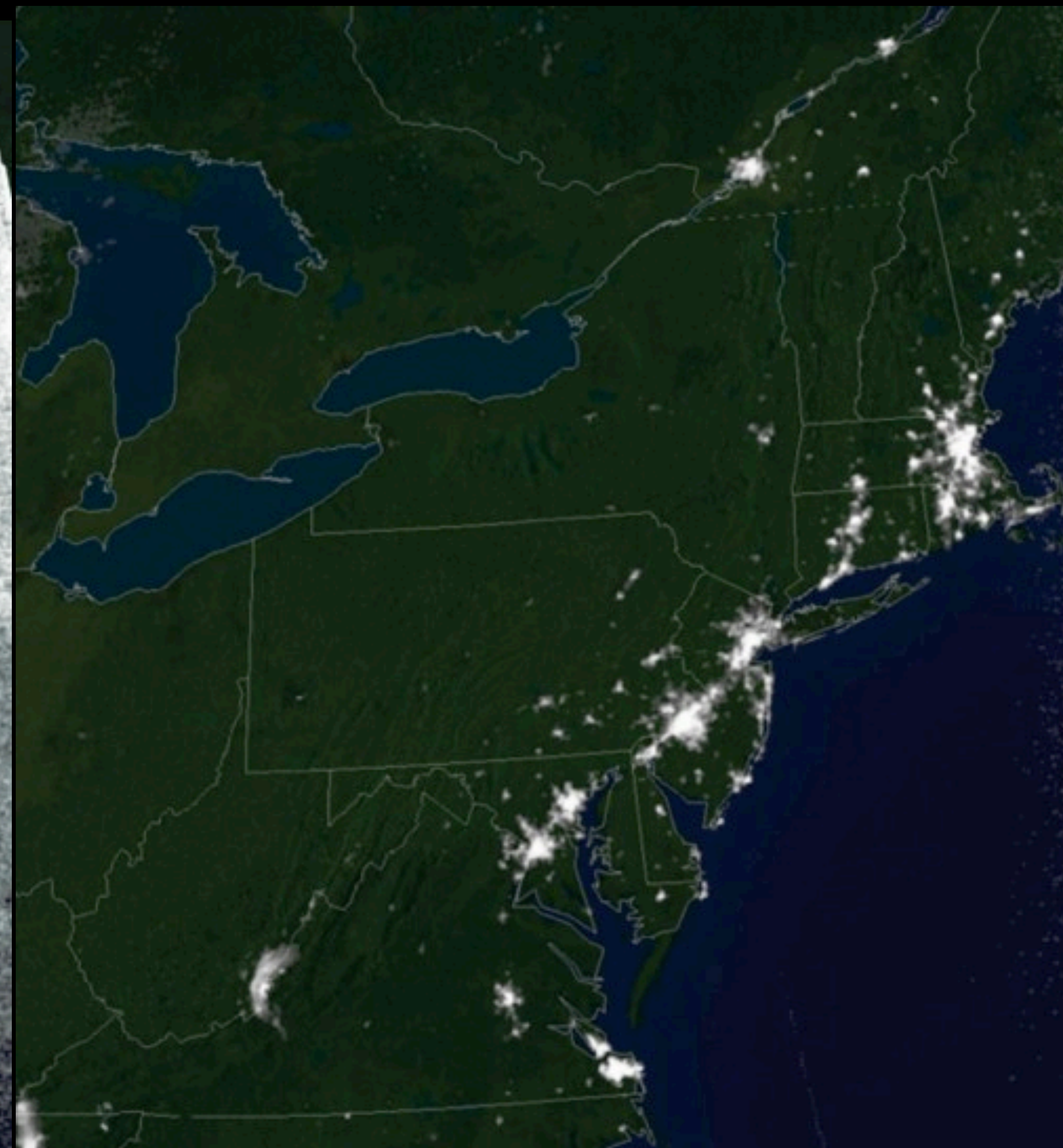


Images by NOAA/DMSP.

storage is the key enabler

- smart grid requires rapid response capability
  - ☞ colossal electric cache
- transmission line congestion
  - ☞ colossal electric cache
- load leveling
  - ☞ colossal electric cache
- load following
  - ☞ colossal electric cache

accelerating the rate of discovery

- there is plenty of room at the top:
  we are not up against any natural laws of nature yet
  ☞ time to start thinking beyond lithium

- the field is woefully underfunded by government:
  energy research in total \$1.4B (2006) < ⅙ 1979 figure
  c.f. medical research rose by 4× to \$29B

- the private sector research spending is even bleaker:
  US energy industry < 0.25% revenues
  c.f. pharmaceuticals 18%
  semiconductors 16%
  automotive 3%

accelerating the rate of discovery

- more money ☞ more people
  ☞ sustained effort ☞ the brightest minds
- new approaches: computational materials science
  ☞ Volta partners with Schrödinger, i.e., bring quantum mechanics to battery engineering
  ☞ high-throughput computing screens candidate materials before lab testing begins
- confine chemistry to earth-abundant elements readily available, i.e., not to those potentially subject to cartel pricing

how to think about inventing in this space

- look at the economy of scale of modern electrometallurgy: aluminium smelter
- bauxite, cryolite, petroleum coke, capital cost of $5000/annual tonne, 14 kWh/kg
  - ☞ virgin metal for less than $1.00/kg
- how is this possible?
  - ☞ we don't make aluminium in little beakers
- to make metal by the tonne we have giant cells, literally large halls in which liquid metal pools on a single cathode spread over the entire floor

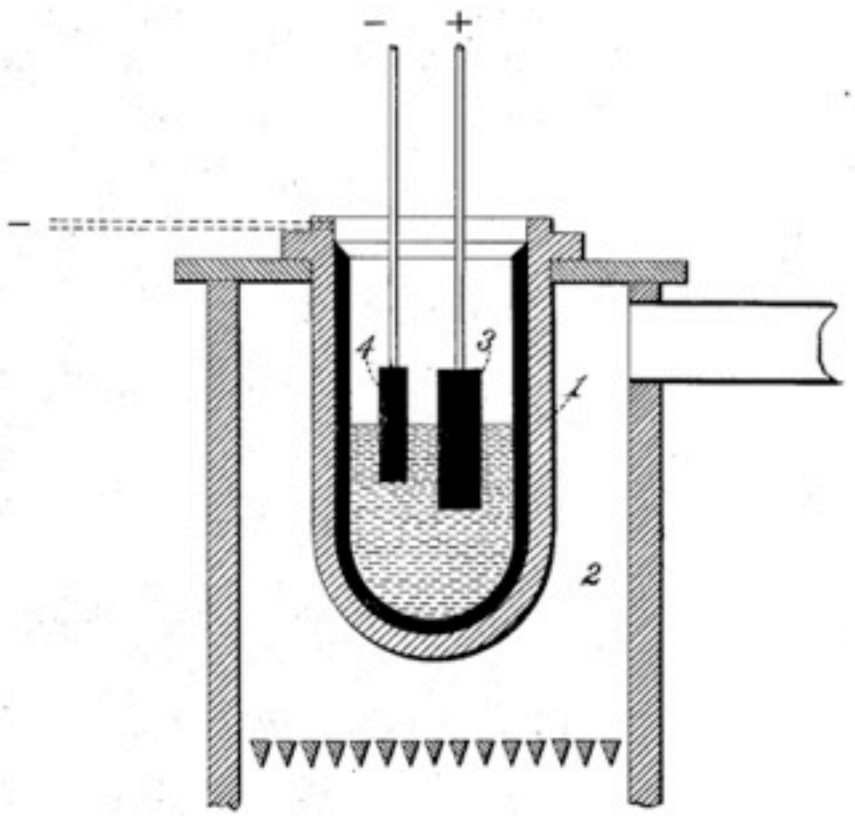
a modern aluminium smelter

(No Model.)

C. M. HALL.

PROCESS OF ELECTROLYZING CRUDE SALTS OF ALUMINIUM.

No. 400,666. Patented Apr. 2, 1889.



WITNESSES:

E. Newell.
F. E. Gaither.

INVENTOR,

Charles M. Hall
by Darwin S. Wolcott
Att'y.

UNITED STATES PATENT OFFICE.

CHARLES M. HALL, OF OBERLIN, OHIO.

PROCESS OF ELECTROLYZING CRUDE SALTS OF ALUMINIUM.

SPECIFICATION forming part of Letters Patent No. 400,666, dated April 2, 1889.

Application filed August 17, 1888. Serial No. 282,955. (No specimens.)

To all whom it may concern:

Be it known that I, CHARLES M. HALL, a citizen of the United States, residing at Oberlin, in the county of Lorain and State of Ohio, have invented or discovered certain new and useful Improvements in the Manufacture of Aluminium by Electrolysis of its Fused Salts, of which improvements the following is a specification.

In applications filed July 9, 1886, and February 2, 1887, and serially numbered 207,601 and 226,206, respectively, I have described and claimed processes for the reduction of aluminium by dissolving alumina in a bath formed of a fused fluoride salt of aluminium and then separating the aluminium by an electric current. In the process described in application, Serial No. 207,601, I employed a bath formed of the fluorides of sodium and aluminium, (represented by the

compound, which occurs sooner in the bath composed of the fluorides of sodium and aluminium than in that composed of the fluorides of potassium and aluminium, necessitates a comparatively frequent renewal of the bath.

The object of the invention described herein is to provide a bath wherein the objections heretofore mentioned do not obtain, and which can be used continuously without changes or renewal, except to supply loss occurring from evaporation.

In the accompanying drawings forming a part of this specification is shown a construction of apparatus applicable for carrying out my improved process.

In the practice of the present invention I form an electrolyte or bath of the fluorides of calcium, sodium, and aluminium, the fluorides of calcium and sodium being obtained in the form of fluor-spar and cryolite, respect-

G 900 19 D / 15

175,711

INDEXÉ

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BLÉTRY FRÈRES
INGÉNIEURS CIVILS
2 Boulevard de Strasbourg 2
PARIS

MÉMOIRE DESCRIPTIF

déposé à l'appui d'une demande d'un

Brevet d'Invention de Quinze Ans

Pour "Procédé électrolytique pour la préparation de l'aluminium."

Par Monsieur Paul Louis Toussaint Héroult,

Représenté par BLÉTRY FRÈRES, Ingénieurs Civils.

Original.

Tel fig!

En principe, le procédé que je désire Breveter pour la préparation

how to think about inventing in this space:

pose the right question

start with a giant current sink

convert this...

aluminium potline

350,000 A, 4 V

...into this

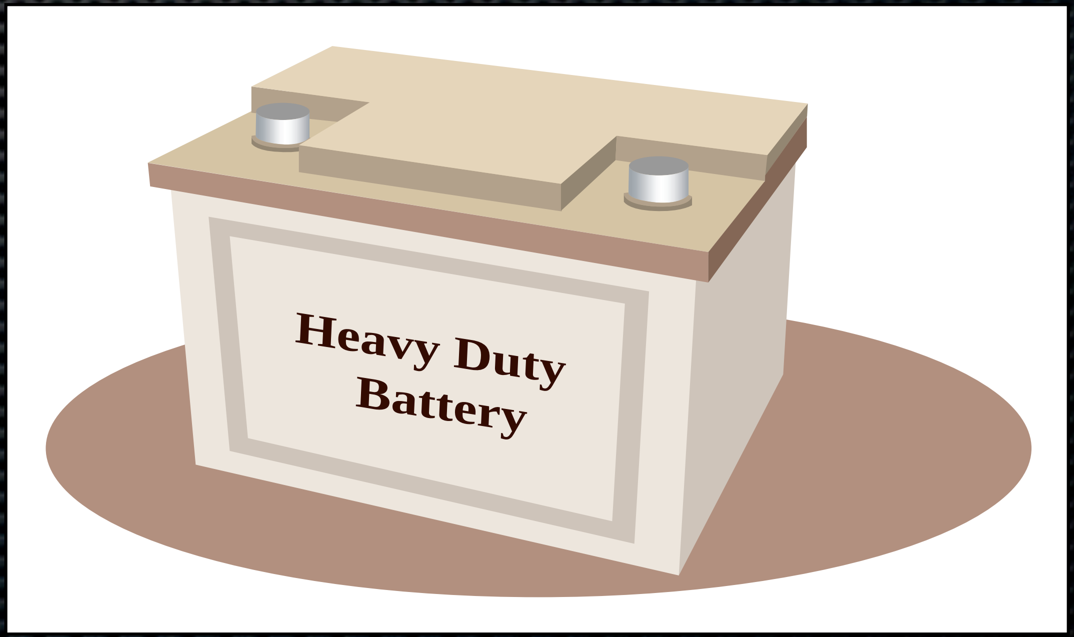


Image by MIT OpenCourseWare. Adapted from Donald Sadoway.

The result of work started 3 years ago under sponsorship by the MIT Deshpande Center and the Chesonis Family Foundation:

☞ reversible ambipolar electrolysis, a.k.a.,

liquid metal battery

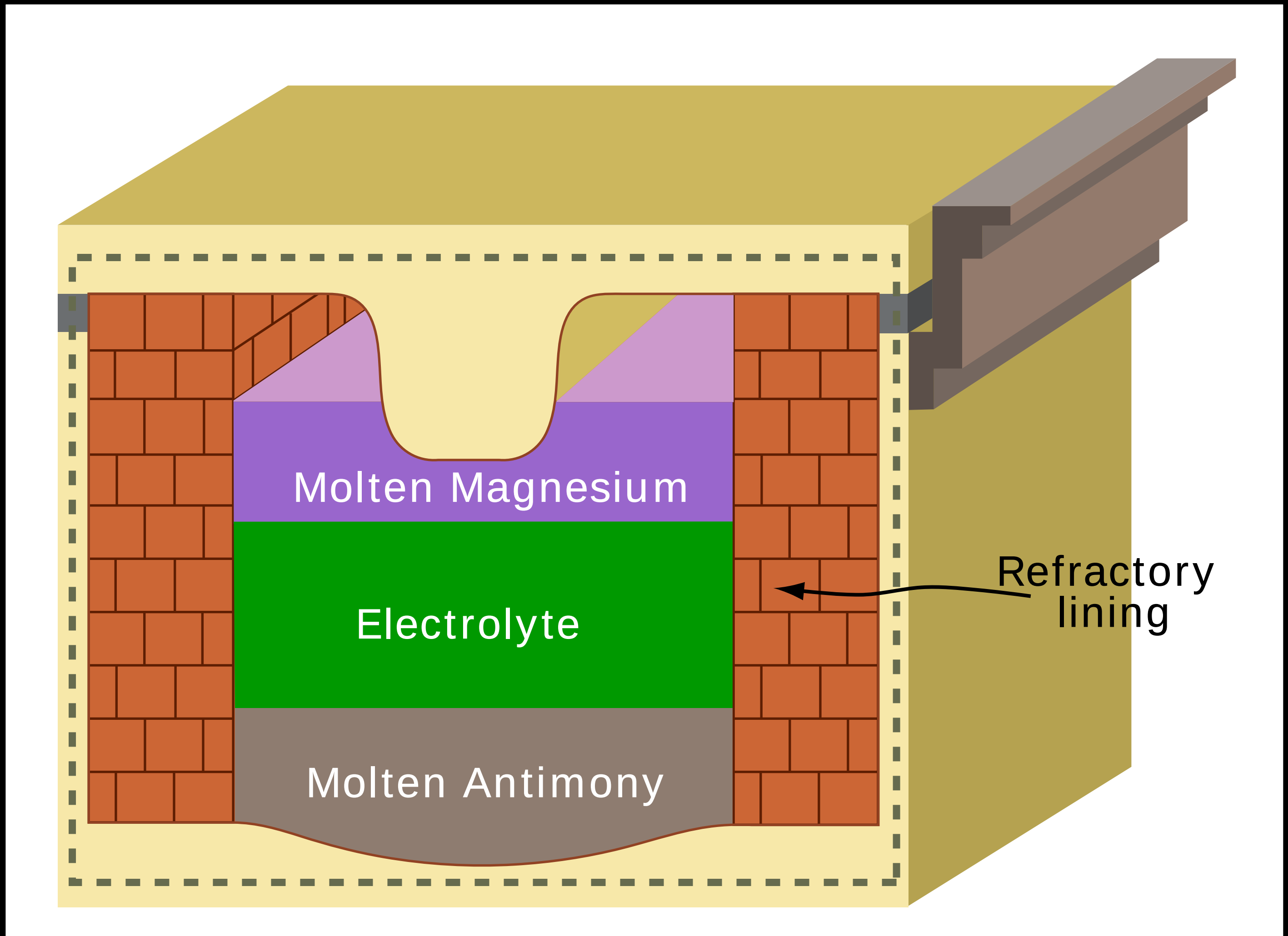
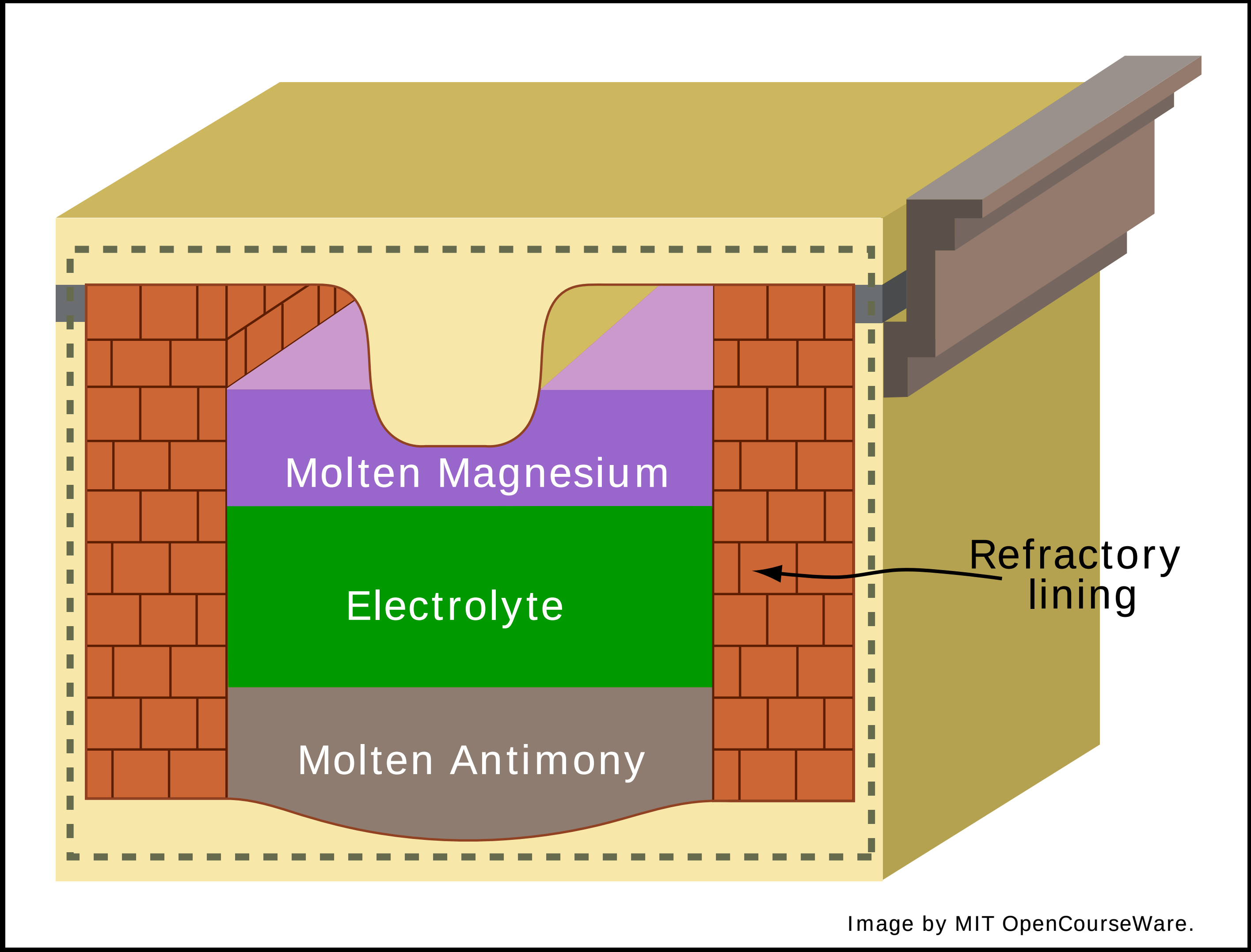


Image by MIT OpenCourseWare.

on discharge

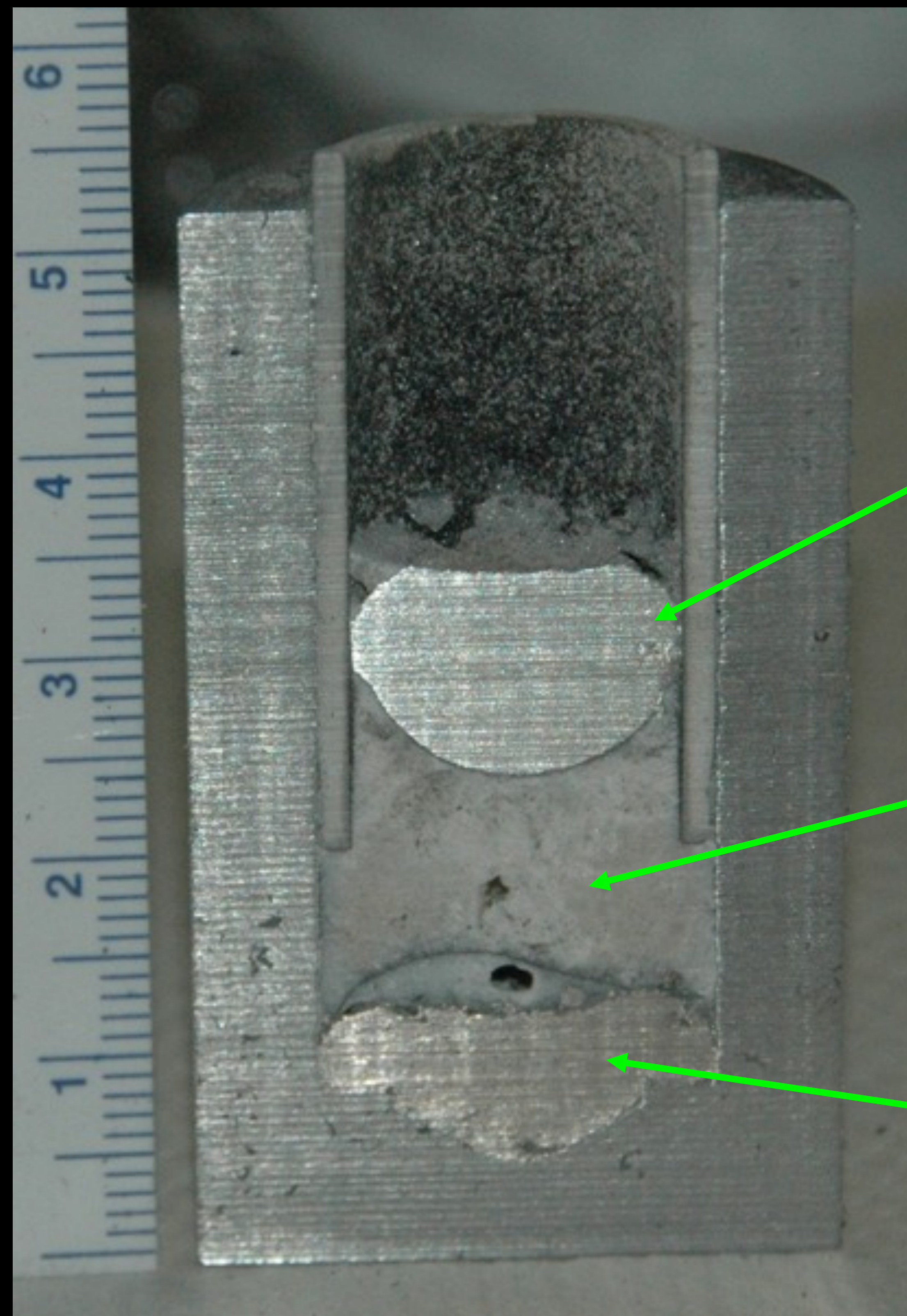
$$Mg_{(liquid)} \Rightarrow Mg^{2+} + 2\,e^-$$

$$Sb_{(liquid)} + 3\,e^- \Rightarrow Sb^{3-}$$



liquid metal battery

cell section after cycling 48 h at 700°C



attributes of all-liquid battery

- ✏ all-liquid construction eliminates reliance on solid-state diffusion
  - ☞ long service life

- ✏ liquid-liquid interfaces are kinetically the fastest in all of electrochemistry
  - ☞ low activation overvoltage

attributes of all-liquid battery

- ✏ all-liquid construction eliminates any reliance on solid-state diffusion
  - ☞ long service life
- ✏ liquid-liquid interfaces are kinetically the fastest in all of electrochemistry
  - ☞ low activation overvoltage
- ✏ all-liquid configuration is self-assembling
  - ☞ expected to be scalable at low cost

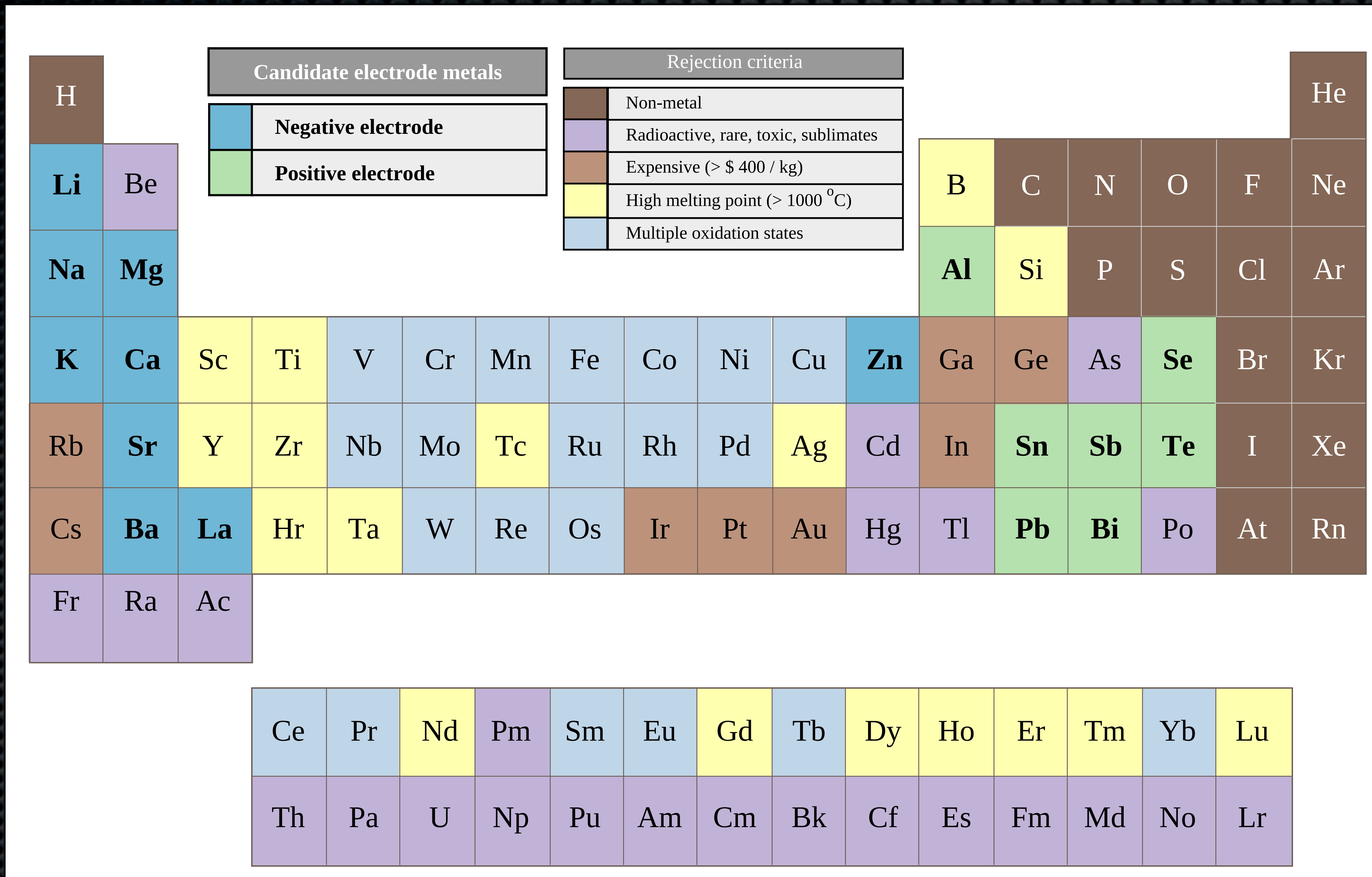
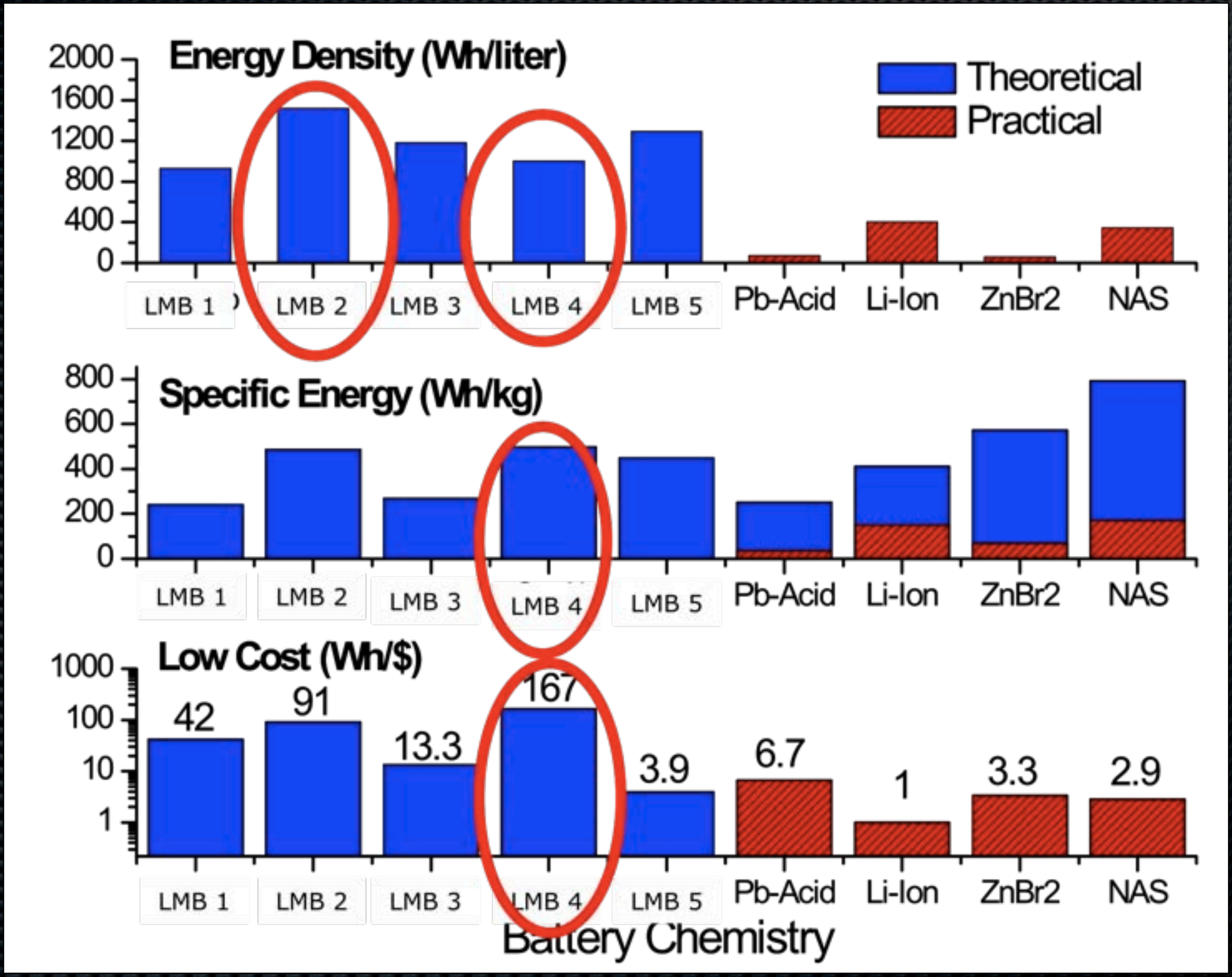
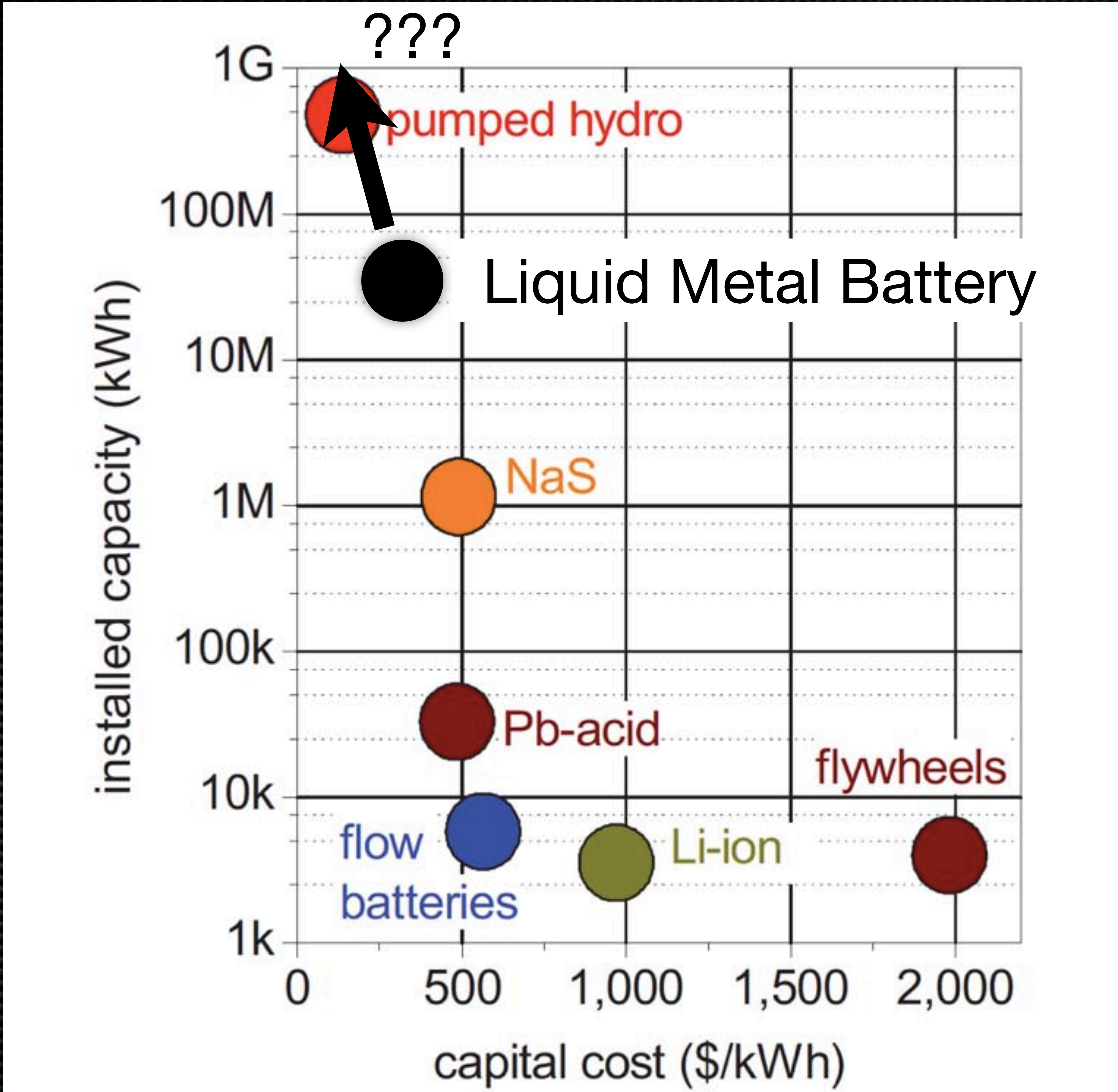


Image by MIT OpenCourseWare.

cost / performance

better than lithium-ion, cheaper than lead acid

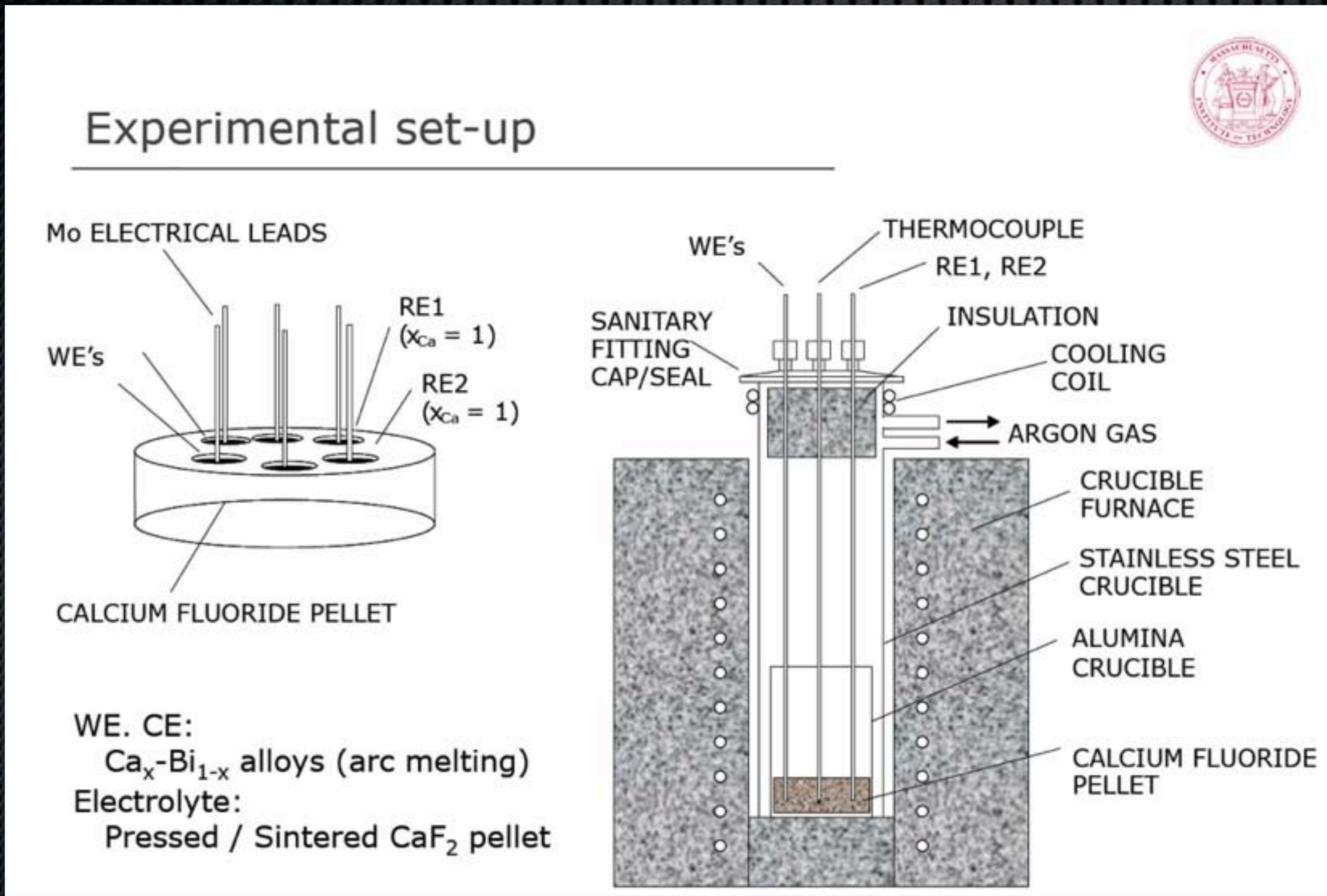



???
1G
100M
10M
1M
100k
10k
1k
installed capacity (kWh)
pumped hydro
Liquid Metal Battery
NaS
Pb-acid
flywheels
flow
batteries
Li-ion
0
500
1,000
1,500
2,000
capital cost ($/kWh)

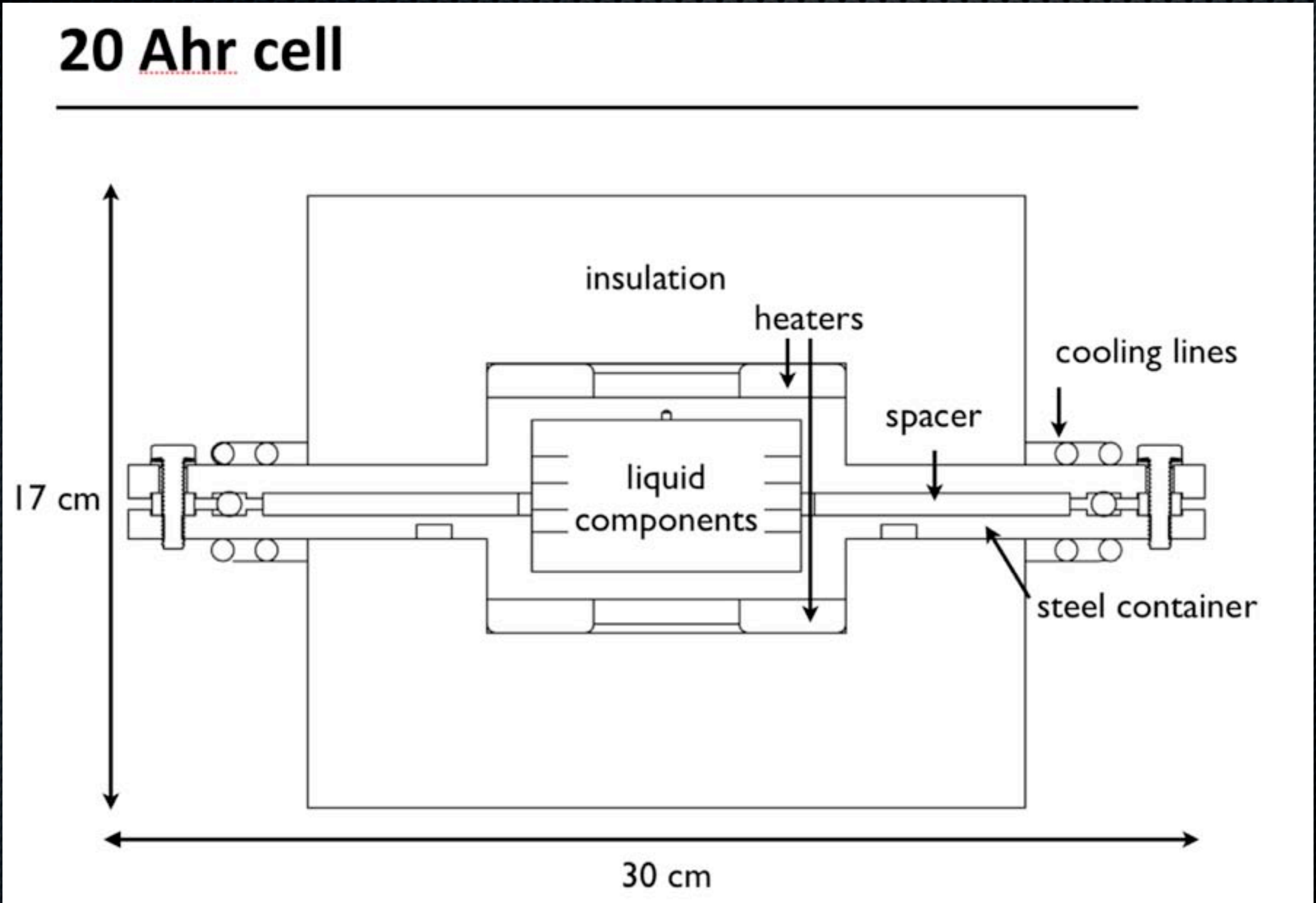
opportunities for basic science

- ✏ database is spotty: alloys lacking widespread commercial use
- ✏ theory not ready to predict properties of liquid metals and alloys
  - ☞ properties must be measured
- ✏ emf data in molten salts require verification with candidate metal couples
  - ☞ *"доверяй, но проверяй"*
    ...*trust, but verify*...

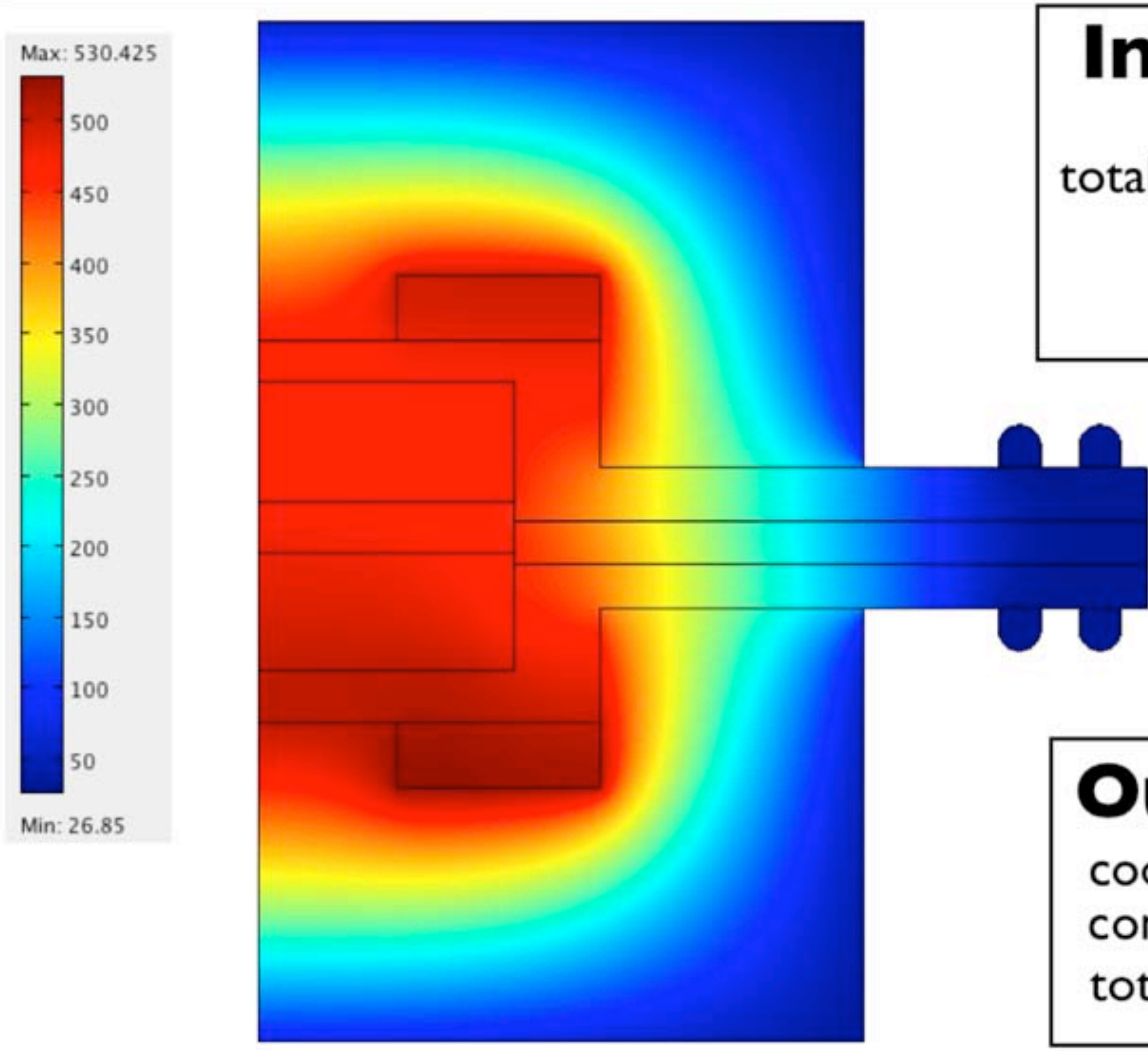
activity measurements of Ca - Bi alloys



scaling laws: towards self-heating cell



Results: Addition of insulation



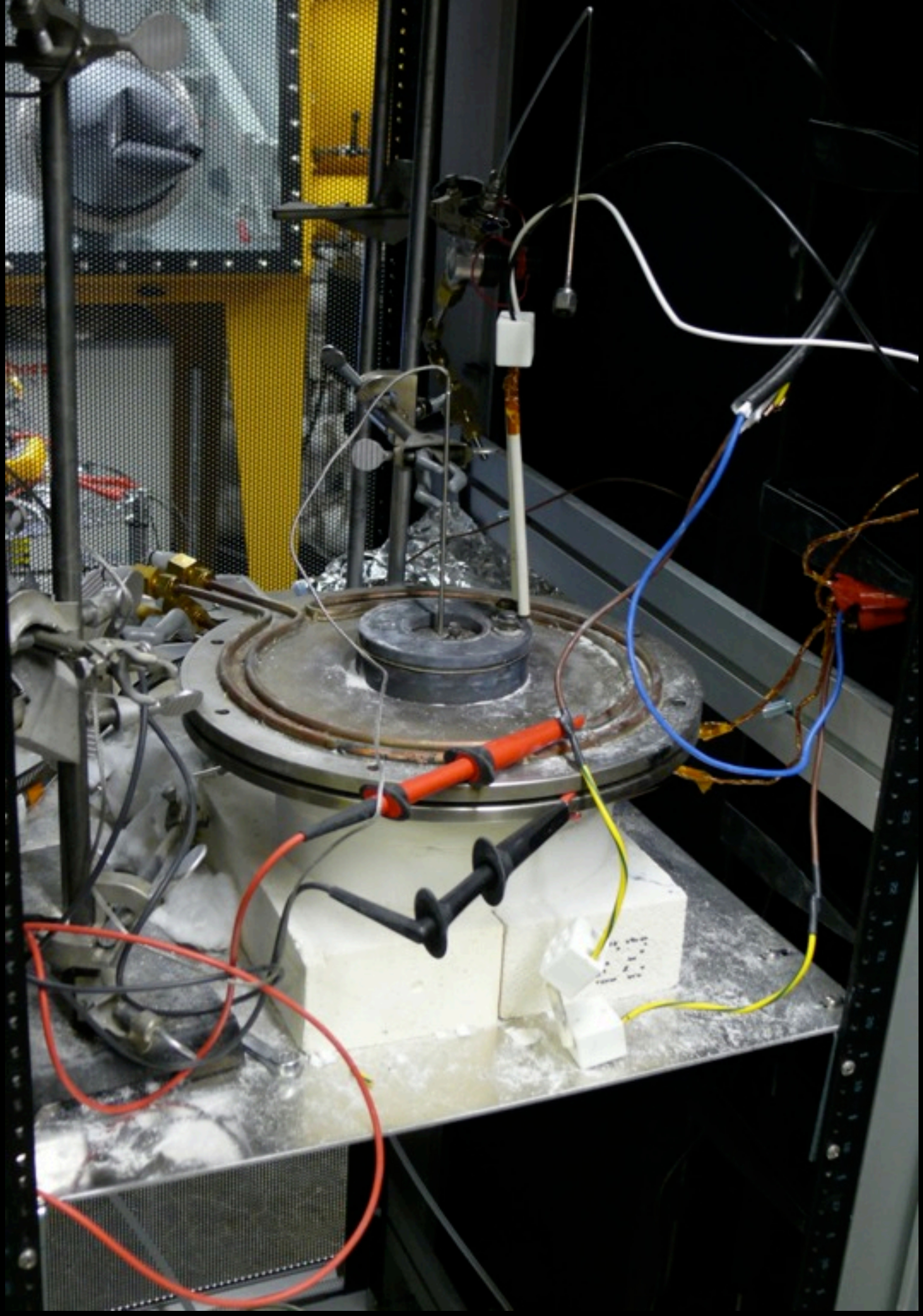
Input

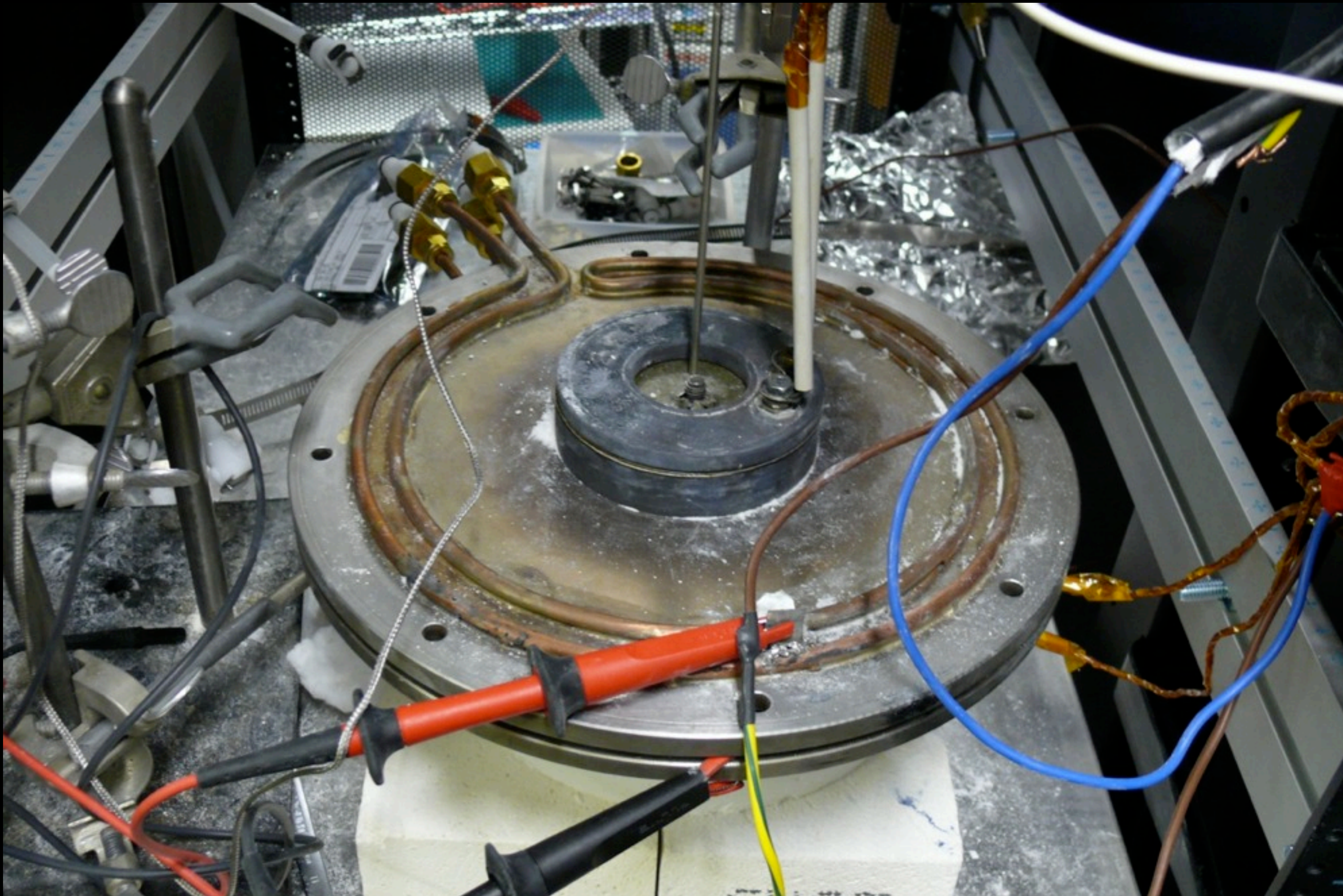
total = 934.6 W

Output

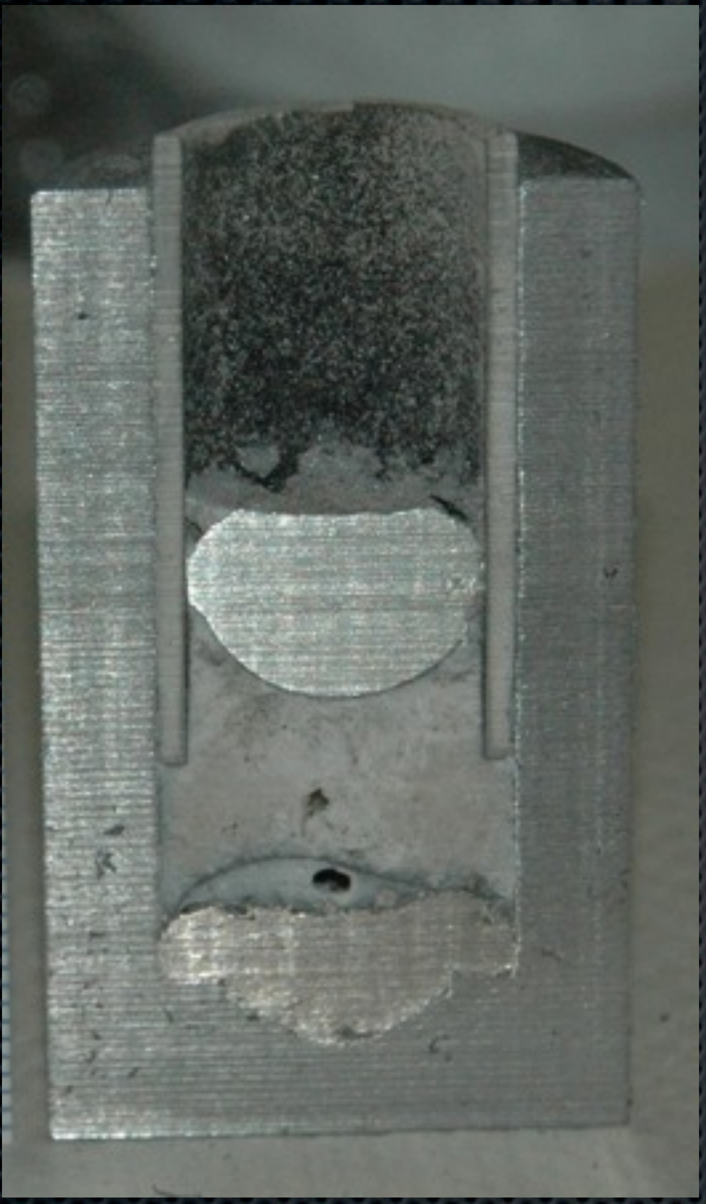
cooling lines = 719 W
convective = 146.5 W
total = 865.5 W

$$Q_{source} = 7.2 \left[\mathrm{W/cm^3} \right]$$





next steps



- cycle performance data
- analysis of failure modes
- self heating cell
- cell optimization
- cost model

tethered in the wireless age ☞ portable power

enabling radical innovation:

biomedical devices **transportation**

Images of an implantable defibrillator and an electric car have been removed due to copyright restrictions.

motivation

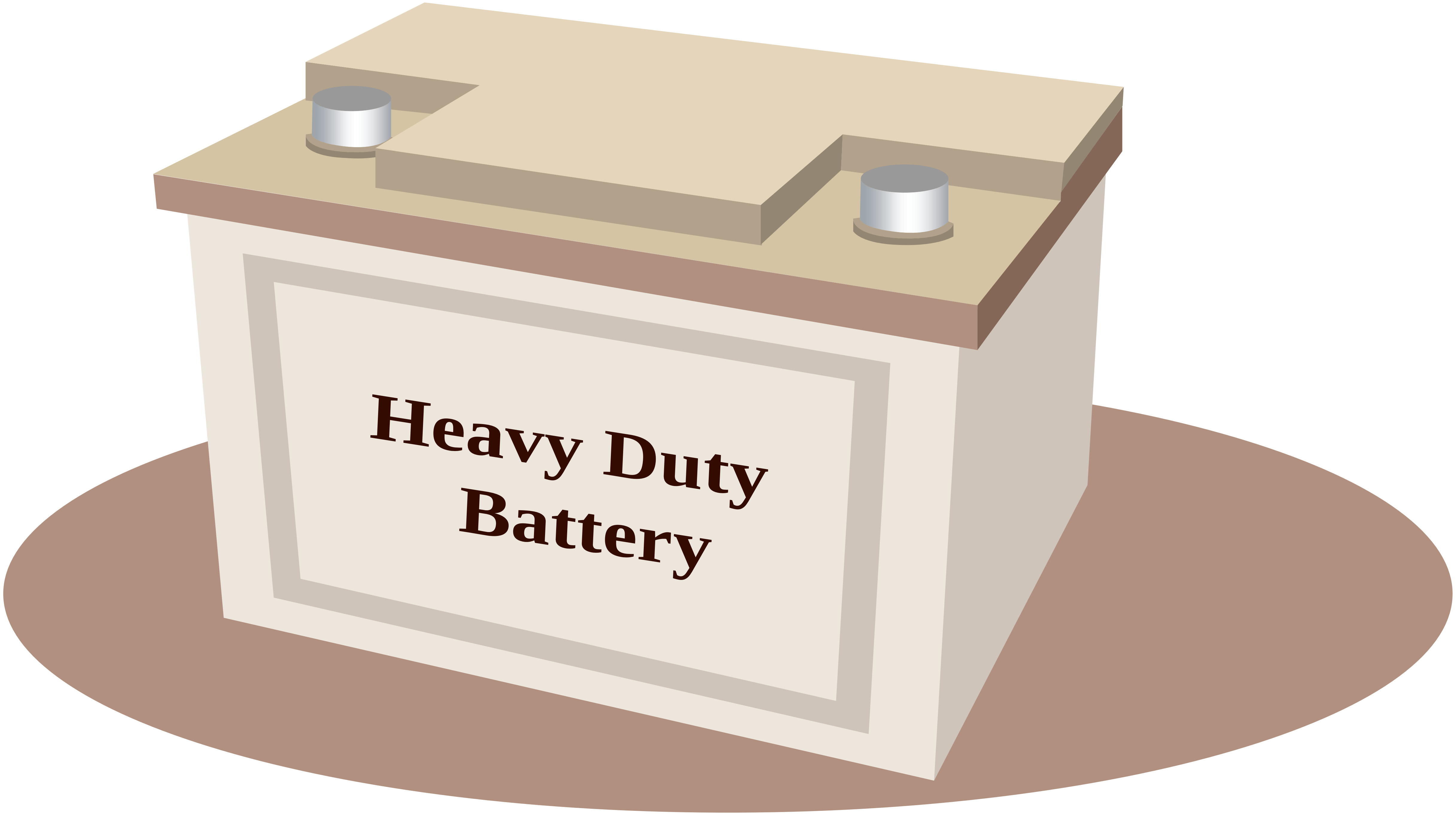
Imagine driving this:

motivation (continued)

without the need for this:

Image by Mirjana Chamberlain-Vucic on Flickr.

relevant enabling technology



The message

There's plenty of room at the top: we are far from hitting the ceiling set by nature.

The road to success is paved with advanced materials.

A bit of automotive history

1888 Frederick Kimball, Boston:

first electric passenger car

why now the renewed interest?

answer: **CARB**

to improve urban air quality

CARB set new standards, including...

CARB Implementation Dates for ZEVs

1998 2% new car sales†

2001 5% new car sales†

2003 10% new car sales†

1991 NESCAUM formed

1992 MA adopts CA standards

✏ in the minds of many policy makers, ZEV implies EV

Problems with EV propulsion

1. **range**: function of energy density of the **battery**.
   Compare gasoline @ 13,000 (theo.) / 2600 Wh/kg
   with the lead-acid **battery** @ 175 (theo.) / 35 Wh/kg

2. **time to refuel**: charge 40 kWh in 5 minutes?
   ➩ 220 V × 2200 A!!!
   When you pump gasoline @ 20 ℓ/min,
   your energy transfer rate is about 10 MW!
   (Hint: energy density of gasoline is 10 kWhth/ℓ.)

Problems with EV propulsion

3. **cost**:

(1) light but safe means higher materials costs,

e.g., less steel, more aluminum;

and higher processing costs,

e.g., fewer castings, more forgings...

(2) to reduce load on the **battery** requires

high efficiency appliances ➫ costly

(3) low cycle life — **batteries** priced @ $4,000 to $8,000

lasting about 2 years

Battery basics

what is a battery?

a device for exploiting **chemical** energy

to perform **electrical** work

i.e., an **electrochemical** power source

the design paradigm?

choose a chemical reaction with

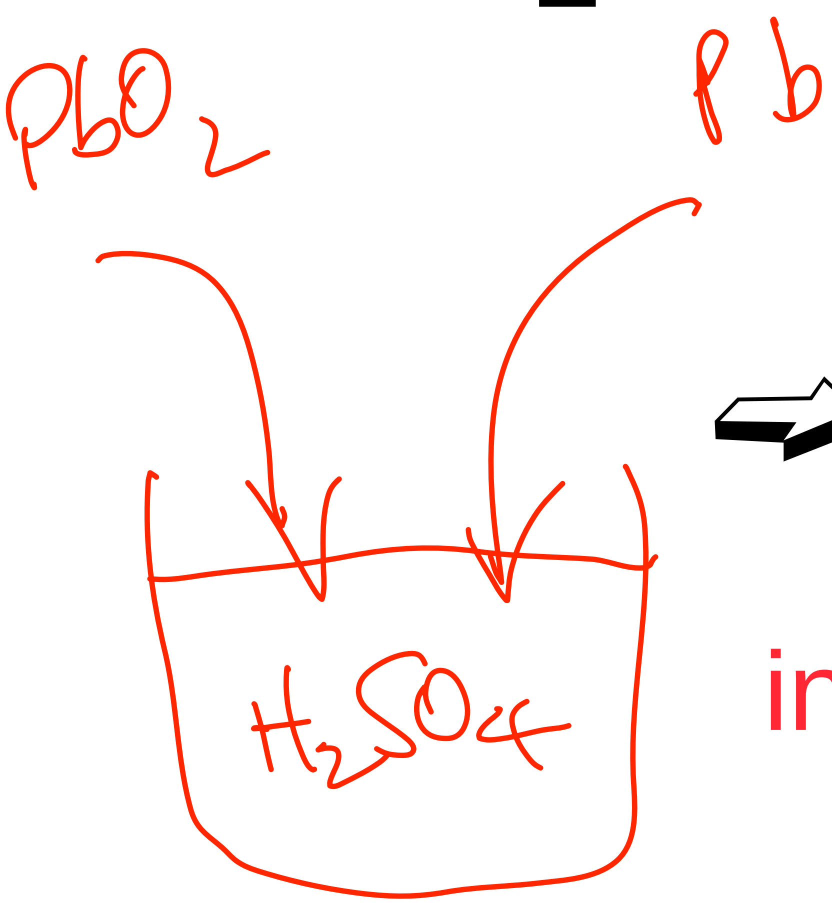
a **large driving force** (ΔG) and **fast kinetics**

to cause the reaction to occur by steps

involving **electron transfer**

A simple chemical reaction

$$PbO_2 + Pb + H_2SO_{4\,(aq)}$$



$$\Rightarrow 2\,H_2O + PbSO_4$$

intimate mixing of all reactants

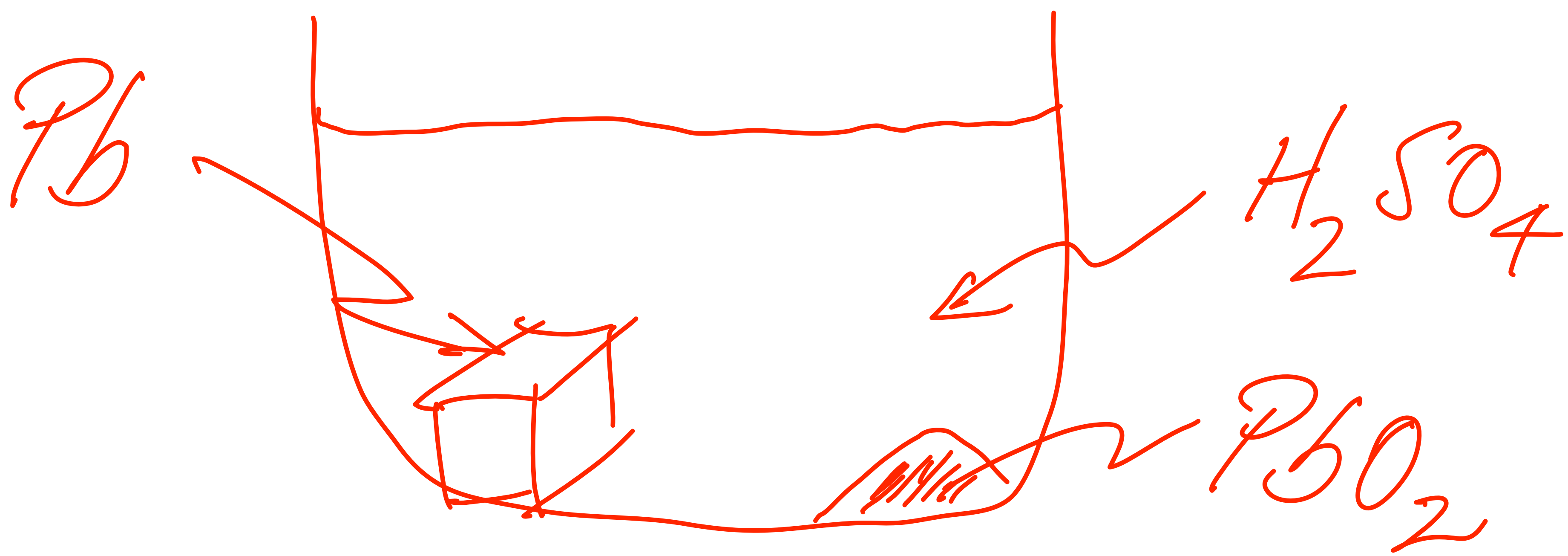
Same reaction, but not so simple

$$Pb + SO_4^{2-}{}_{(aq)} \Rightarrow PbSO_4 + 2e^-$$

insoluble in water

$$PbO_2 + 4H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2e^- \Rightarrow 2H_2O + PbSO_4$$

reactants physically separated

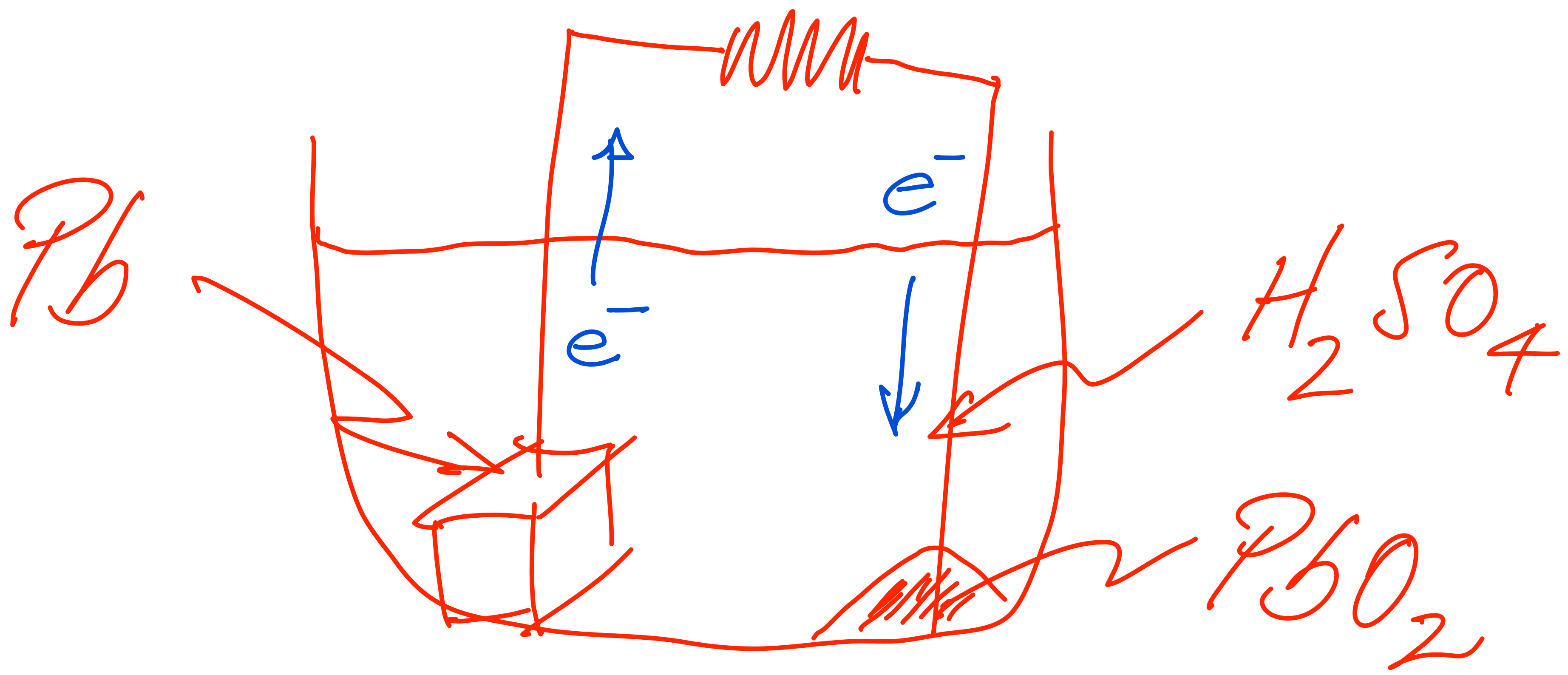


Electrons in motion

$Pb + SO_4{}^{2-}{}_{(aq)} \Rightarrow PbSO_4 + 2e^-$

$PbO_2 + 4H^+{}_{(aq)} + SO_4{}^{2-}{}_{(aq)} + 2e^-$

$\Rightarrow 2H_2O + PbSO_4$

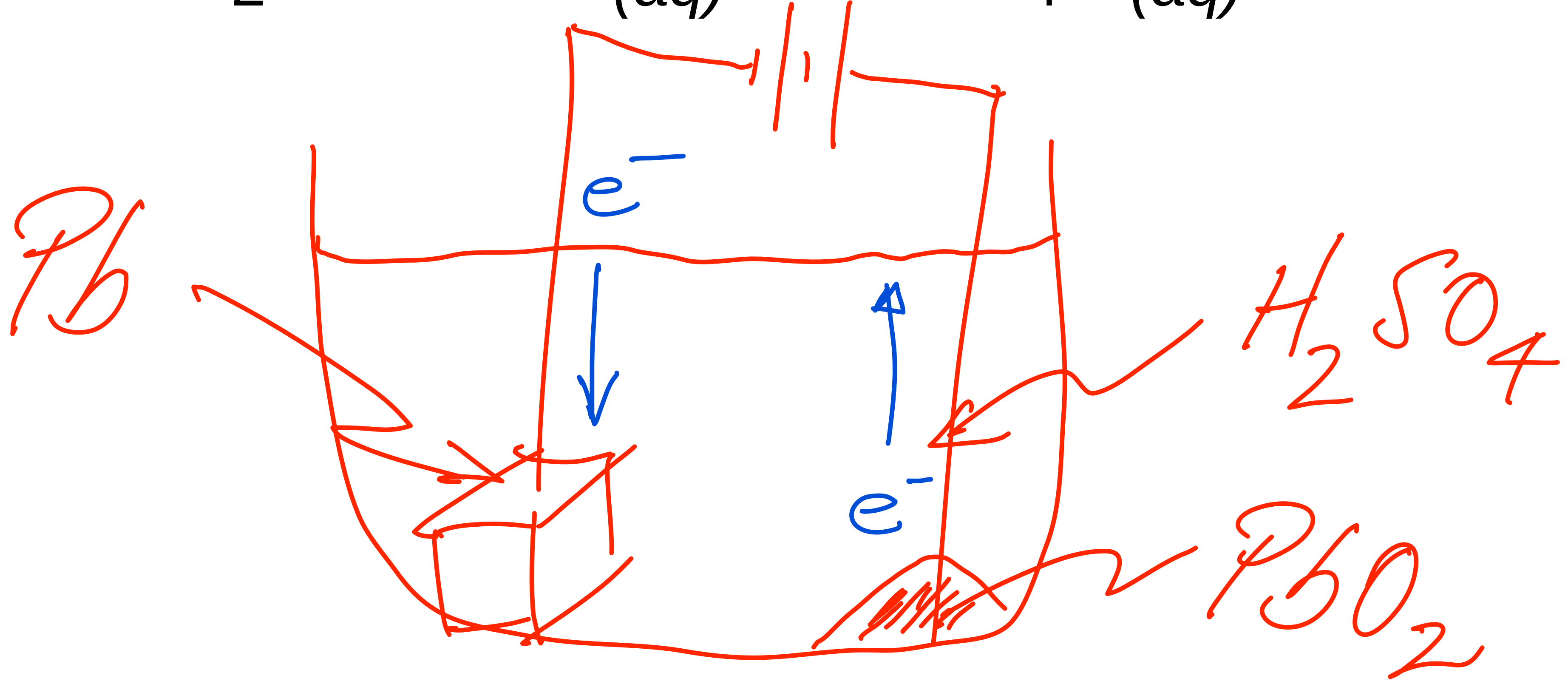


Electrons in motion

$PbSO_4 + 2\ e^- \Rightarrow Pb + SO_4^{2-}{}_{(aq)}$

$2\ H_2O + PbSO_4 \Rightarrow$

$PbO_2 + 4\ H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\ e^-$



The lead-acid battery

anode:

$$Pb + SO_4^{2-}{}_{(aq)} \Rightarrow PbSO_4 + 2\,e^-$$

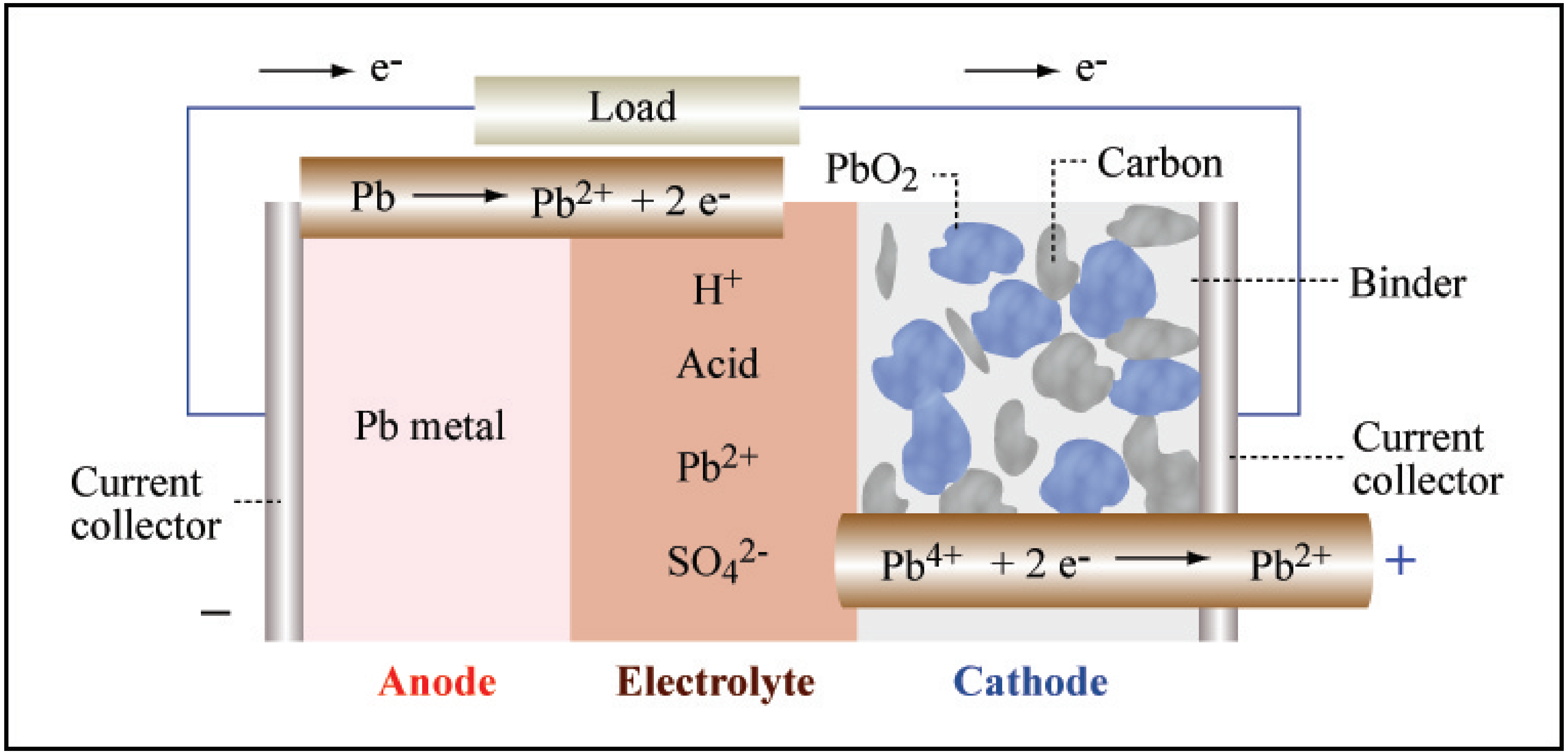
⊖ $$Pb^0 \Rightarrow Pb^{2+} + 2e^- \quad (oxid^n)$$

cathode:

$$PbO_2 + 4\,H^+{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2\,e^- \Rightarrow 2\,H_2O + PbSO_4$$

⊕ $$Pb^{4+} + 2\,e^- \Rightarrow Pb^{2+} \quad (red^n)$$

Lead-acid battery on discharge



The nickel metal-hydride battery

cathode:

$$NiOOH_{(aq)} + 2\,H_2O + e^- \Rightarrow Ni(OH)_{2(aq)} + OH^-_{(aq)}$$

anode:

$$MH + OH^-_{(aq)} \Rightarrow M + H_2O + e^-$$

electrolyte: 30% $KOH_{(aq)}$ (alkaline)

The nickel metal-hydride battery

cathode:

$$NiOOH_{(aq)} + 2\,H_2O + e^- \Rightarrow Ni(OH)_{2(aq)} + OH^-_{(aq)}$$

$$Ni^{3+} + e^- \Rightarrow Ni^{2+}$$

anode:

$$MH + OH^-_{(aq)} \Rightarrow M + H_2O + e^-$$

$$H \Rightarrow H^+ + e^-$$

The lithium ion battery

anode (-)

$$Li_{in\ carbon} \rightarrow Li^+ + e^-$$

cathode (+)

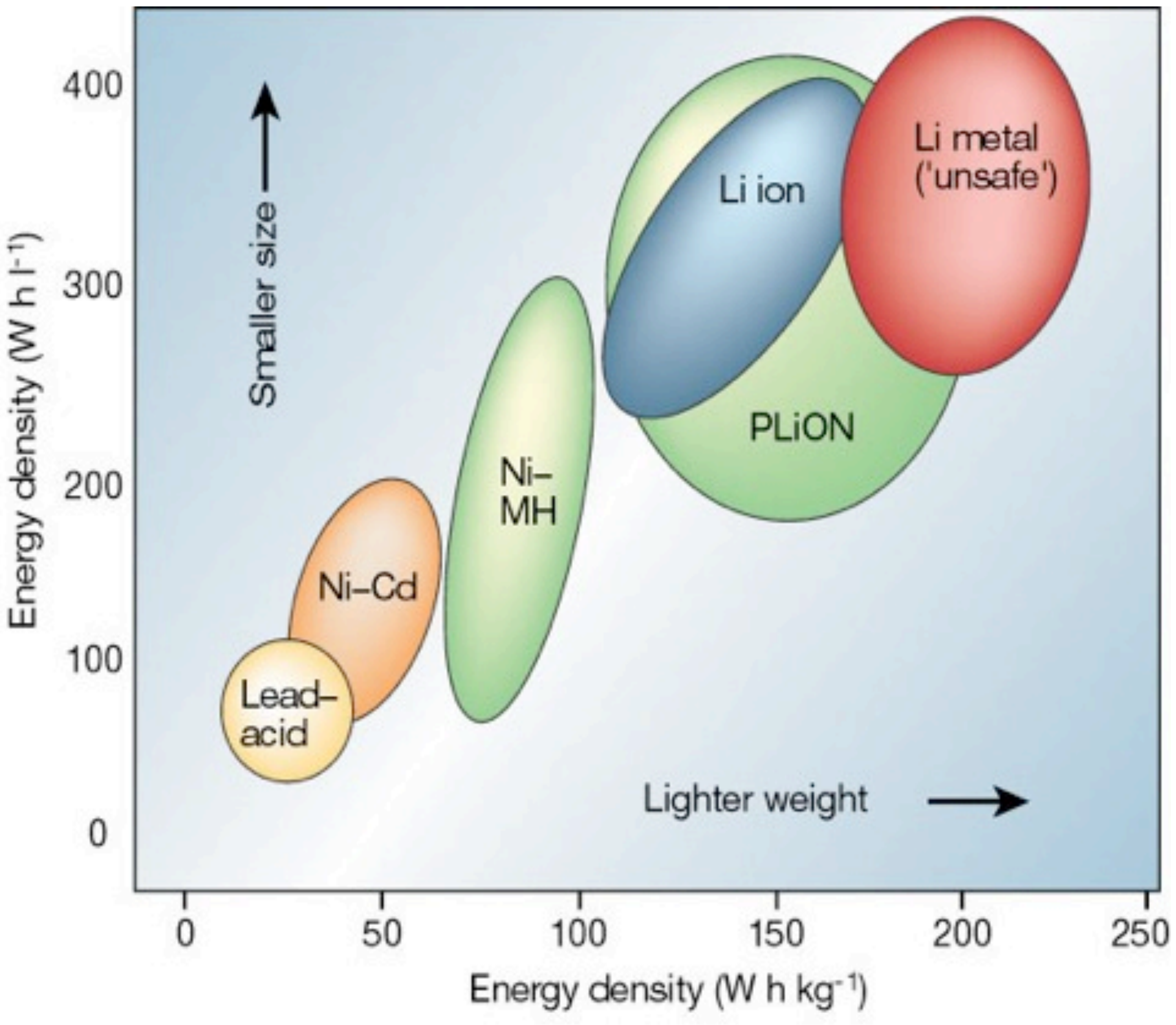
$$Li^+ + e^- + Li_xCoO_2 \rightarrow Li_{1+x}CoO_2$$

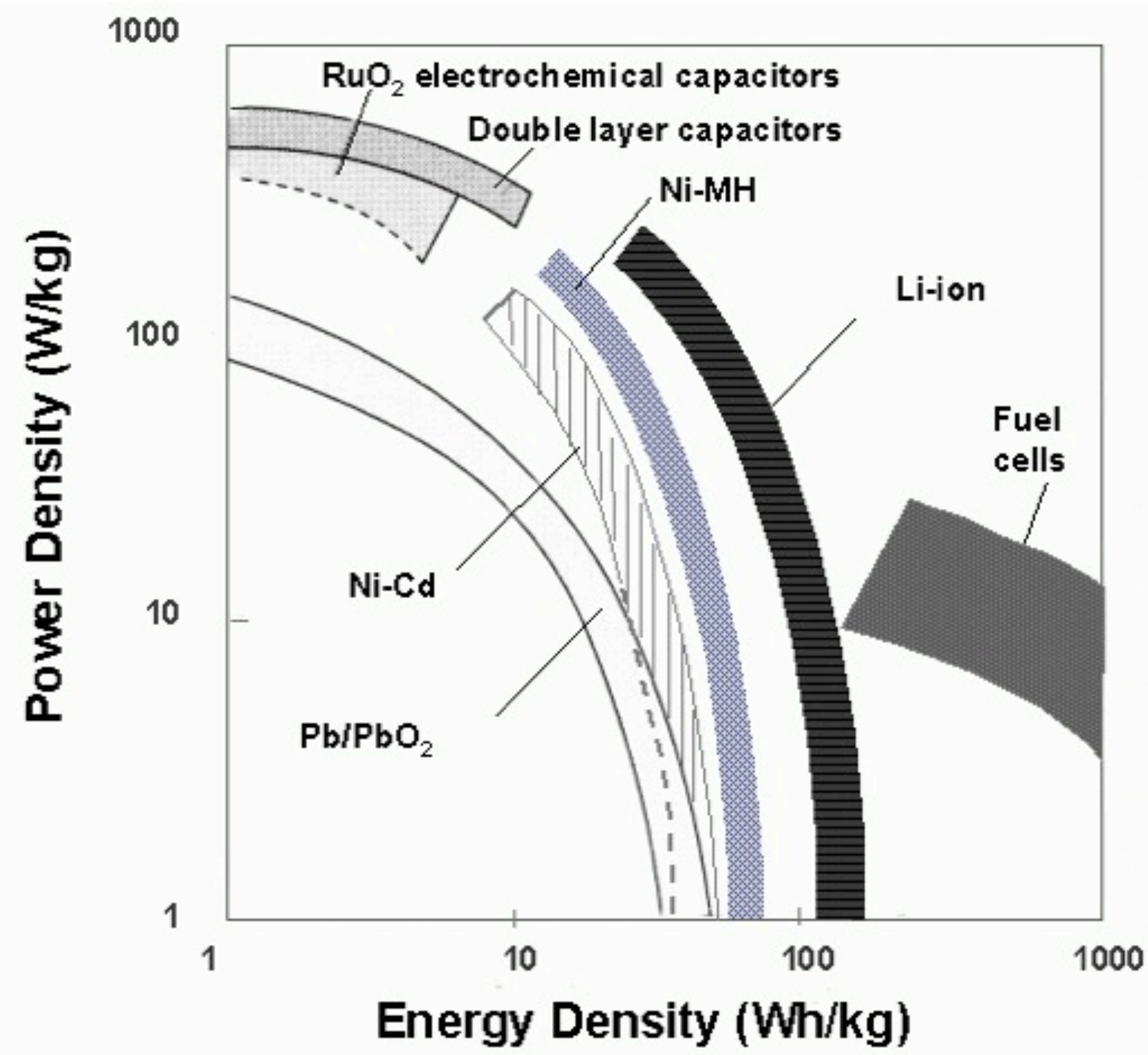
$$Li^+ + e^- + Co^{4+} \rightarrow Li^+ + Co^{3+}$$

electrolyte: 1 M $LiPF_6$ in

1:1 ethylene carbonate – propylene carbonate

Battery Performance Metrics





[1] J.-M. Tarascon and M. Armand, *Nature* 414, 359 - 367 (2001)

Ragone plot

Warhol, "Marilyn Diptych" (1962) Tate Gallery

Please see Andy Warhol, "Marilyn Diptych," 1962.

Sadoway, “GM EV1 Diptych” (2005) Private Collection

1 Wh/kg storage capacity

☞ 1 mile driving range

USABC Long-term Performance Goals

operating temp.	-40 to 85ºC
specific energy	**200 Wh/kg @ C/3**
energy density	300 Wh/L @ C/3
specific power	400 W/kg
power density	600 W/L
cycle life	1000 cycles @ 80% DOD
service life	10 years
ultimate price	~ $100/kWh for 40 kWh packs

new thresholds in performance

Today $LiCoO_2$, $LiNiO_2$, $LiFe(PO_4)$ all use only one electron per metal (e.g. Co^{4+}/Co^{3+})

47.88 22	50.9415 23	51.9961 24	54.93805 25	55.847 26	58.93320 27	58.6934 28
Ti	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**
Titanium	Vanadium	Chromium	Manganese	Iron	Cobalt	Nickel

⇒ theoretical capacity limited **<< 300 mAh/g**

The Future compounds where metal cycles over multiple redox steps

breaking the one-electron barrier

In the presence of Mn,

$$Li^{+} + 2e^{-} + Li_{x}NiO_{2} \rightarrow Li_{1+x}NiO_{2}$$

$$Li^{+} + 2e^{-} + Ni^{4+} \rightarrow Li^{+} + Ni^{2+}$$

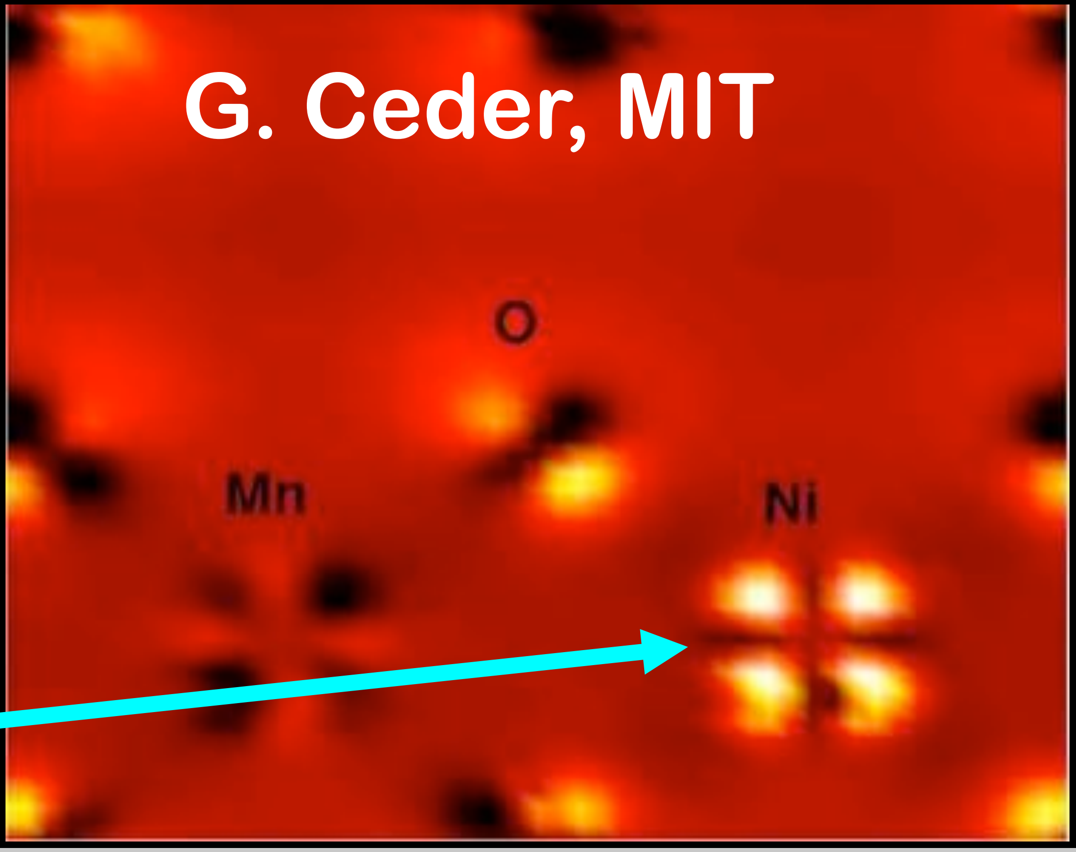
☞ theoretical capacity

≈ **600 mAh/g !**

≈ **540 Wh/kg !**

c.f. 150 Wh/kg in Li ion

two-electron change around Ni upon Li intercalation



breaking the one-electron barrier

Your wildest dream

$$Li^{+} + 3e^{-} + Li_{x}CrO_{3} \rightarrow Li_{1+x}CrO_{3}$$

$$Li^{+} + 3e^{-} + Cr^{6+} \rightarrow Li^{+} + Cr^{3+}$$

☞ theoretical capacity

≈ **1000 mAh/g !**

≈ **700 Wh/kg !** ☞ **700 mi**

breaking the one-electron barrier

Your wildest dream

$Li^+ + 3e^- + Li_xMnO_4 \rightarrow Li_{1+x}MnO_4$

$Li^+ + 3e^- + Mn^{7+} \rightarrow Li^+ + Mn^{4+}$

☞ theoretical capacity

≈ **1000 mAh/g !**

≈ **700 Wh/kg !** ☞ **700 mi**

supervalent battery: beyond lithium

- energy density ∝ (ion charge)^2
- can Li become a strategic resource?

limitations of lithium

Please see: Abuelsamid, Sam. "Forget Peak Oil. Are We Facing Peak Lithium?" *AutoblogGreen*, January 30, 2007. LaMonica, Martin. "Electric-Car Race Could Strain Lithium Battery Supply." *CNET Green Tech*, October 31, 2008. Kempf, Herve. "Limited Lithium Supplies Could Restrict Electric Car Growth." *EV World*, October 9, 2008. Kahya, Damian. "Bolivia Holds Key to Electric Car Future." *BBC News*, November 9, 2008. "The Trouble with Lithium 2: Under the Microscope." Meridian International Research, May 29, 2008.

supervalent battery: beyond lithium

- energy density ∝ (ion charge)^2
- can Li become a strategic resource?
- with MITEI support we have begun searching for redox couples based upon ions of valence ≥ 3, e.g., Al^{3+}

supervalent battery: beyond lithium

- energy density ∝ (ion charge)^2

- can Li become a strategic resource?
- with MITEI support we have begun searching for redox couples based upon ions of valence ≥ 3, e.g., Al^{3+}
  - ☞ not just intercalation reactions but also metatheticals

The hydrogen fuel cell

anode:

$$H_2 \Rightarrow 2\,H^+ + 2\,e^-$$

cathode:

$$\tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \Rightarrow H_2O$$

electrolyte:

proton (H^+) conductor,

i.e., proton exchange membrane (PEM)

✏ both electrode reactions occur on substrates made of platinum-group metals

The hydrogen fuel cell

anode:

$$H_2 \xrightarrow{Pt} 2\,H^+ + 2\,e^-$$

cathode:

$$\tfrac{1}{2}\,O_2 + 2\,H^+ + 2\,e^- \xrightarrow{Pt} H_2O$$

electrolyte:

proton (H^+) conductor,

i.e., proton exchange membrane (PEM)

✏ both electrode reactions occur on substrates made of platinum-group metals

The hydrogen fuel cell

technical issues:

- ✏ hydrogen on board? pure H_2? $LaNi_5$?
- ✏ generation of hydrogen?

    water electrolysis?

    cracking of natural gas or even gasoline?
- ✏ electrode stability:

    corrosion, contamination, mechanical disturbance,

    conversion efficiency
- ✏ electrolyte stability: breakdown, impurities

potential showstoppers

Cost: noble-metal electrodes !!!

Cost: no infrastructure for H_2 delivery

Effectiveness: will this truly reduce CO_2 emissions?

…in summary

- **One size does not fit all:**

  different applications call for different power sources.

- **Batteries have been around for a long time:**

  user community justifiably frustrated at present state of battery development.

- **Big changes are under way:**

  ingress of materials scientists invigorating the field; computational materials science accelerating the rate of discovery ***if we make the investment.***

…in summary

✏ **Development of human resources:**

electrochemical science & engineering need sustained support to attract and retain the best and brightest

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