Energy Technologies at Scale: Nanoscience by the Ton

2014 International Symposium on Energy Technology and Strategy

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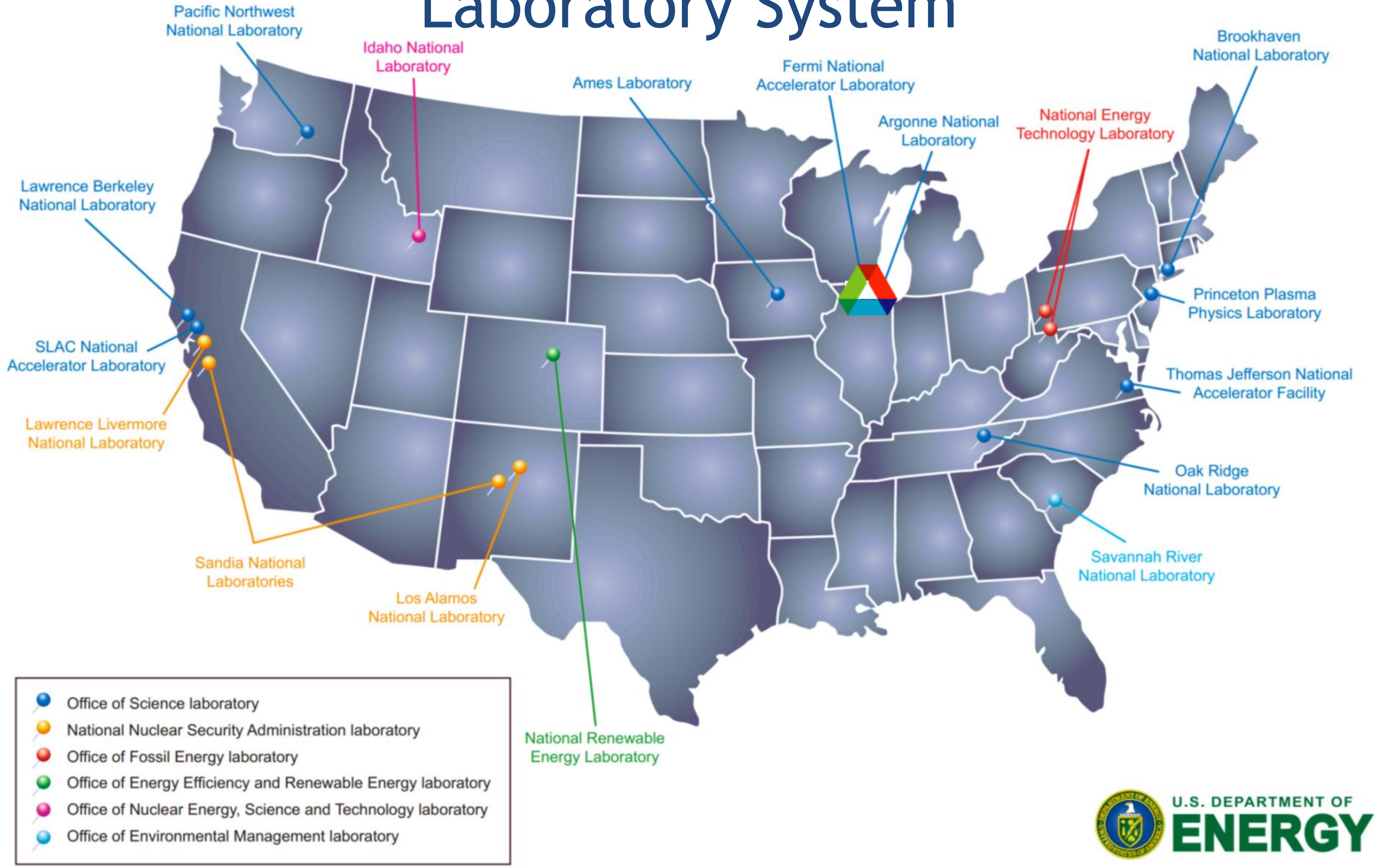
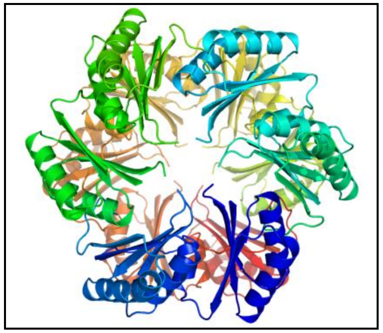
Argonne – a vital part of DOE National Laboratory System



U.S. DEPARTMENT OF ENERGY

Argonne's mission: To provide science-based solutions to pressing global challenges

Energy
Science



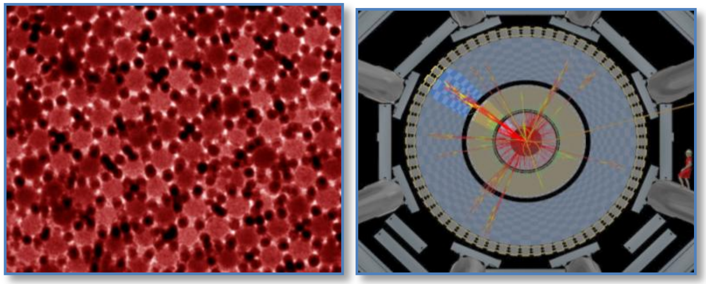
Environmental
Sustainability

Nuclear and
National Security

Use-Inspired Science and Engineering…

…Discovery and Transformational Science and Engineering

Major User Facilities



Science and Technology Programs

Major research areas and key priorities

Hard x-ray sciences

Leadership computing and computational science

Energy storage

Materials for energy

Sustainable transportation

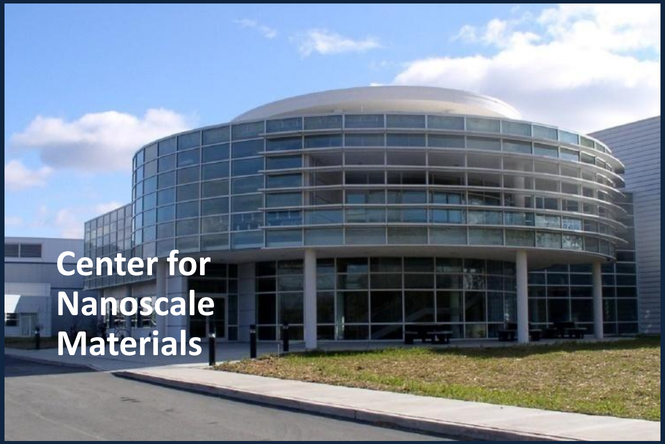
Nuclear energy and security

Biological and environmental systems

Argonne's world-class suite of user facilities

Advanced Photon Source

Argonne Tandem Linear Accelerator System

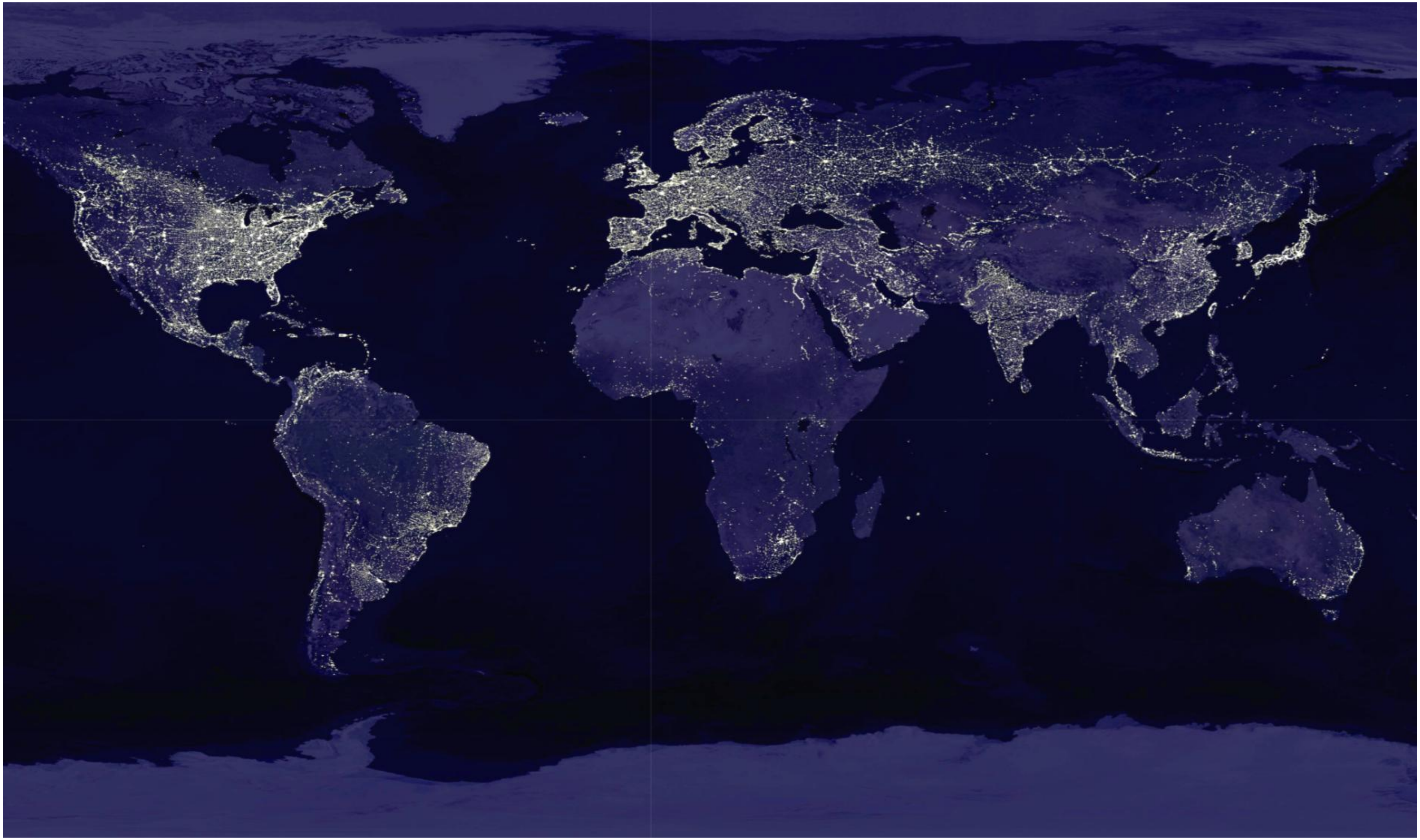


Center for Nanoscale Materials

Argonne Leadership Computing Facility

Electron Microscopy Center

Today, our mission is to solve the world's greatest challenges – with scalable solutions

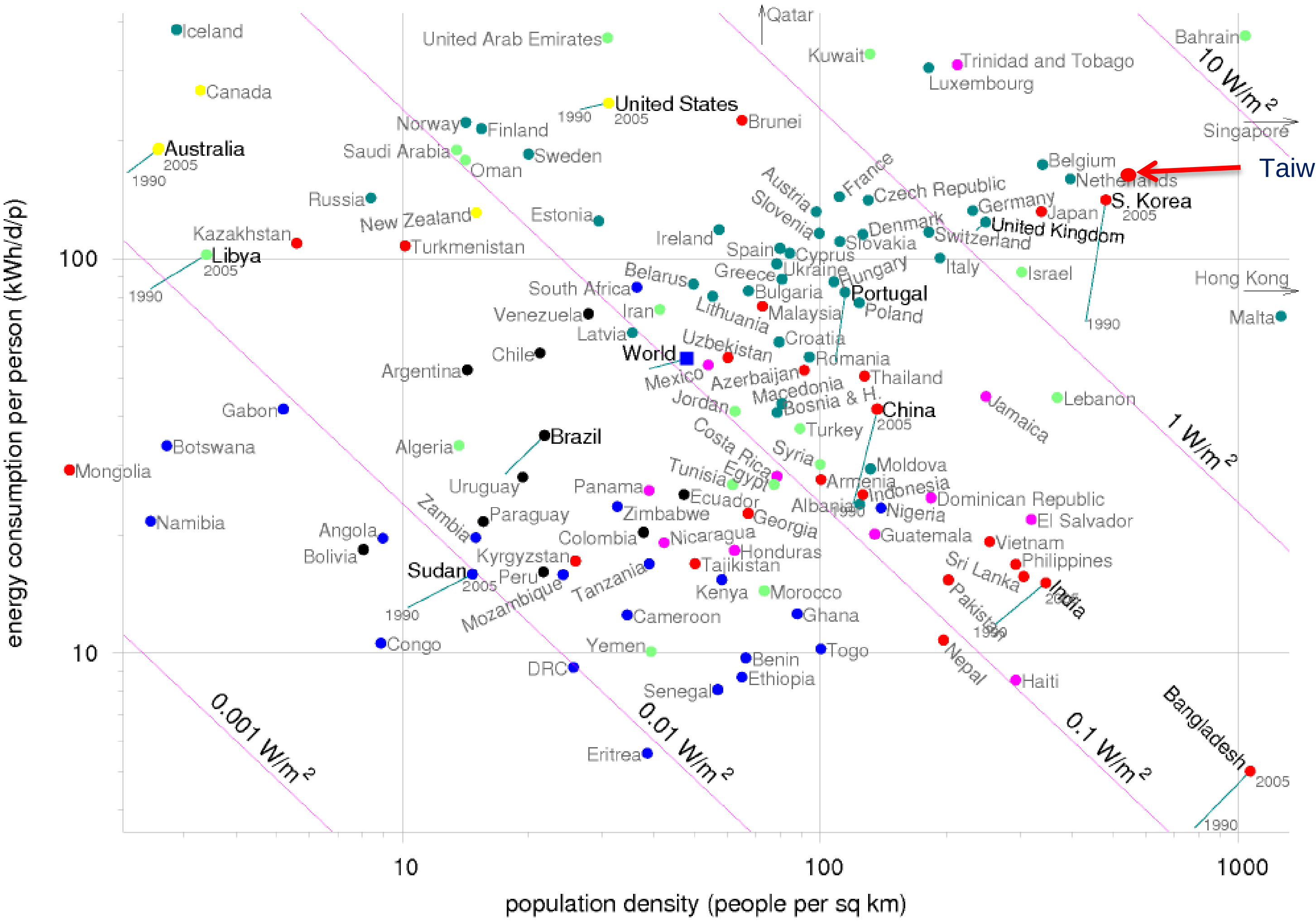


Outline

- Scale : generation, storage and transmission of energy from renewable sources
- Cost : technology measured in $/kg
- Science
  - 20th century condensed matter physics has evolved along with its technologies --- transistor, laser, display --- to maximise information capacity in dense packages for consumption
  - how will our science evolve along with 21st century technology pulls?
- How much headroom, and how?

Sources of renewable energy and the needs of the planet

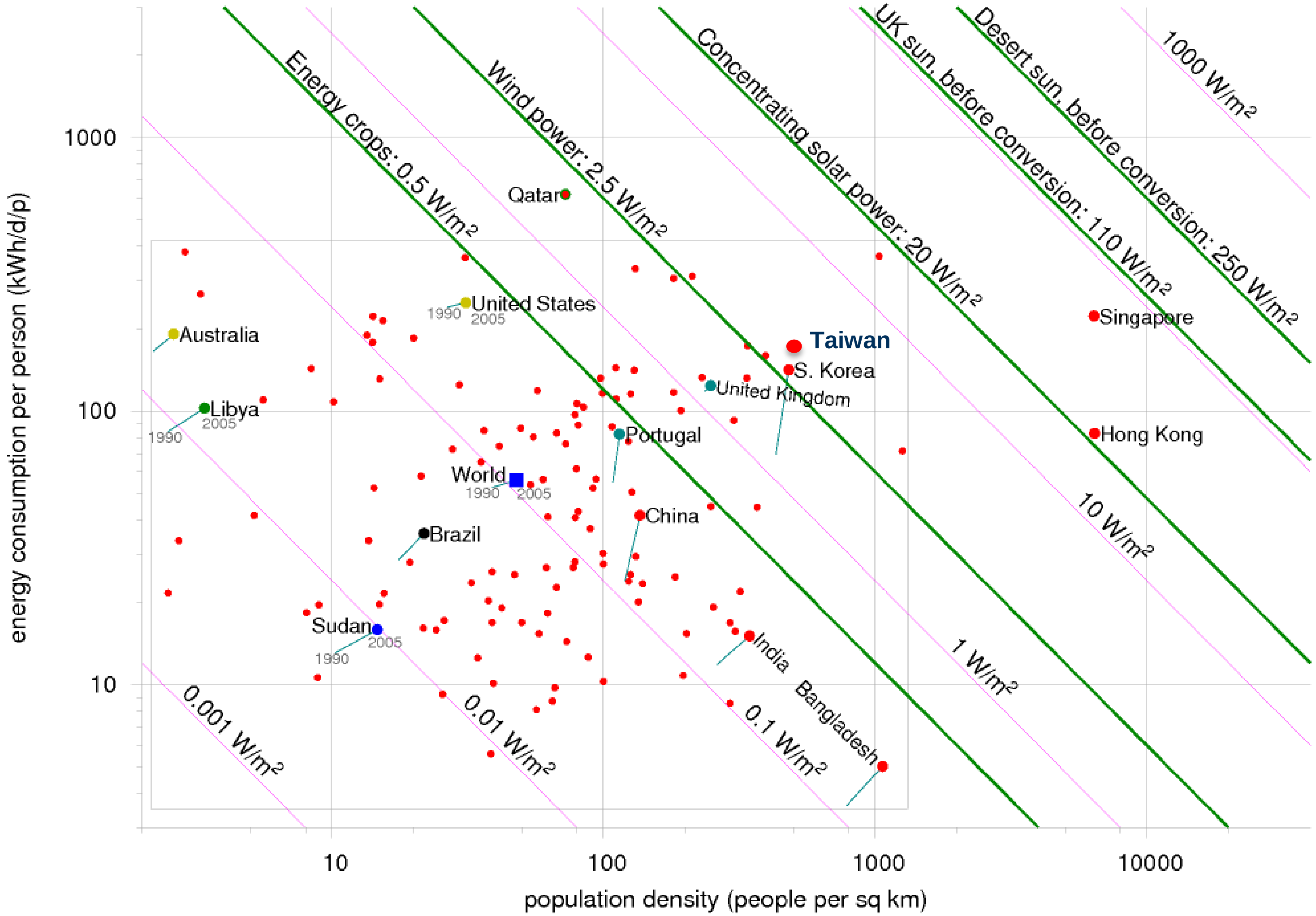
Energy usage per square meter



Taiwan (2013)

Courtesy D J Mackay, UK DECC

Renewables must be deployed on country-sized scale



Courtesy D J Mackay, UK DECC

Solar: the energy input

- Solar insolation is the major energy input to the planet
- Mean radiative solar flux =341.5 W/m^2
- This energy gets redistributed into other degrees of freedom
  - thermalised into infra-red --- “heat”
  - wind energy
  - wave energy
  - rainfall

How much do we need ?

USA average power consumption = 3 TeraWatt (Taiwan ~ 0.16 TW)

10 kW per person (Taiwan ~ 7kW)

5 billion microwave ovens

Solar flux on 10,000 km^2 = Delaware + Rhode Island

Solar photovoltaics in the USA

Photo courtesy SEPA

- The US uses 3 TeraWatts of power, averaged over the day
- In 2011 2 GigaWatts (peak) installed in US (about 20GW worldwide)
- Unfortunately the rating assumes 1kW/m^2 intensity of insolation (mid-day in Arizona)
- In practice, the average power is probably 20-30% of peak (at best) – so this is 0.02% of demand ....
- Can we scale this up ?

https://financere.nrel.gov/finance/content/calculating-total-us-solar-energy-production-behind-the-meter-utility-scale

Technologies by volume

Global shipments of silicon wafers

1st quarter 2012

2033 million square inches[1]

[1] Source: semi.org

1.2 square kilometers

[Global Foundries Fab 8 in Malta NY]

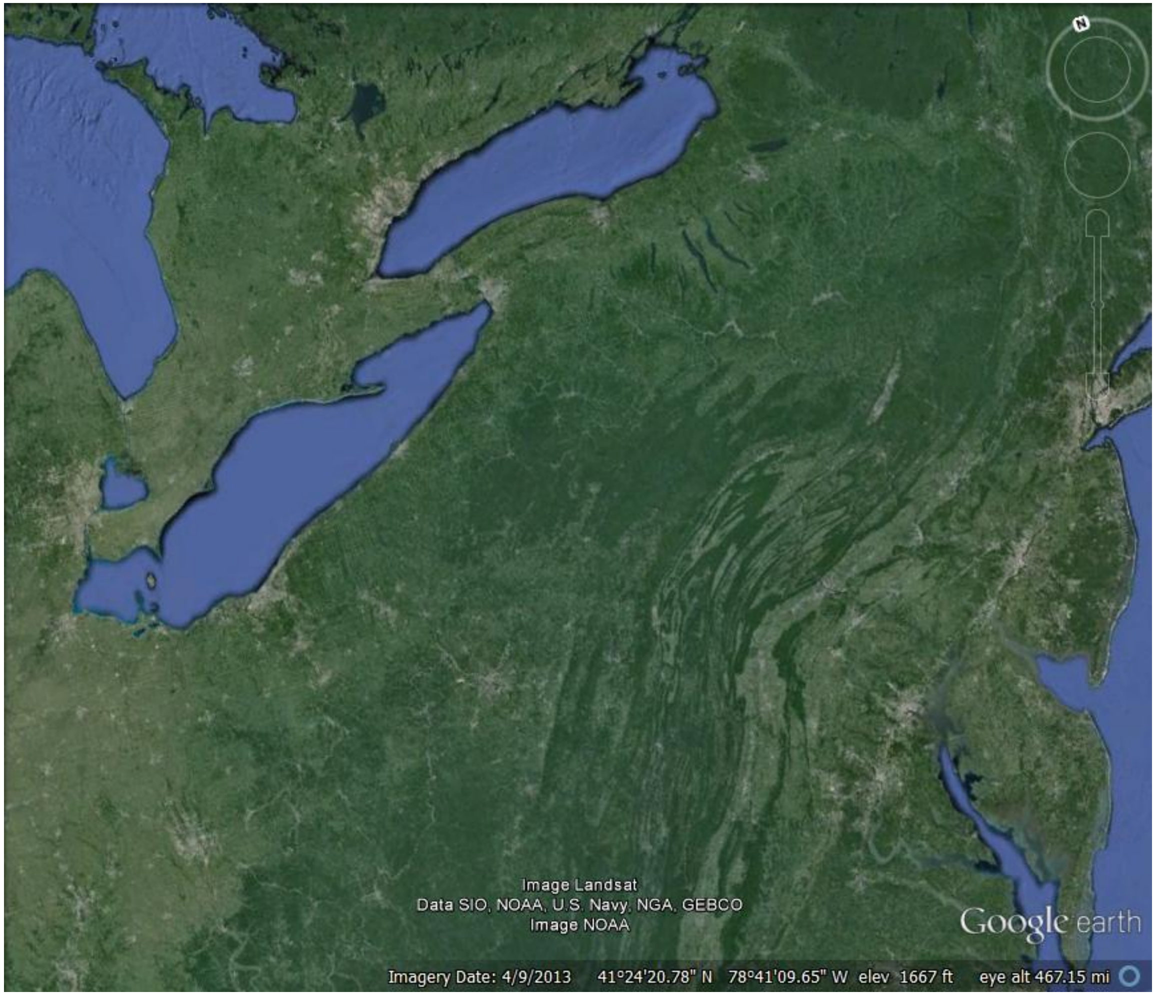
2011 Solar PV Capacity in USA – 2 GW (peak)
10 square kilometers

3 TW @ 300 W/m^2 (Full insolation in AZ) 10000 km^2

3 TW @ 80 W/m^2 40,000 km^2
State of the art PV - 30% efficient

3 TW @ 30W/m^2 100000 km^2
Typical solar PV installation ~ 10% efficient

3 TW @ 5W/m^2 600000 km^2
Typical installed PV under cloudy conditions



Challenges of geography, efficiency, and cost

	Power density Watt/m^2
Full insolation Arizona desert	300
Concentrated solar power (desert)	15-20
Solar photovoltaic	5-80
Biomass	1-2
Tidal pools/tidal stream	3-8
Wind	2-8
Rainwater (highland)	0.3
US energy consumption (all sources)	0.3

In the US:
Solar + wind + storage + grid infrastructure = Sustainable economy

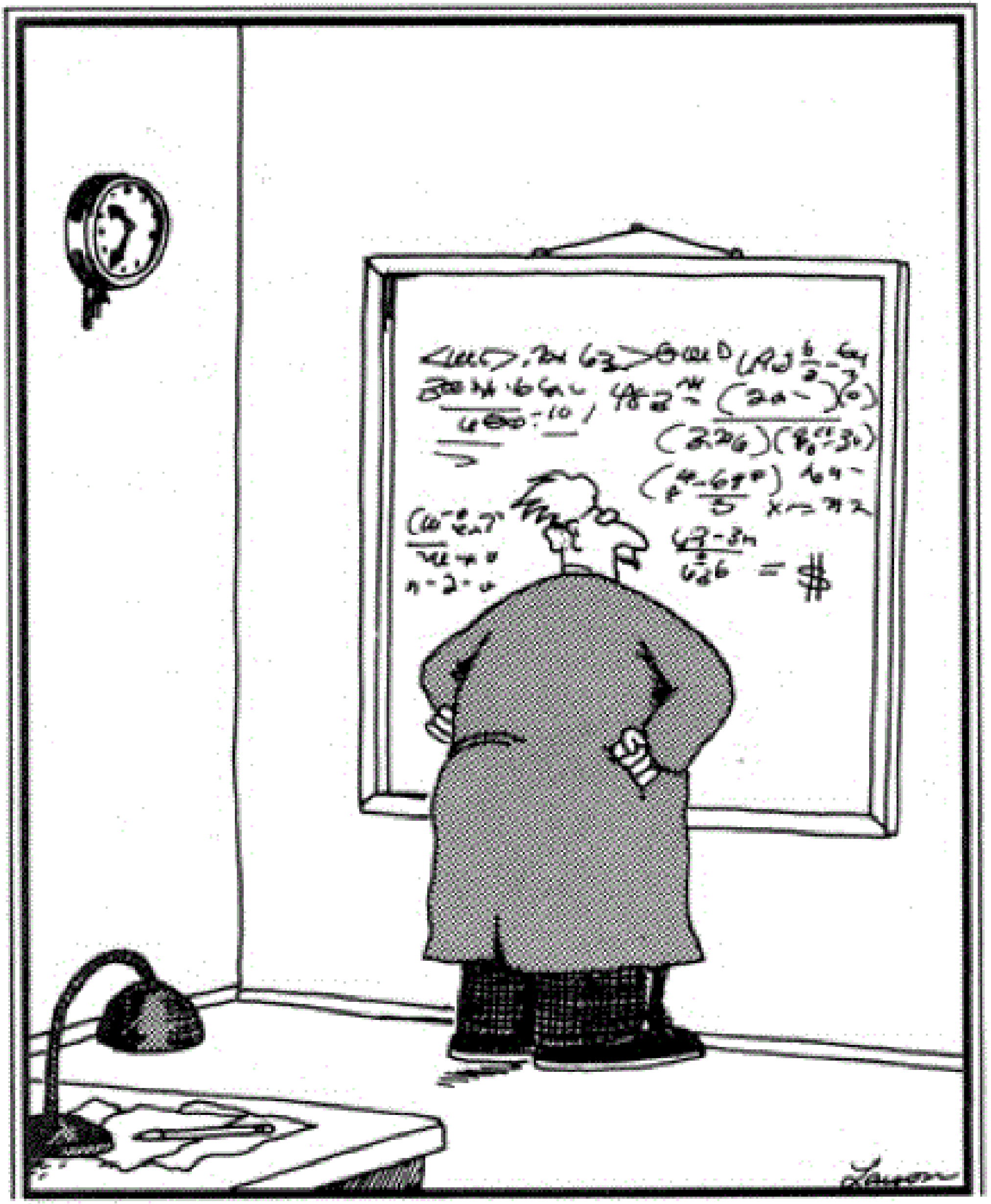
In the Global South:
Solar + storage+ refrigeration+ lighting = Education and healthcare

Backing up grid renewables with storage

3 Terawatts x 12 hours equals:

9 times the **annual** energy generated by the Hoover Dam

10^8 tons of Li-ion batteries: ~ 10^3 times current production



Einstein discovers that time is actually money

The (energy) cost of making things

Materials are energy, and energy is money

Energy input accounts for:

- 1/3 cost of steel ($1/kg)
- 1/2 cost of aluminum ($2.50/kg)

iPad
Cost: $500
Weight: 0.6 kg
$1,000/kg

Boeing 787-9
$243M
180,000kg
$1,500/kg

Honda Civic 1.8
$16,000
1,210 kg
$13/kg

Ground beef
$10/kg

Enercon E-126
7.58 MW
$10M
6,000 tons
$1.5/kg
Payback
in 3-4 years
at 10¢/kWh

The cost of things is their energy input

	Price/$	Energy consumed kWh	Implied cost of energy $/kWh	Time to breakeven at 10c/kWh
1 kg steel*	1.00	7.5	0.13	
1 kg Al	2.50	16.2	0.15	
1 kg hamburger	10.00	1.9X50(1)	0.11	
1 liter diesel	0.80	10	0.08	
1 kg wheat flour	1.00	4.3	0.23	
E-126 wind turbine (2)	$10M/6000 ton= $1.50/kg			3.5 years
Solar panel	$1/Watt			4 years

*1/3 of the cost of steel is the energy input

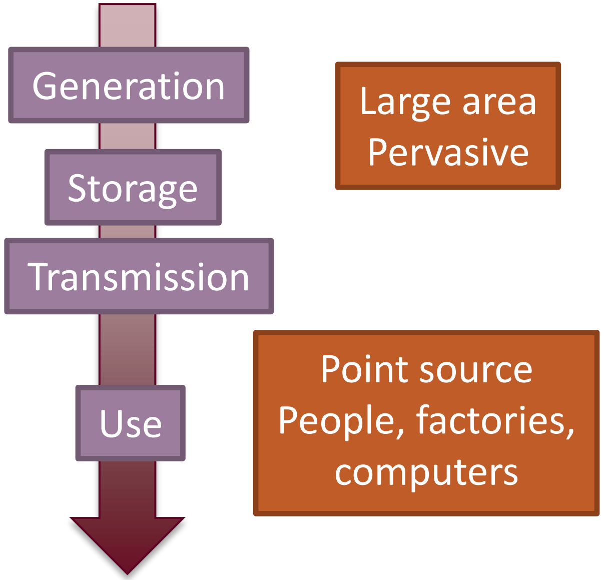
(1) Energy factor – David Pimentel 1997

(2) Bloomberg New Energy Finance's Wind Turbine Price Index 7 Feb 2011

How much headroom for new technologies ?

Transformative materials technologies for the electrified economy

- Solar PV for electricity generation (or solar to fuel)
- Ultracapacitors/batteries for electrical storage
- Superconductors for electrical transmission/motors
- Thermoelectrics for refrigeration/scavenging
- Light emitting diodes for electrical lighting
- Membranes for water purification/desalination



Generation

Storage

Transmission

Use

Large area
Pervasive

Point source
People, factories,
computers

Point use is easier: smaller scale for fabrication, straightforward path to introduction
Large scale disruptive technologies are very hard

Aside from the grid, we have no examples of implementing wide scale "by the ton" electrical materials technology

Why electrical storage?

- Rechargeable lithium-ion batteries already a $40B business (2011)
  - Improving at few percent per annum
  - Can we do this faster?
- Laggard technology
  - Around 1% theoretical efficiency; (lighting ~80%, solar PV ~30%)
  - Can we do something much better?
- Scale – To back up U.S. power use (~3 TeraWatt) for 12 hours takes:
  - 9x annual energy production of the Hoover Dam
  - 1,000x the annual production of Li-ion batteries
  - Can we do something at scale?

Argonne's comprehensive energy storage portfolio

Applied Research
EERE, OE, DoD
Argonne Battery Dept (80)

Research Facilities
Materials Engineering Research Facility (MERF), Battery Post-Test Facility, Cell Fabrication Facility

Contract Research
Industry

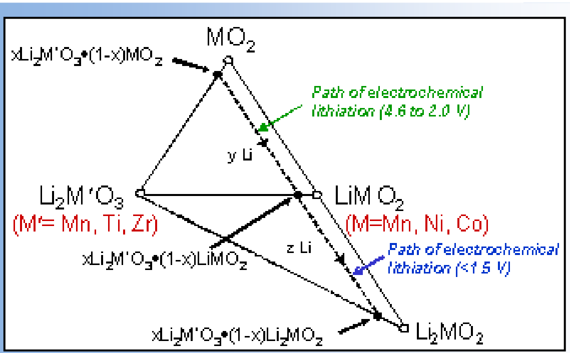
Technology Transfer
IP Generation, Scale up

Argonne Transportation Center

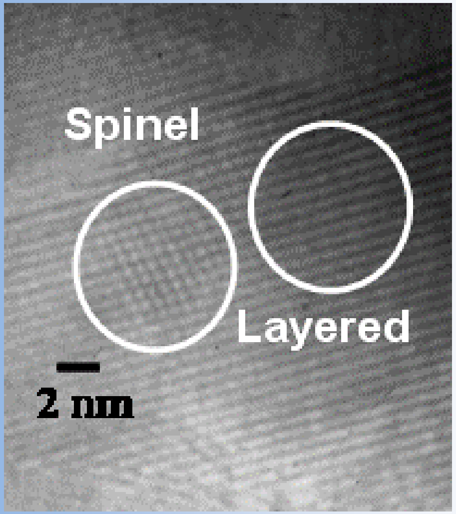
Basic Research
OS, BES
EFRC – CEES (60)
Universities
LDRD Funding

JCESR
Joint Center for Energy Storage Research (120)

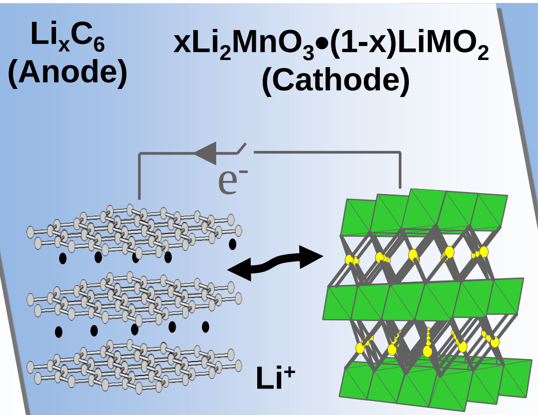
Argonne's Li-ion battery research program: From fundamental research to cars on the road



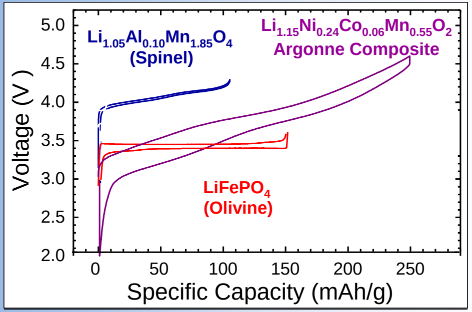
Discovered new composite structures for stable, high-capacity cathodes



Tailored electrode materials



Created high-energy Li-ion cells with double cathode capacity, enhanced stability

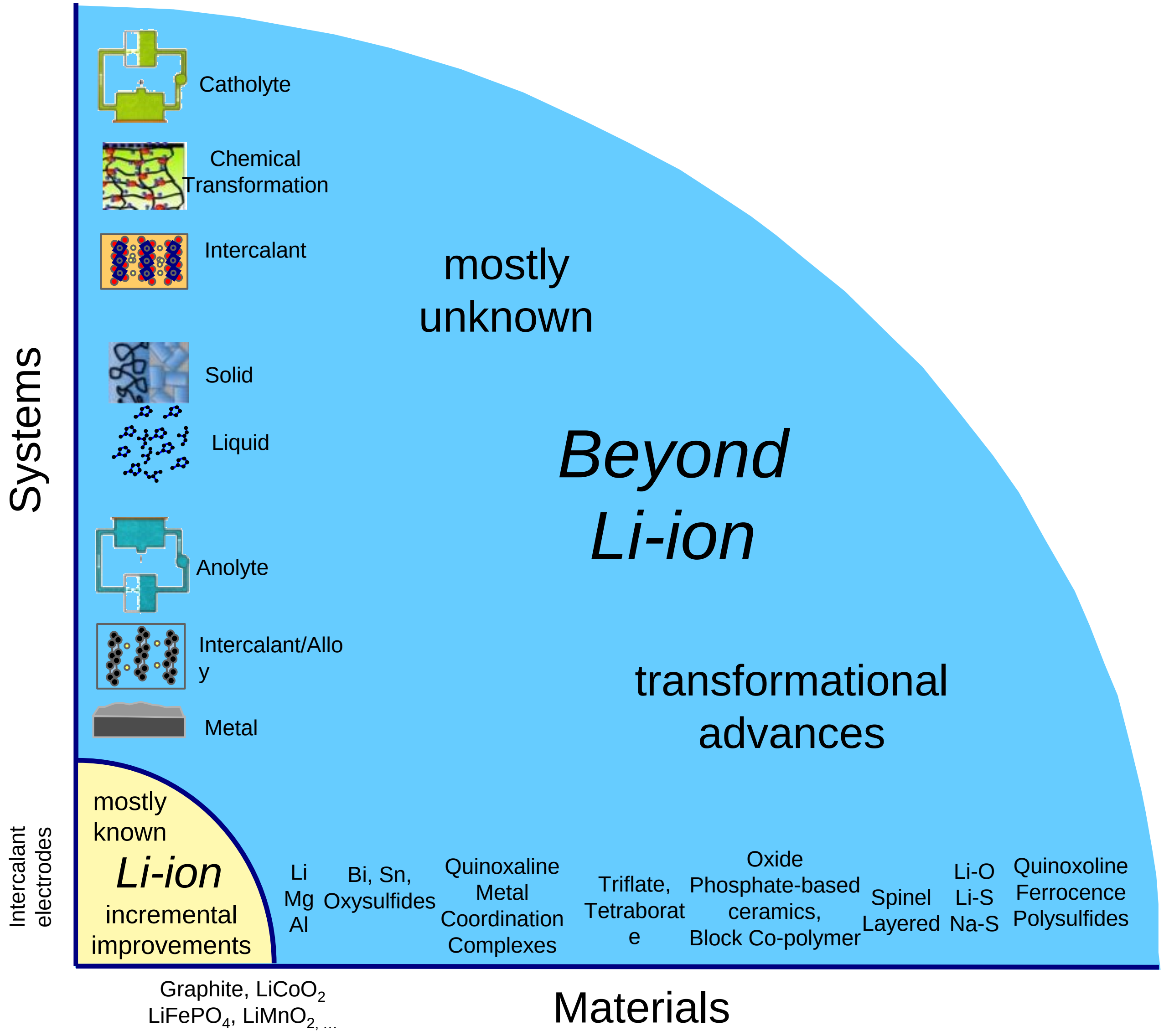


Licenses to materials cell manufacturers and automobile companies

Argonne provides scale-up research in energy storage, offers testing facilities to users

JCESR: Strong affiliate group extends market reach

Opportunity space beyond lithium-ion is large, unexplored and rich



Systems

Catholyte

Chemical Transformation

Intercalant

Solid

Liquid

Anolyte

Intercalant/Alloy

Metal

mostly
unknown

Beyond
Li-ion

transformational
advances

mostly
known

Li-ion

incremental
improvements

Intercalant
electrodes

Li
Mg
Al

Bi, Sn,
Oxysulfides

Quinoxaline
Metal
Coordination
Complexes

Triflate,
Tetraborate

Oxide
Phosphate-based
ceramics,
Block Co-polymer

Spinel
Layered

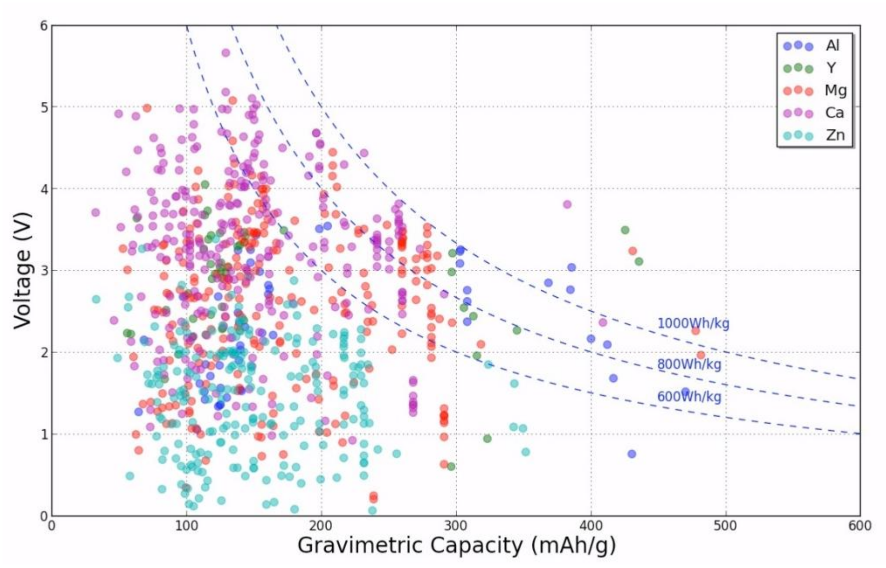
Li-O
Li-S
Na-S

Quinoxoline
Ferrocence
Polysulfides

Graphite, $LiCoO_2$
$LiFePO_4$, $LiMnO_2$, ...

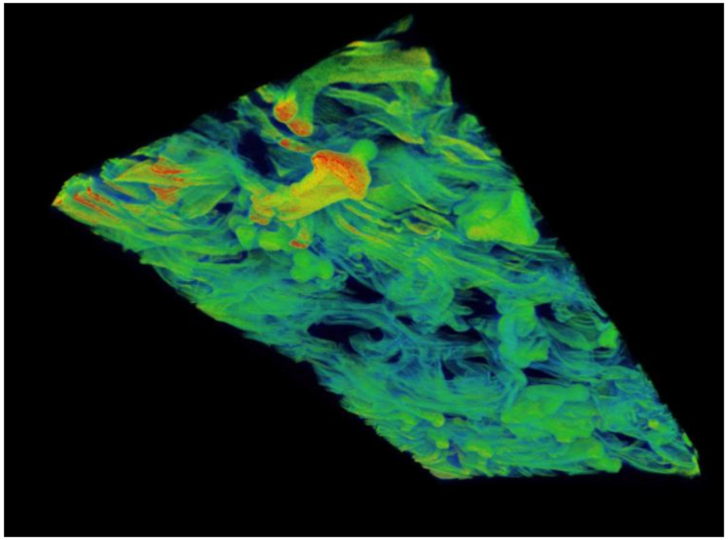
Materials

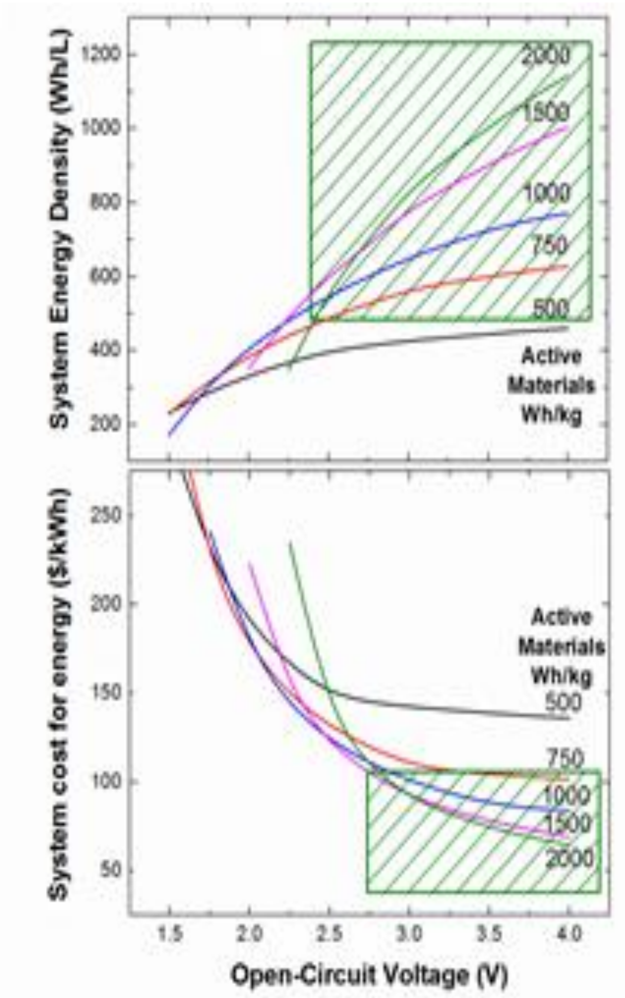
Pruning the search tree



Screening of 1,800 intercalant hosts

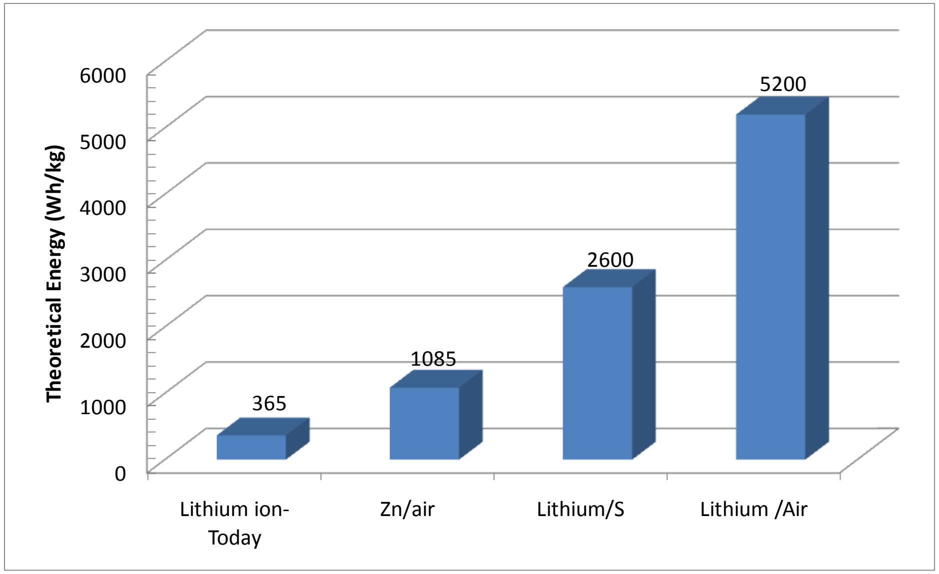
In operando
X-ray

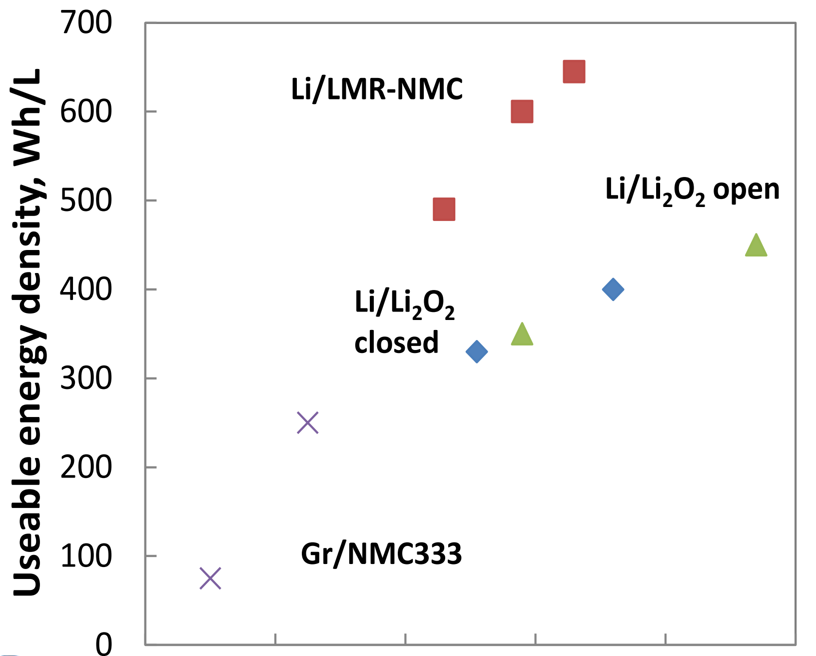




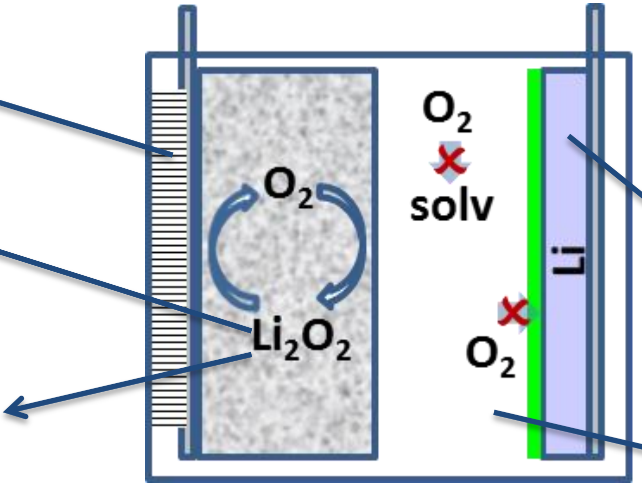
Systems analysis and
techno-economic modeling

Assessing the near-term challenges of lithium-air batteries





100 kWh$_{use}$, 80 kW$_{net}$ 360 V battery
Systems-level calculation
– ANL, GM, Berkeley NL



Oxygen ingress

Lithium peroxide is an insulator

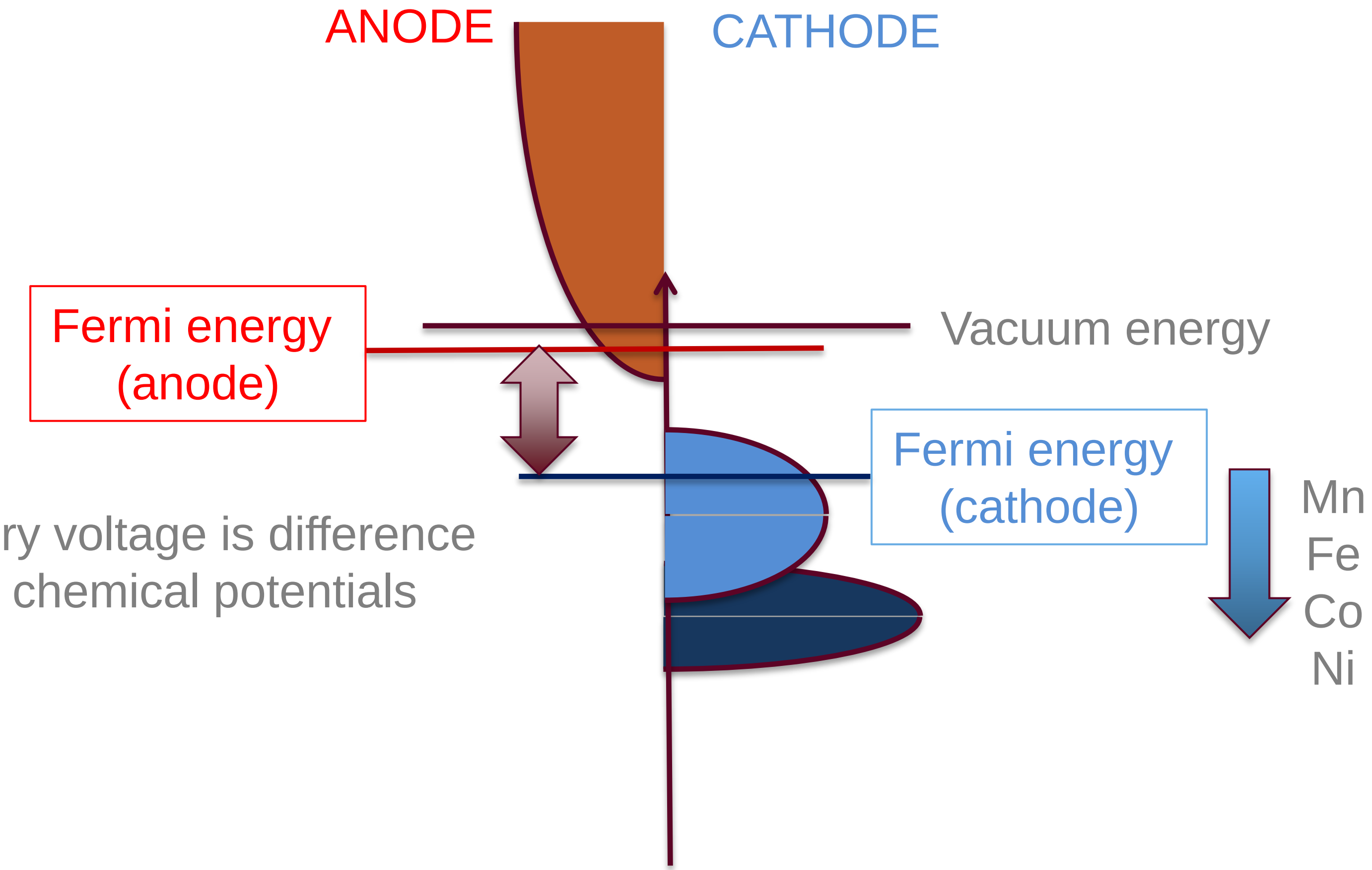
Lithium peroxide growth/dissolution irreversible

Li metal very reactive, forms dendrites

Electrolyte unstable on oxygen electrode

Does this motivate fundamental science?

Battery basics

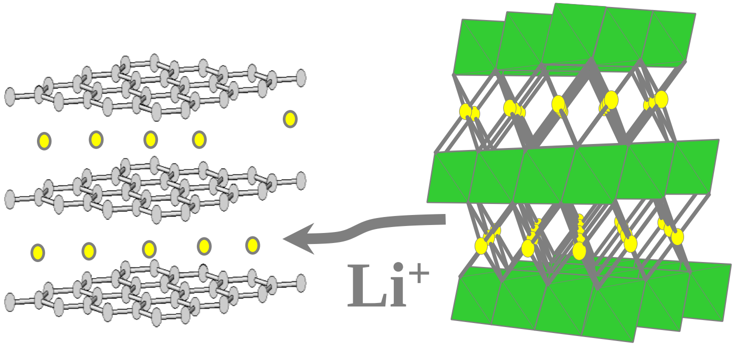


Battery voltage is difference in chemical potentials

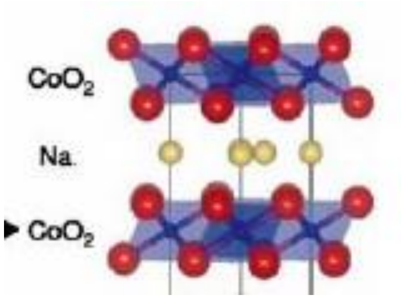
Want high density of states and deep levels (cathode)
Want high density of states and shallow levels (anode)
Must be able to reversibly shift chemical potentials by ion transport (Li^+)
Non-reactive electrolyte

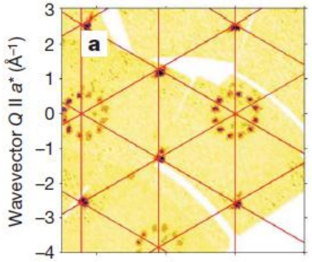
Energy dense materials are strongly correlated

Li-ion battery, commercialised by Sony in 1991
$Li_x C_6$ (anode) / $Li_{1-x} CoO_2$ (cathode)
x limited to ~ 0.5



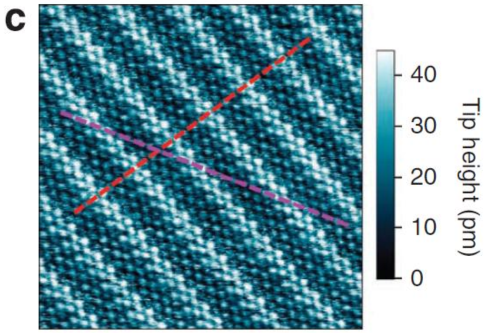
$Na_x CoO_2$
Enhanced thermopower, 5K superconductor
vacancy ordered phases

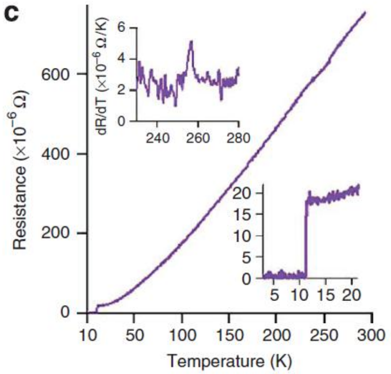




Roger et al. 2007 doi:10.1038/nature05531

CaC_6
12K superconductor; 250K CDW





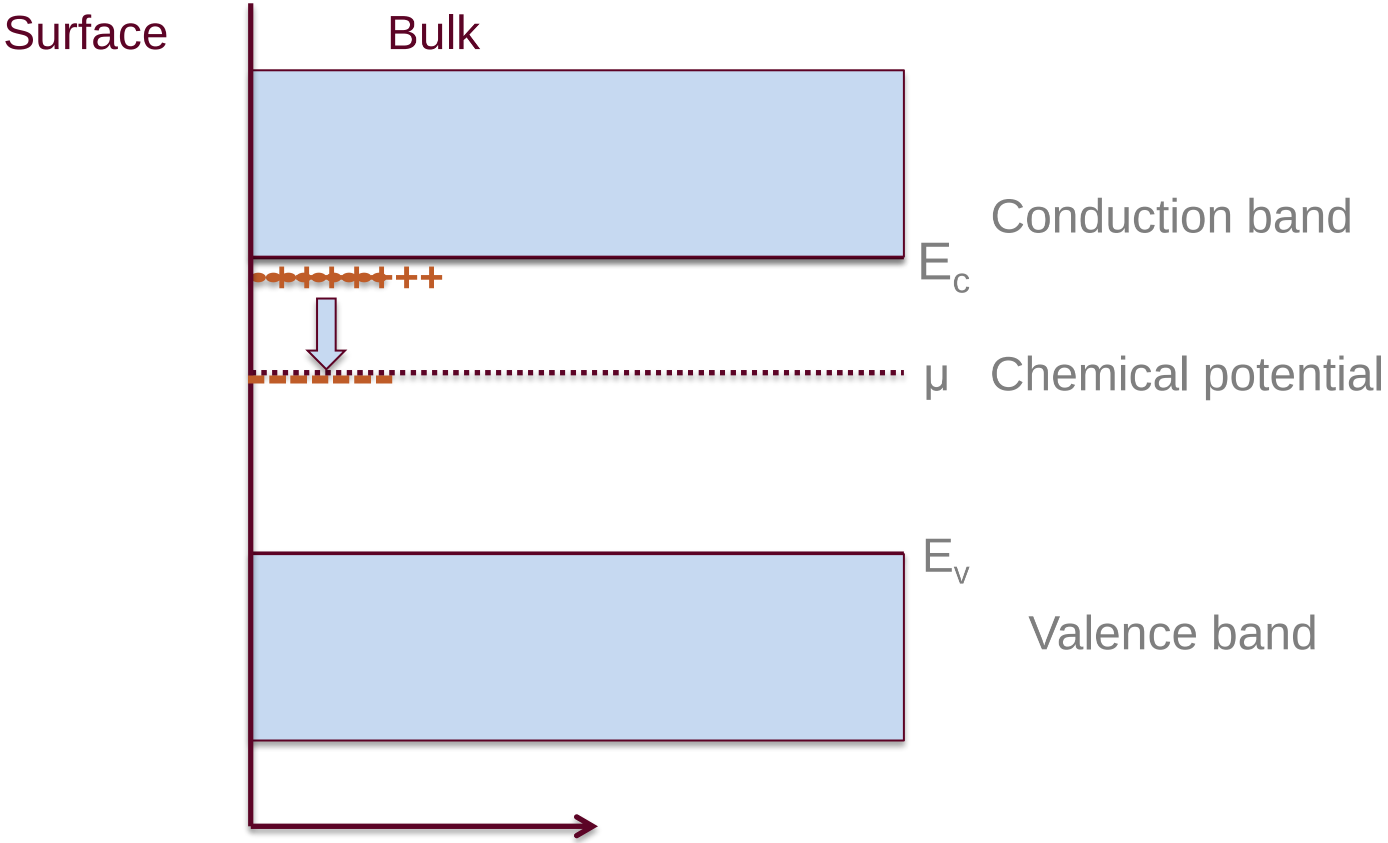
This is not an accident!

Rahnejat et al 2011 DOI: 10.1038/ncomms1574

Energy dense materials are strongly correlated

- Cathodes are best made from “strongly correlated” materials
  - Strongly bound, narrow bands with a large density of states
  - Also need large ratio of Li to transition metal (weight)
  - But they often have Mott transitions/Jahn Teller effects which lead to insulating behavior
- Anodes are usually made from weakly correlated materials
  - TiO_2 , graphite, graphene, C_{60} ---- weakly bound states, chemical potential near vacuum
  - But lowish density of states means there is less capacity: eg LiC_6 is the maximum capacity of Li in graphite

Doping of conventional semiconductor



Surface

Bulk

Conduction band

E_c

μ Chemical potential

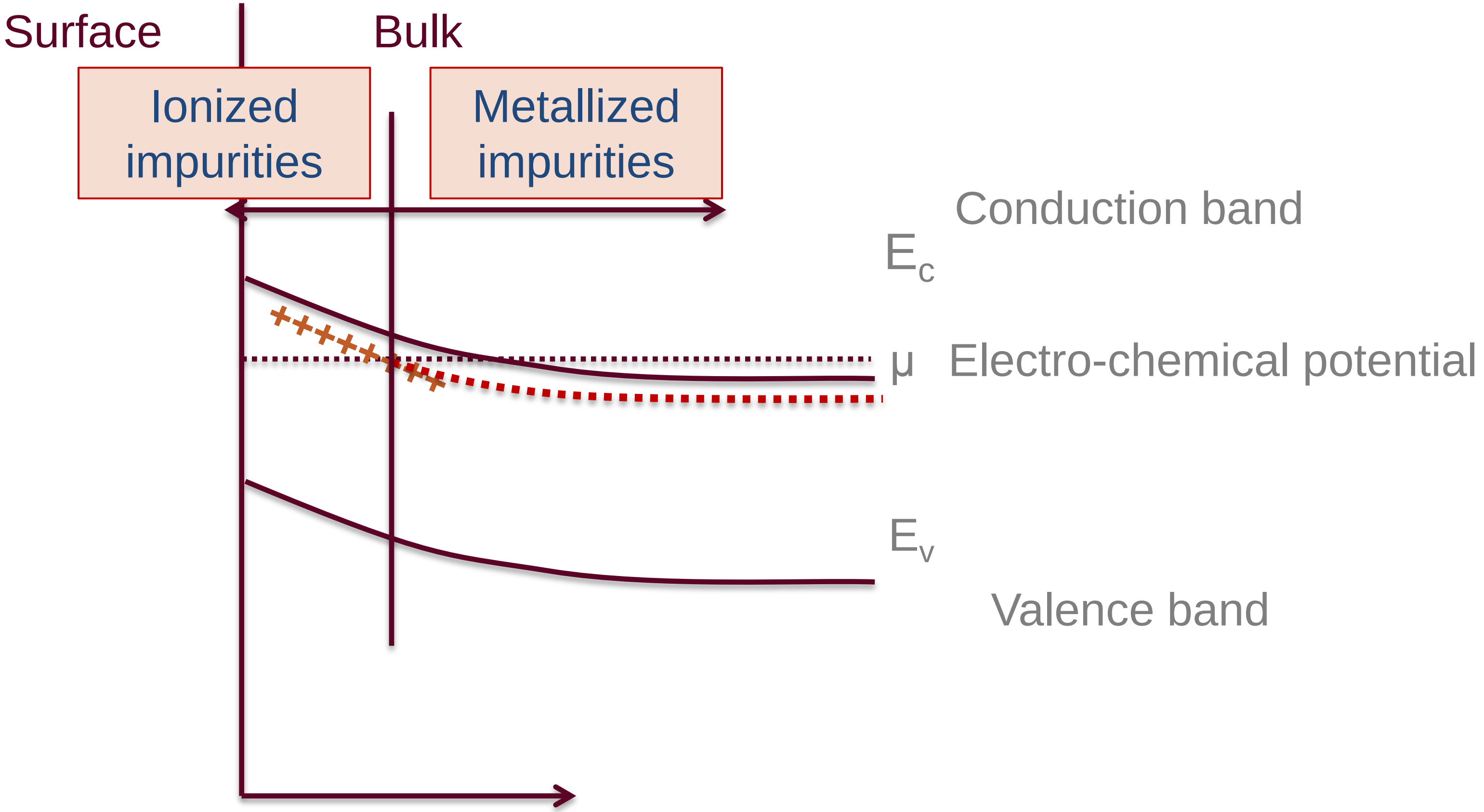
E_v

Valence band

Add dopant (including associated electron) near the interface

Dopants ionize and electrons delocalise

Doping of conventional semiconductor



Charge separation introduces electrical potential which shifts the band edge

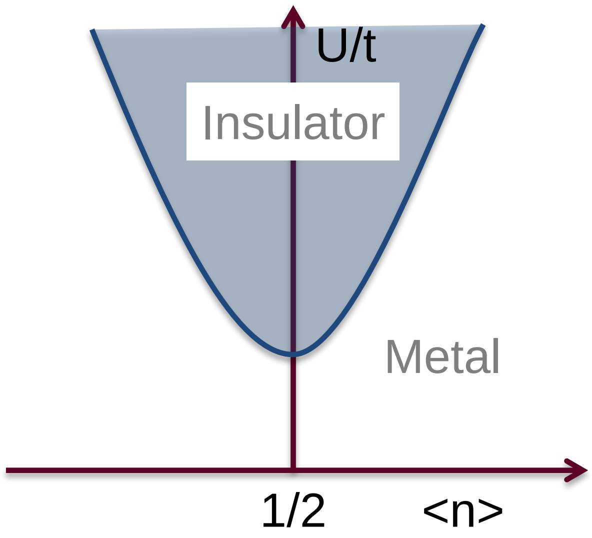
Weakly bound carriers metallize , depletion layer at interface

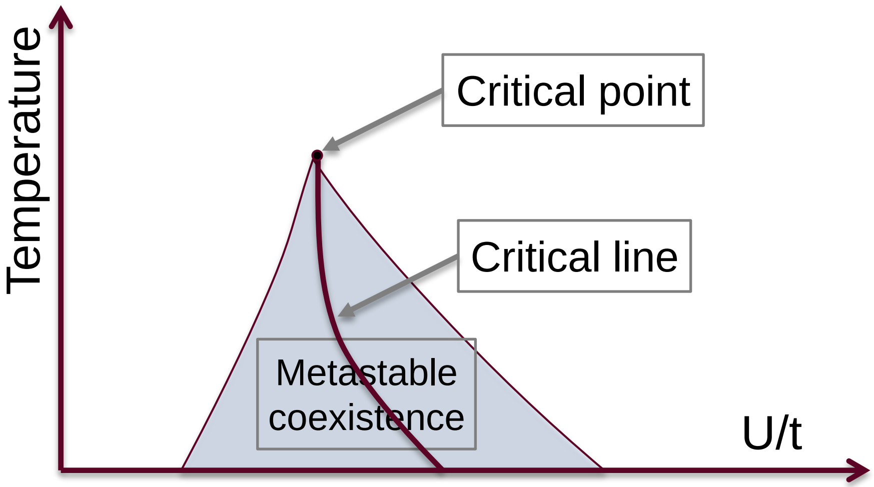
Mott insulator

- Generic model due to Mott, Hubbard --- competition between hopping “t” and Coulomb “U”

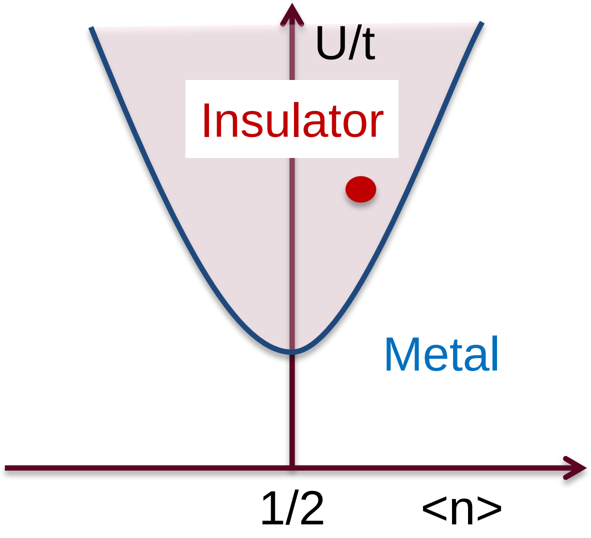
$$H = \sum_{ij} t_{ij} \hat{c}_i^\dagger \hat{c}_j + \sum_i U \hat{n}_{i\uparrow} \hat{n}_{j\downarrow}$$

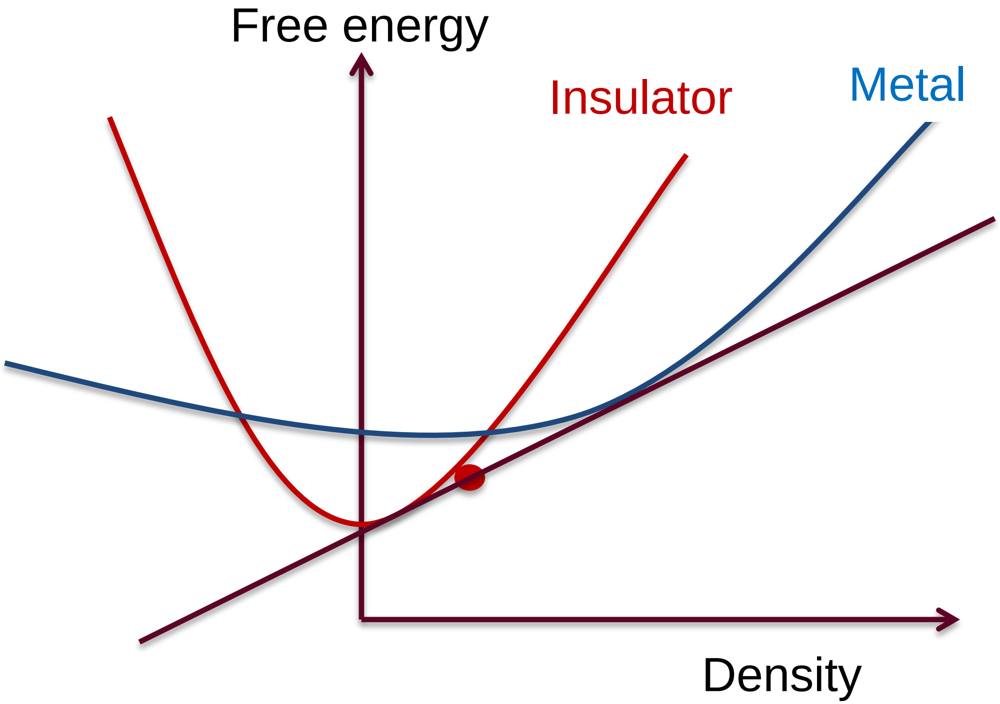
- Near half-filling, induces insulating/magnetic states by a discontinuous first-order phase transition





Doping of a Mott insulator

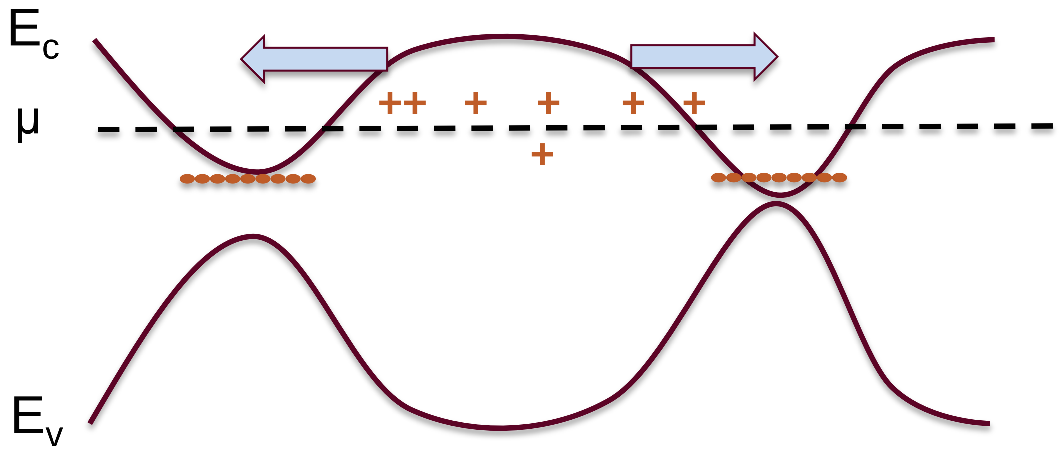




Expect phase separation and an inhomogeneous state
“Frustrated” by Coulomb interaction

Inhomogeneous phases in Mott systems

Mobile donors diffuse to form metallic puddles and screen Coulomb repulsion of phase-separating carriers



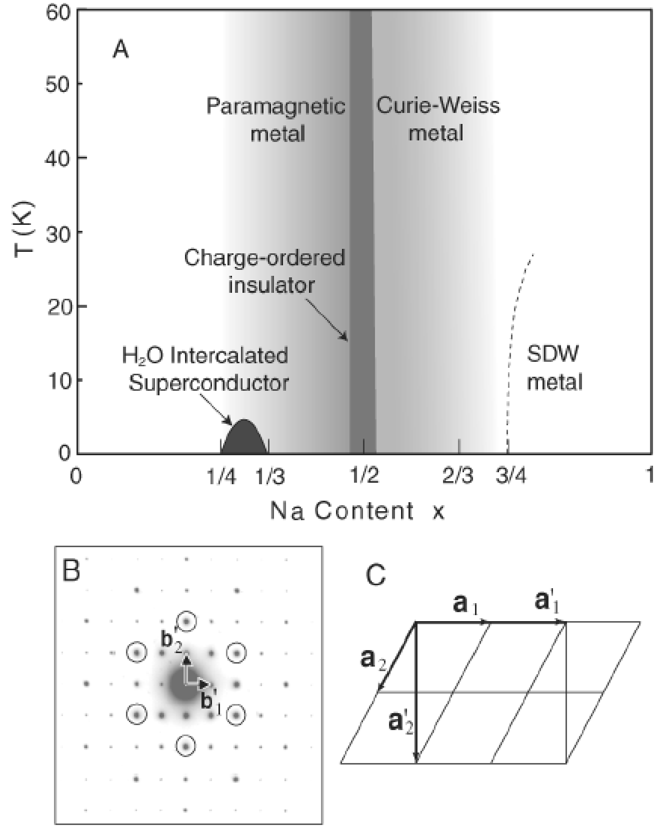
This is a generic feature of any system with a first-order phase transitions separating stable phases of differing electron density

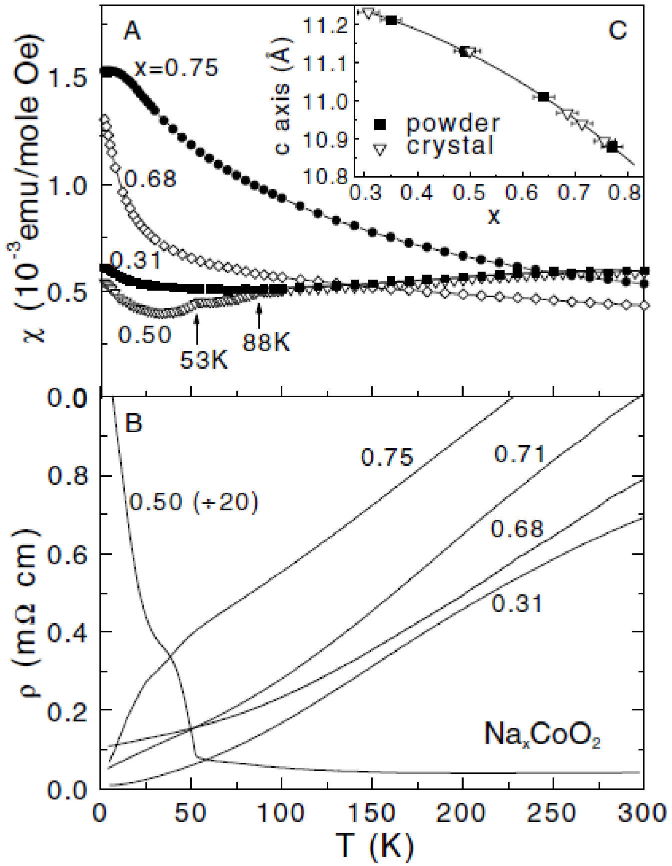
Particularly prevalent when dopant species are highly mobile – e.g. O vacancies and Li ions

VOLUME 92, NUMBER 24 PHYSICAL REVIEW LETTERS week ending 18 JUNE 2004

Charge Ordering, Commensurability, and Metallicity in the Phase Diagram of the Layered Na_xCoO_2

Maw Lin Foo,[1] Yayu Wang,[2] Satoshi Watauchi,[1,*] H.W. Zandbergen,[3,4] Tao He,[5] R. J. Cava,[1,3] and N. P. Ong[2,3]

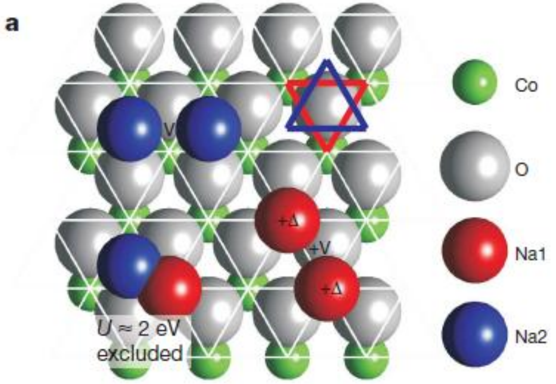




Patterning of sodium ions and the control of electrons in sodium cobaltate

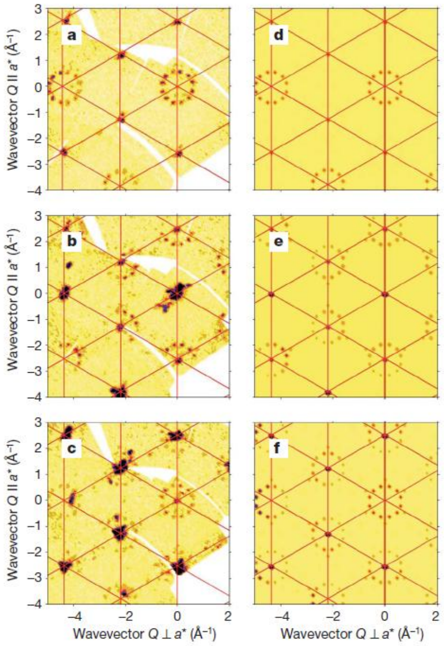
Vol 445 | 8 February 2007 | doi:10.1038/nature05531

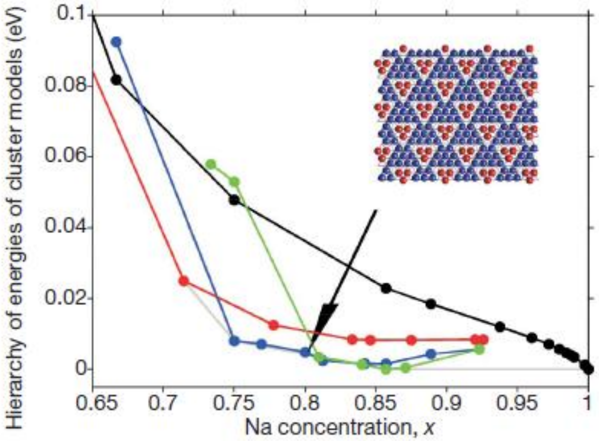
M. Roger[1], D. J. P. Morris[2], D. A. Tennant[3,4], M. J. Gutmann[5], J. P. Goff[2], J.-U. Hoffmann[3], R. Feyerherm[3], E. Dudzik[3], D. Prabhakaran[6], A. T. Boothroyd[6], N. Shannon[7], B. Lake[3,4] & P. P. Deen[8]



Ordered trivacancy phase

of $Na_{0.8}CoO_2$



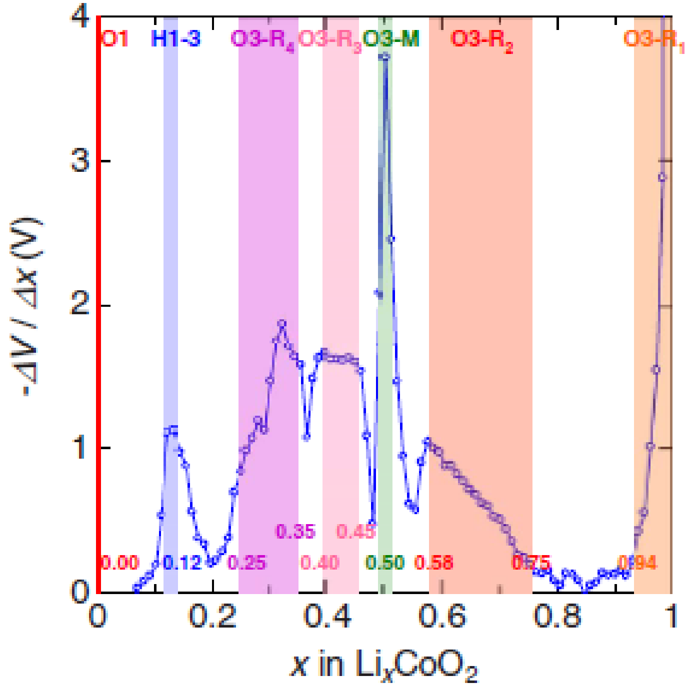


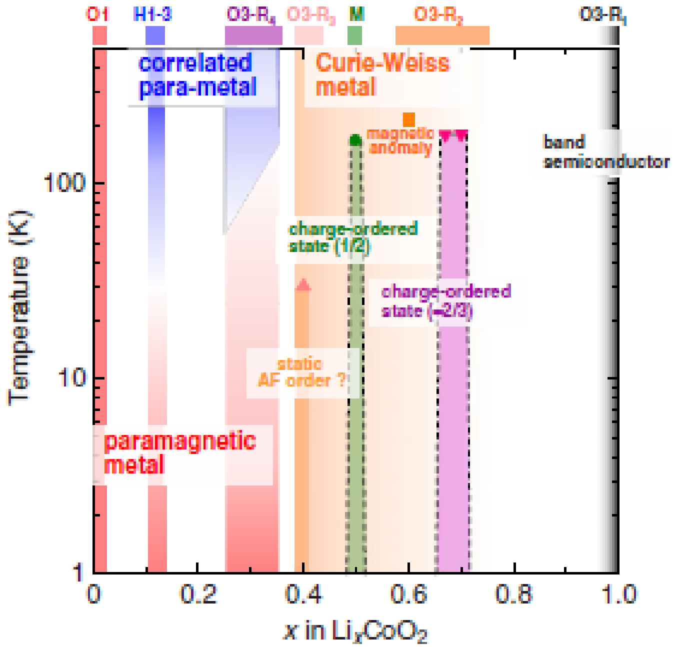
PHYSICAL REVIEW B **80**, 165114 (2009)

Electronic phase diagram of the layered cobalt oxide system Li_xCoO_2 ($0.0 \leq x \leq 1.0$)

T. Motohashi,[1,2] T. Ono,[2,3] Y. Sugimoto,[1] Y. Masubuchi,[1] S. Kikkawa,[1] R. Kanno,[3] M. Karppinen,[2,4] and H. Yamauchi[2,3,4]

Derivative of open cell voltage dV/dx indicates biphasic regions

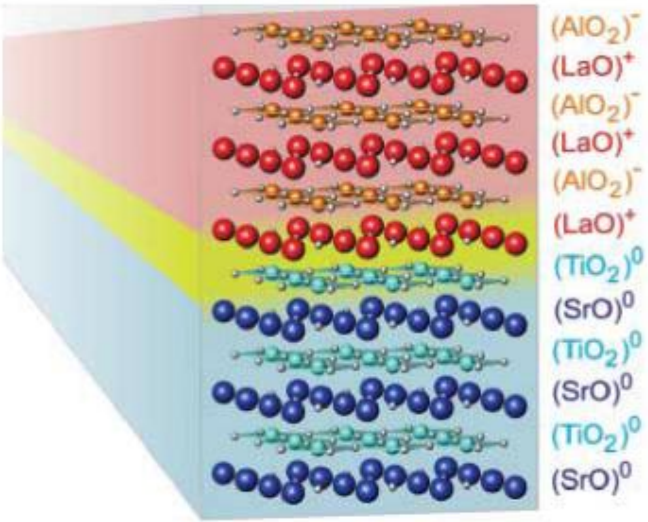


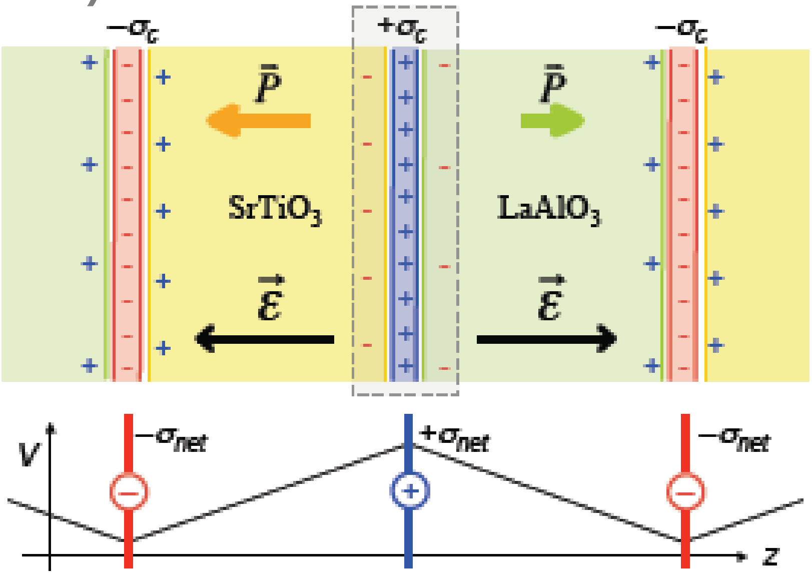


What is actually possible?
A thought experiment

Polar heterostructures demonstrate there is a possible solution

A Ohtomo & H Hwang, Nature **427, 423 (2004)**



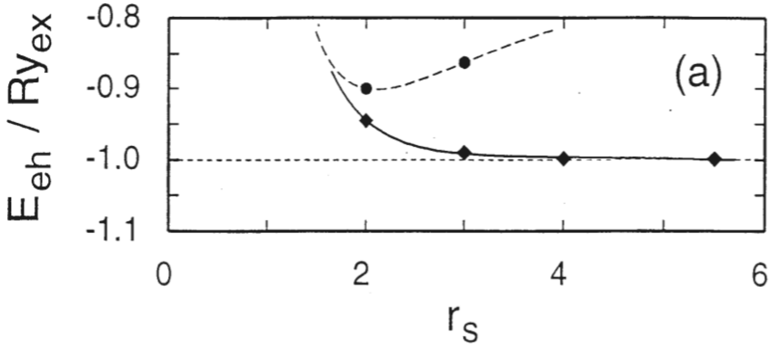


- Once voltage offset = bandgap, chemical potential of carriers controlled by external circuit
- Carriers are lattice-constant sized, so in principle density high
- There are a few issues with materials growth, defects, reconstructed surfaces etc ... currently a fictional and extremely expensive device

Ultracapacitor / Photovoltaic

- Excitons: add electrons and holes in pairs
- Energy cost = Energy gap – binding energy + interaction energy
  - Tuned by external bias ~ 0
- Capacitance is theoretically very large
  - Store one exciton/Bohr radius (Mott density)
- Intrinsic photovoltaic
  - Enormous internal field ~ V/nm
- Quite possibly a high temperature superfluid or an exciton solid unless one is careful

Energy per pair (in exciton Rydberg) as a function of density



$$1/n = \frac{4\pi}{3}(a_{Bohr} r_s)^3$$

Zhu et al, PRB 54, 13575 (1996)

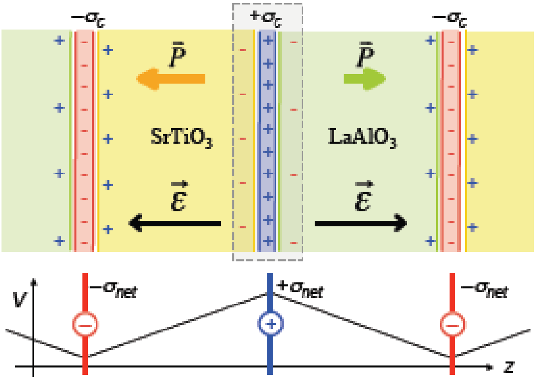
Materials for Energy

Creating transformational technologies: nanoscience by the ton

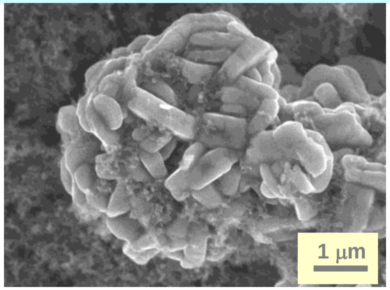
Four magic technologies: storage, photovoltaics, refrigeration and lighting depend on the science of *interfaces.*

- At least two orders of magnitude below optimal performance and too costly
- Devices are unnecessarily complicated, operation is poorly understood, and manufacturing difficult to control
- Major discoveries of new materials classes are rare and random
- There is no predictable path forward

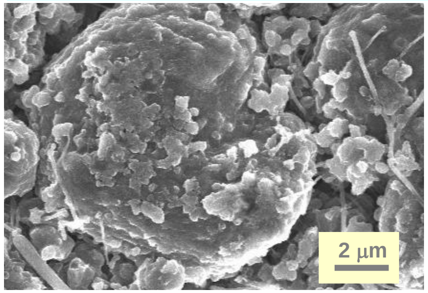
Model "solar battery" with storage density of order gasoline ?



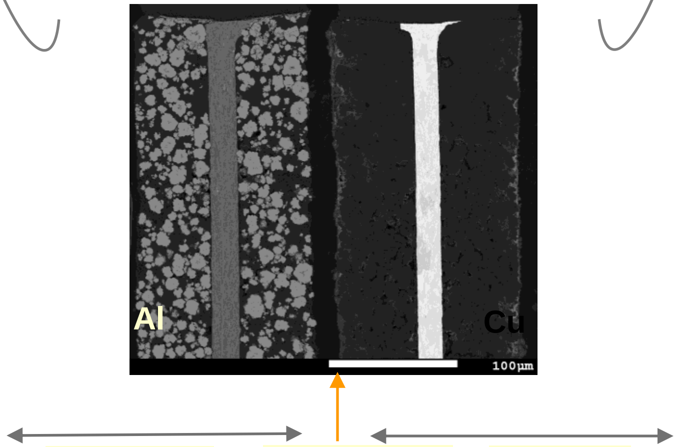
The cathode contains an oxide, carbon additives and PVdF binder



The anode contains graphite, carbon additives and PVdF binder



The cathode comprises an Al current collector coated on both sides. The anode comprises a Cu current collector coated on both sides.



Cathode **Separator** **Anode**

Photo image of an 18650 cell

Nanoscience by the ton

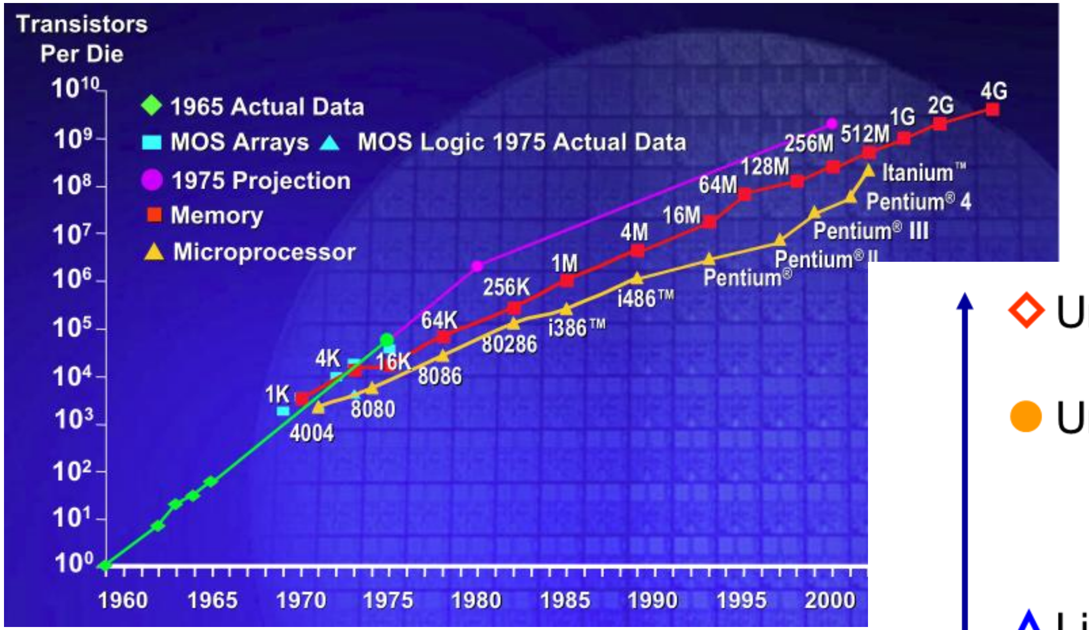
We need a road map for materials development that enables us to escape primitive technologies and have a predictable path forward – this is the science challenge of the next few decades

“Top –down” engineering is not the solution - for example:

- 2/3 of the weight of a PHEV battery is “packaging” – control electronics, safety engineering, casing etc.
- Most of the cost of solar panel installation is *not* the module – power electronics and packaging, installation costs, etc.

Can we learn how to construct functional materials whose properties are defined by precisely controlled interfaces on the nanoscale and which may be manufactured at low cost in enormous volume ....

The consequence of understanding is prediction: Moore's Law for Si *vs*. current strategy for Li-ion batteries



Transformational technologies depend on reliable understanding and control of materials at scales ranging from the atomic to the mesoscale

◇ Unk-HV-HC / Li metal

Safe and reversible cycling of Li metal
Market entry >2021

● Unk-HV-HC / Gr-Si

Discovery of high voltage electrolyte >4.8 V
Discovery of reversible unknown high-voltage high-capacity cathode: 250 mAh/g @ 4.8 V
Market entry > 2019

△ Li_2MXO_4 / Gr-Si

Discovery of path to reversible multi-electron cathode material with 4V cell voltage
Market entry > 2017

■ LMR-NMC / Gr-Si

Stabilization of silicon
Market entry > 2015

◇ LMR-NMC / Gr

Stabilization of LMR-NMC
Market entry > 2013

● LMO / Gr

Nanotechnology fabs of the future ...

Synthesis is king; manufacturing will begin at the nanoscale

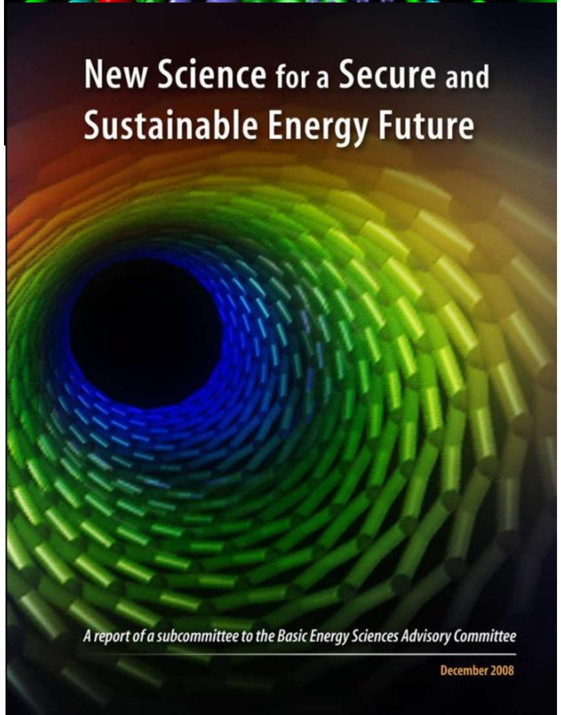
- ***Innovative theory and modeling strategies*** that will span from ‘white boards’ to exascale computing
- ***New synthetic frameworks*** to discover and grow targeted materials classes
- ***New manufacturing strategies*** utilising self-assembly
- ***In situ tools*** to characterize, understand and control materials growth and function

“Where to put the atoms, and how to put them there”

SEPTEMBER 2012

FROM QUANTA TO THE CONTINUUM:
OPPORTUNITIES FOR MESOSCALE SCIENCE

A REPORT FOR THE BASIC ENERGY
SCIENCES ADVISORY COMMITTEE
MESOSCALE SCIENCE SUBCOMMITTEE



New Science for a Secure and
Sustainable Energy Future

A report of a subcommittee to the Basic Energy Sciences Advisory Committee

December 2008

Thank you

Thank you