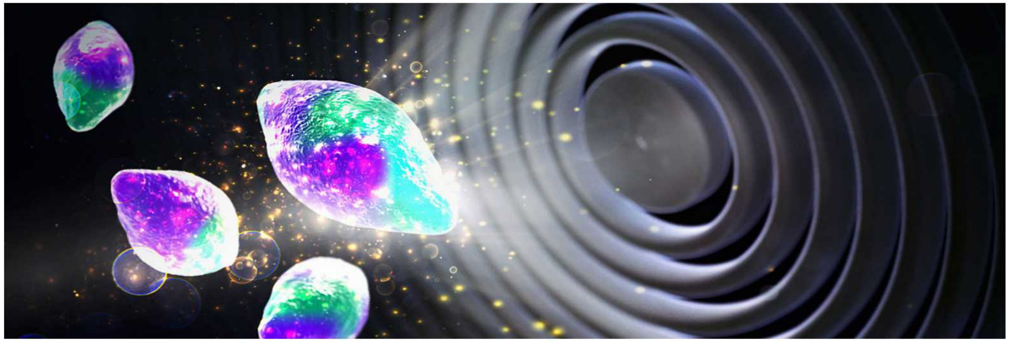
Stanford | ENGINEERING
Materials Science & Engineering

Sandia National Laboratories

SAND2018-3069PE

Electrochemical ion insertion for energy storage and neuromorphic computing



PRESENTED BY

Yiyang Li

This work is supported by the Sandia National Laboratories Truman Fellowship Program, which is funded by the Laboratory Directed Research and Development (LDRD) Program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

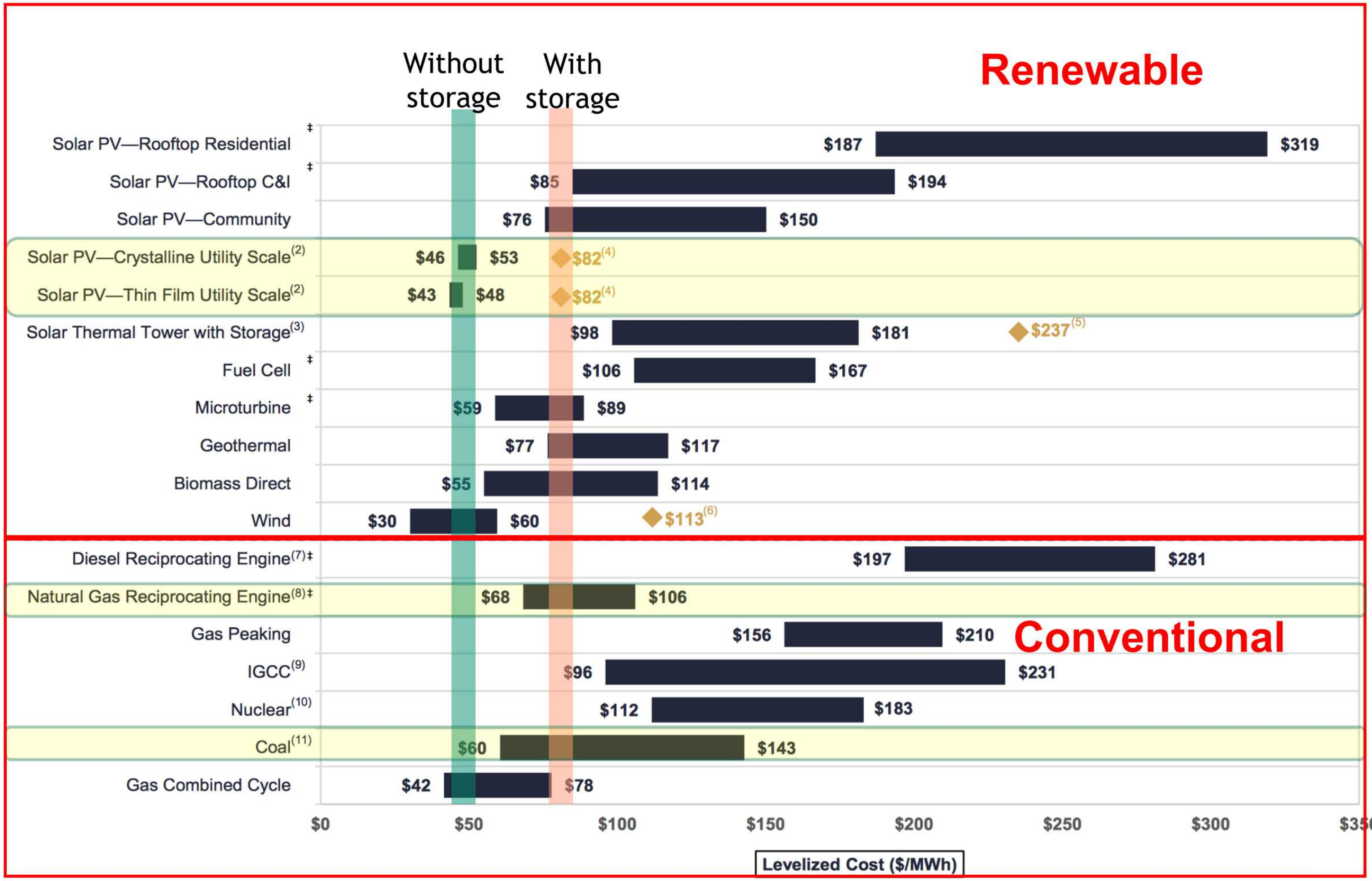
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

7 billion people

16 Terawatt of Power Consumed

NASA

Renewable electricity is cost-effective today



Storage: the key to enabling renewable energy to be used when and where we use it

Source: Lazard

Energy storage in personal transportation

Honda Clarity, Electric

Honda Accord, Gasoline

90g CO_2 /mile
$0.03 / mile

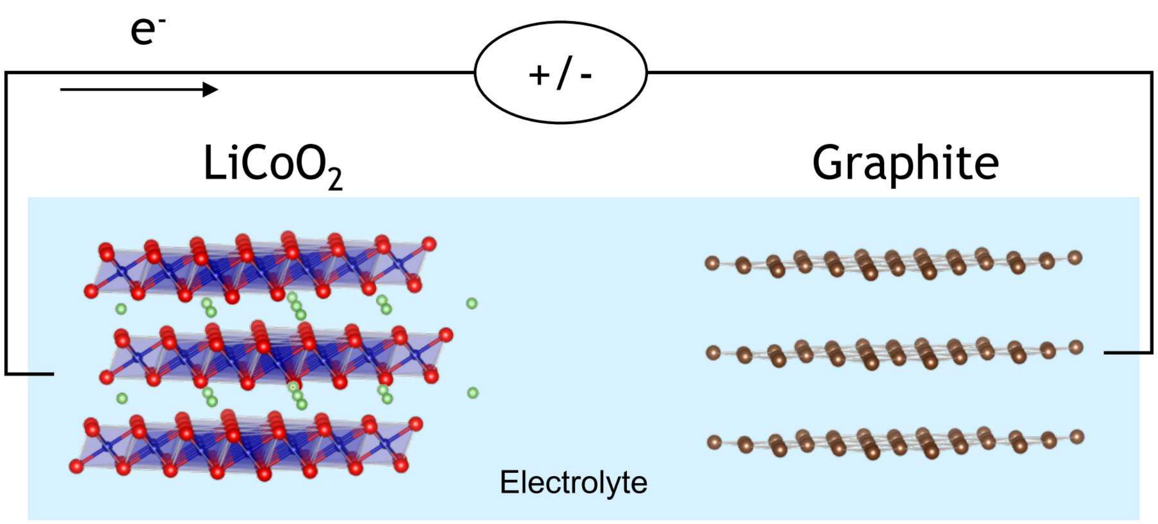
300g CO_2 / mile
$0.10 / mile

Electricity: $0.13/kWh, 300g CO_2 /kWh (SF Bay area), 4 miles/kWh
Gasoline: $3.00/gallon, 9000g CO_2/gallon, 30 miles/gallon

Source: Honda, Tesla

Electrochemical ion insertion

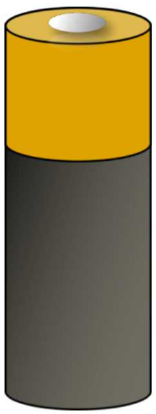
Using electrical signals to dynamically control material composition

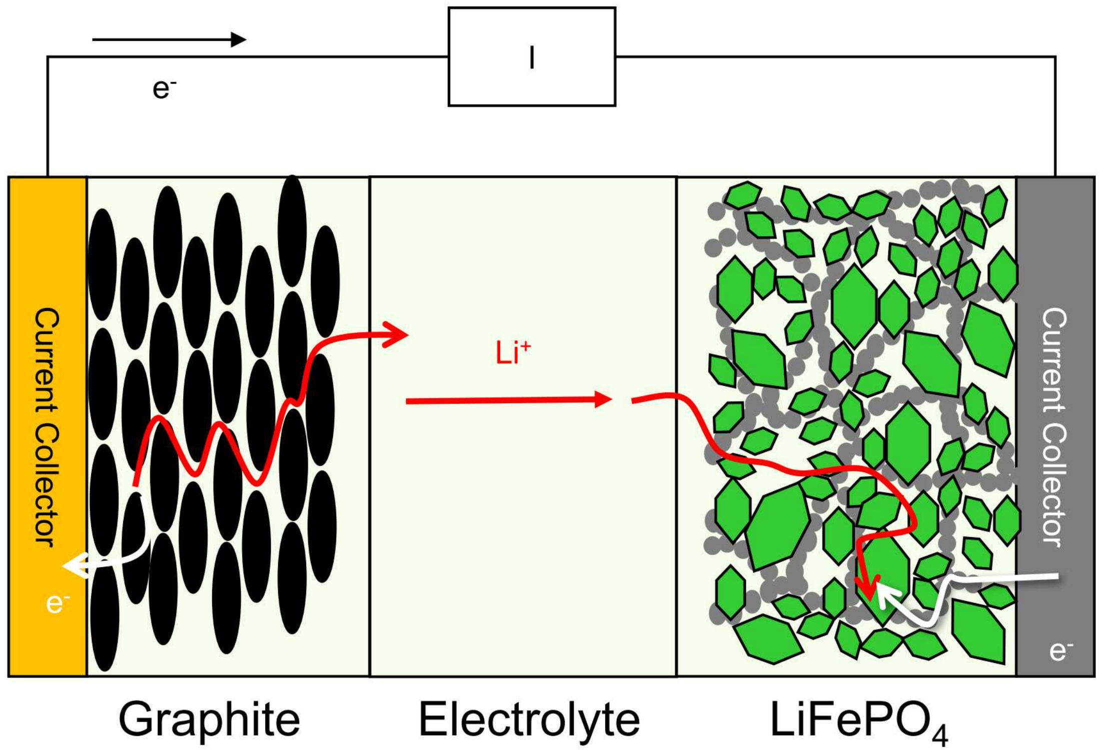


$LiCoO_2 \leftrightarrow CoO_2$ $C_6 \leftrightarrow LiC_6$

Modulating the material composition through current and voltage.
Alter solid-state chemistry through electronic signals

Ion insertion in a Li-ion battery





$$Energy = QV$$
$$Q = e\, n_{Li}$$
$$V = \frac{\Delta G_{rxn}}{e}$$

$$LiC_6 \rightarrow Li^+ + e^- + C_6$$

$$Li^+ + e^- + FePO_4 \rightarrow LiFePO_4$$

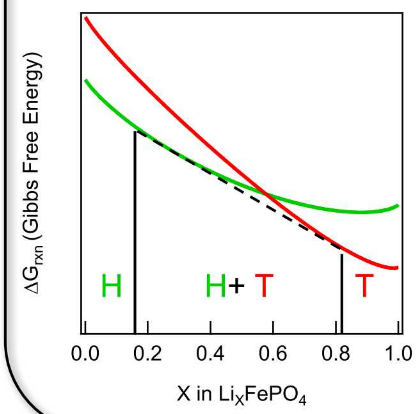
Net Reaction: $LiC_6 + FePO_4 \rightarrow C_6 + LiFePO_4$

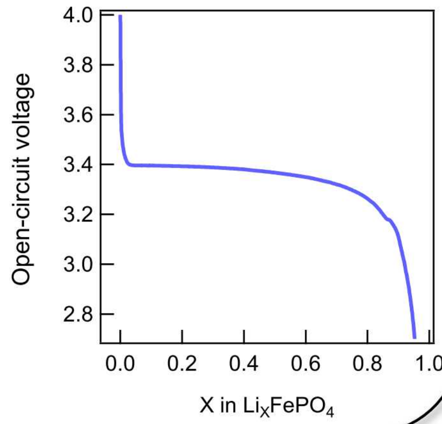
$$\Delta G = -320 \frac{kJ}{mol}$$
$$V = -\frac{\Delta G}{nFe} = 3.4\ V$$

Discharge: inserting Li into Li_XFePO_4
Charge: removing Li from Li_XFePO_4
C-rate: current to (dis)charge in 1 hr
2C: 30 min (dis)charge

Phase separation in Li_XFePO_4

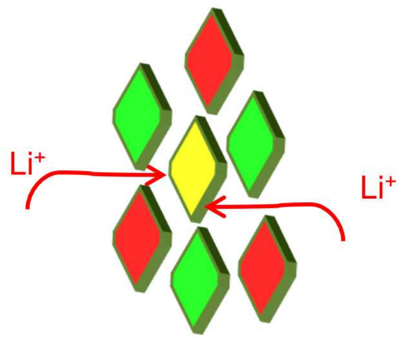
Large miscibility gap



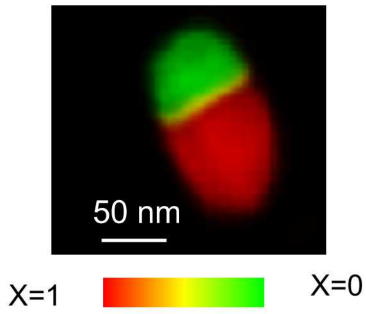


Phase separation

Inter-particle



Intra-particle

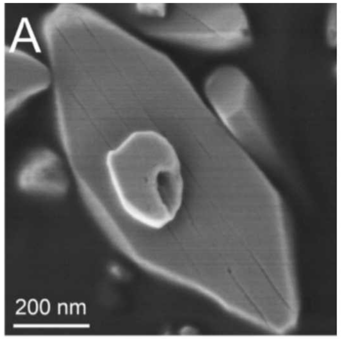


Y. Li et al. *Nature Mater.* **13**, 1149-56 (2014)

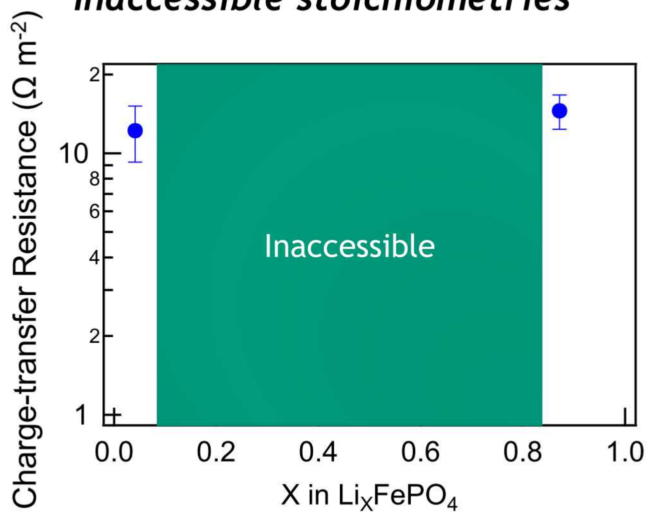
Consequences of phase separation

Mechanical strain

Yu et al. *Nano Lett.* (2015)



Inaccessible stoichiometries

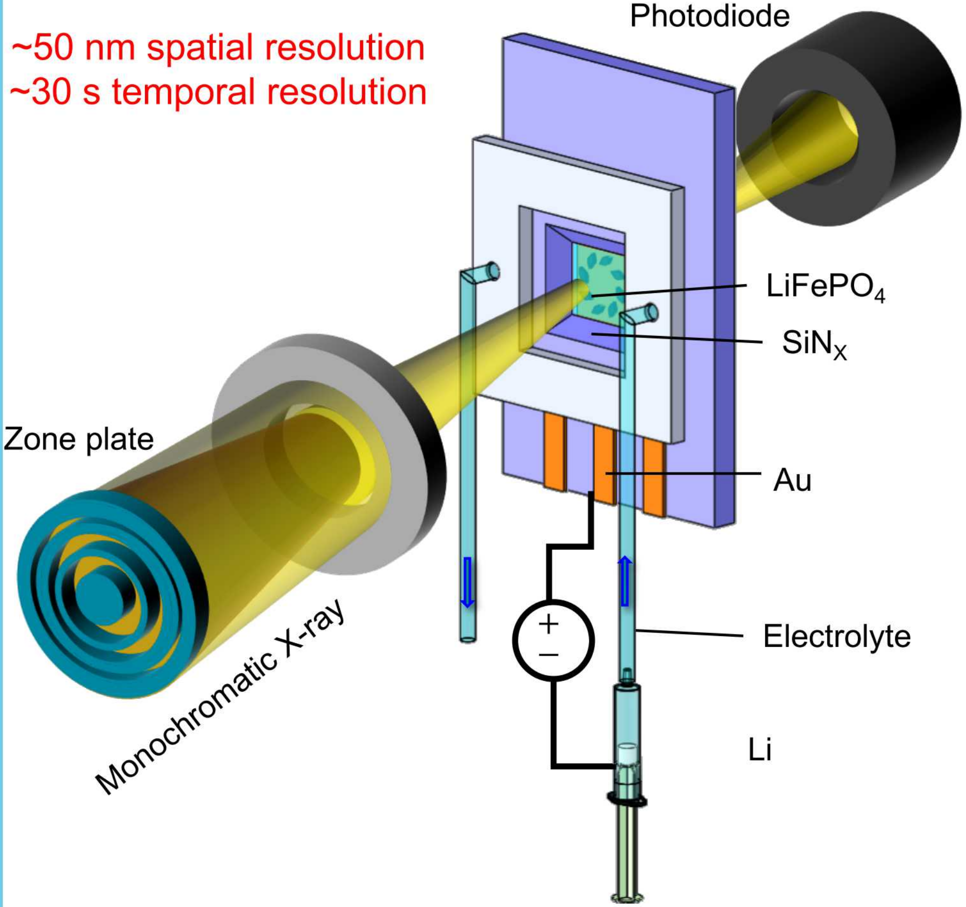


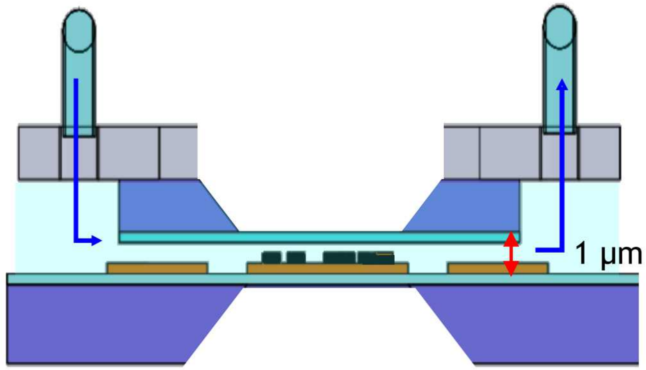
Goal: identify how to control phase separation

Visualizing battery (dis)charge using in situ X-ray microscopy

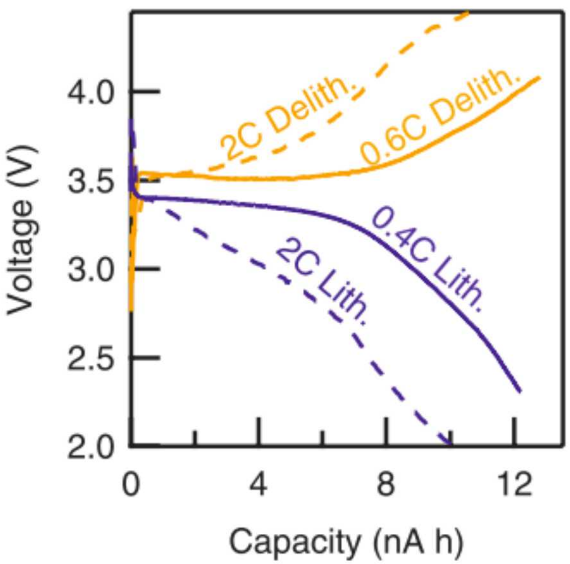
Tracking lithium insertion during cycling

~50 nm spatial resolution
~30 s temporal resolution



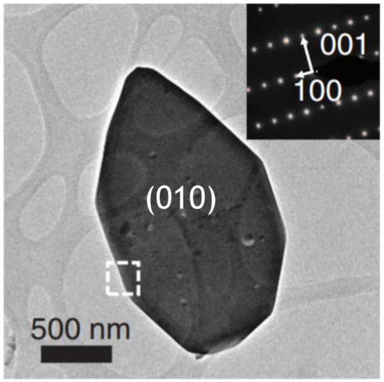


Robust electrochemical cycling

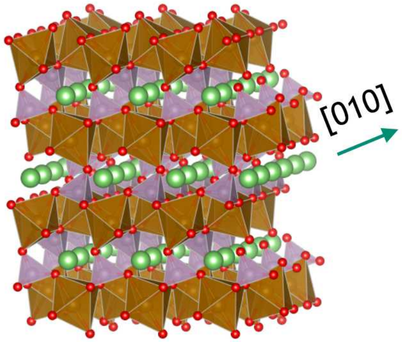


J. Lim*, Y. Li*, et al. *Science*, **353**, 566-571 (2016)
*equal contribution authors

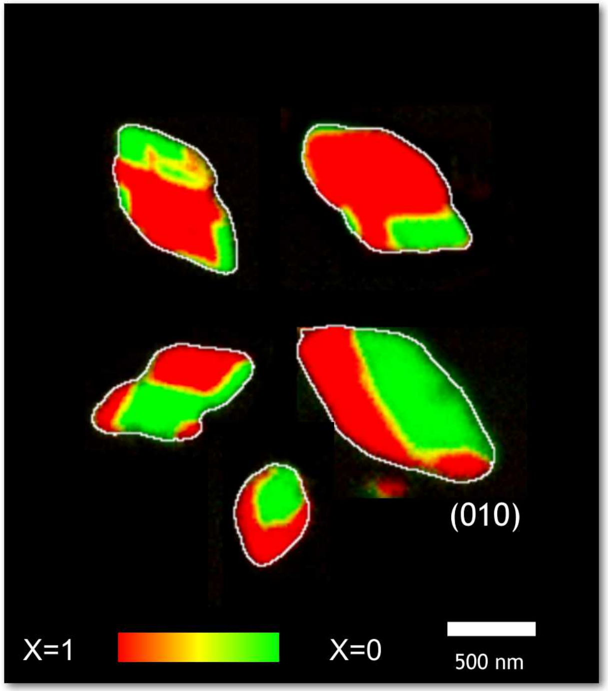
Tracking lithium insertion within particles *in situ*



100-nm thick single crystalline particles



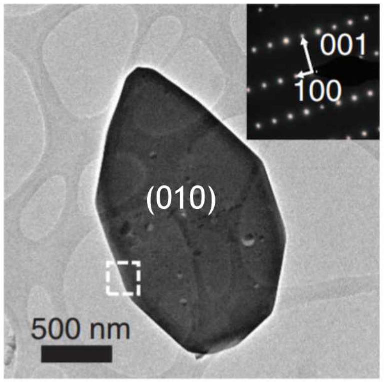
One dimensional lithium conductor



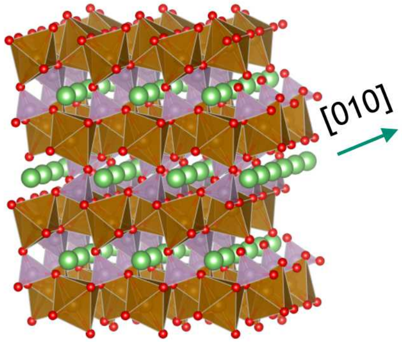
Equilibrium & slow rates

J. Lim*, Y. Li*, et al. *Science*, **353**, 566-571 (2016)
*equal contribution authors

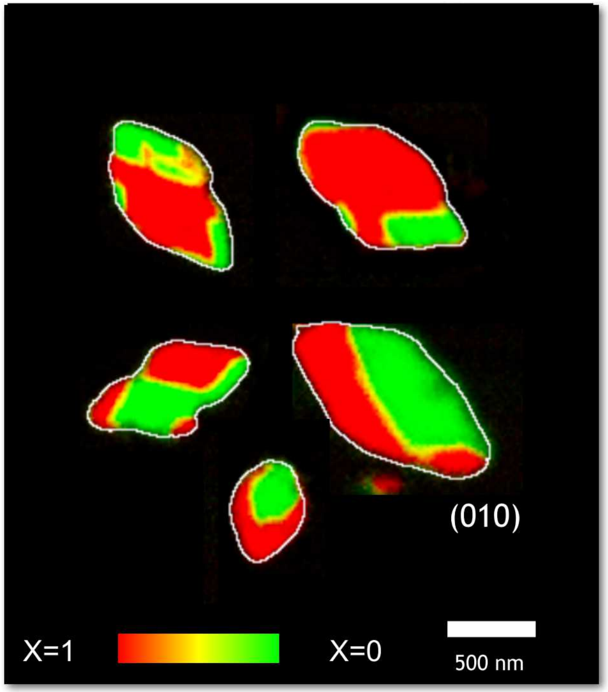
Tracking lithium insertion within particles *in situ*



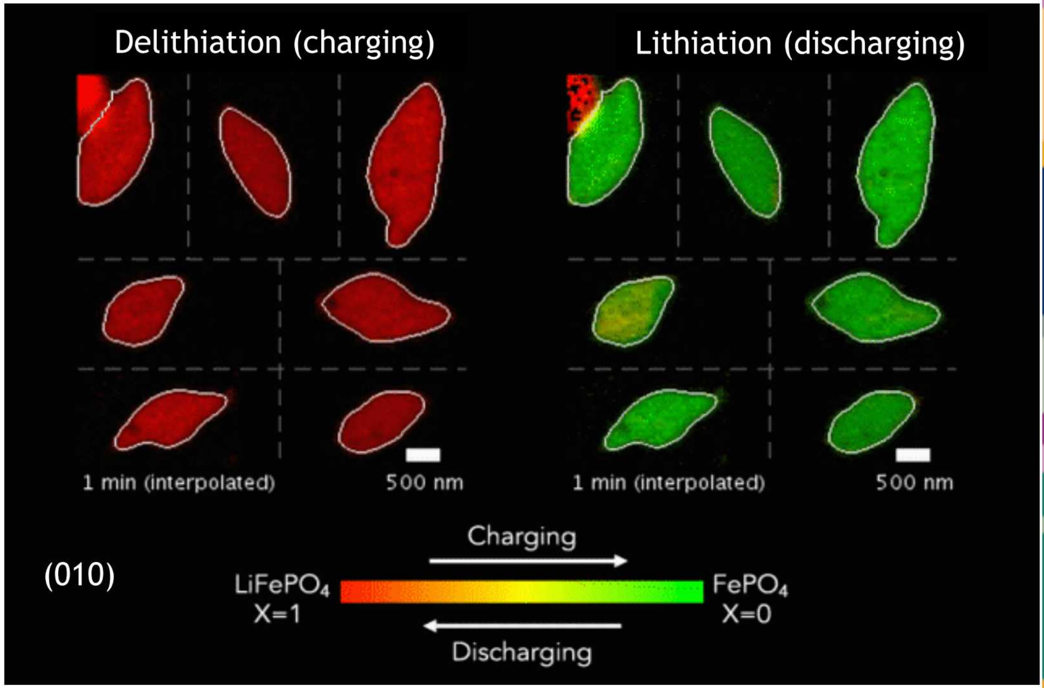
100-nm thick single crystalline particles



One dimensional lithium conductor

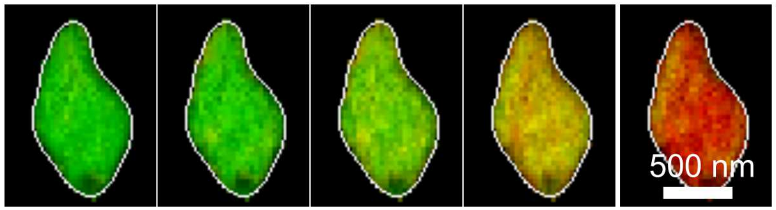


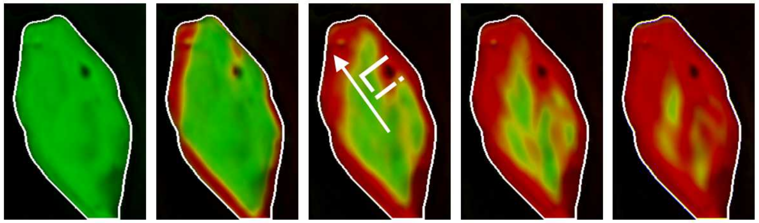
Equilibrium & slow rates



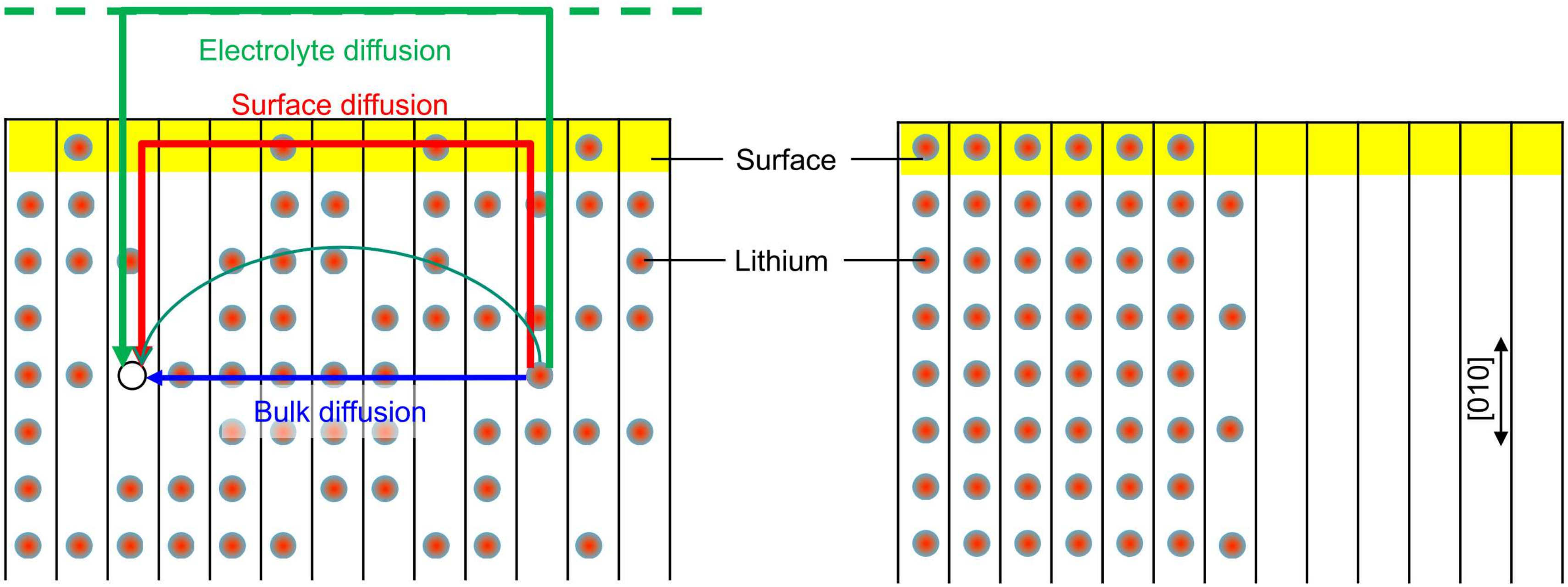
Nonequilibrium lithium insertion

How do we prevent phase separation?



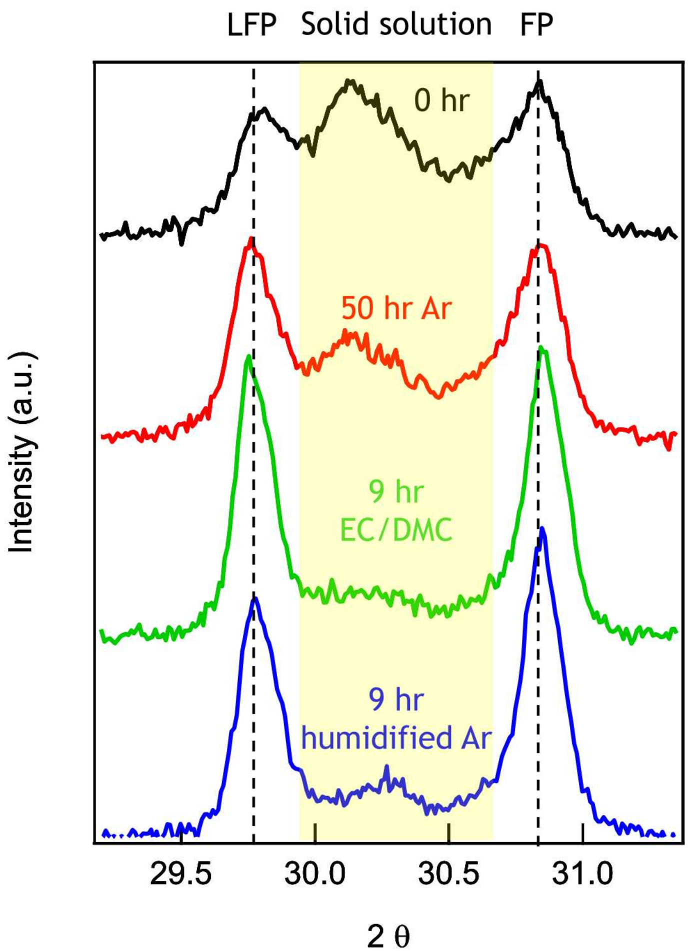


Lithium must diffuse along the non-conducting directions for phase separation



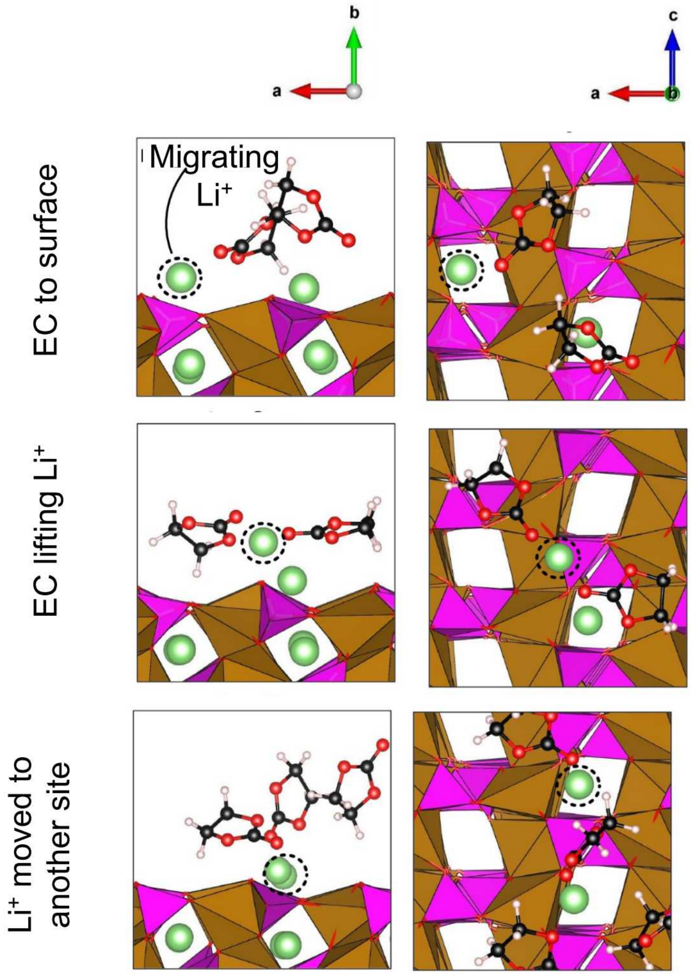
How do we prevent lithium from migrating between channels?

Lithium migration pathway



Fluid molecules enhance phase separation rate. Lithium migrates at the surface

Li, Chen, Islam, Bazant, Chueh et al. submitted



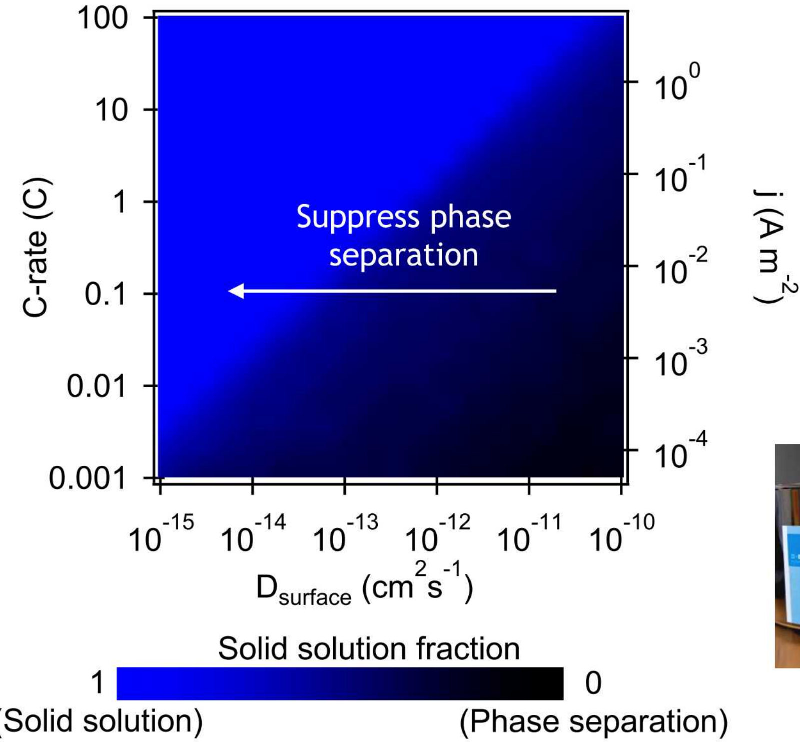
MD shows solvent-assisted lithium migration

Collaboration: Hungru Chen & Saiful Islam, Univ of Bath

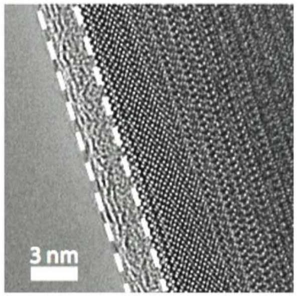
Surface diffusion controls phase separation

Cahn-Hilliard: $$\frac{\partial X}{\partial t} = \nabla \left[\frac{D}{k_B T} X(1-X)\,\nabla \mu_{Li}\right] + j(X, \mu_{Li})$$

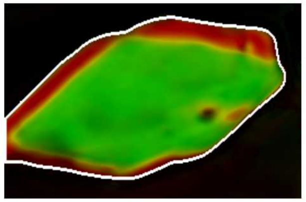
$$\mu_{Li} = \Omega(X)(1-X) + k_B T \ln \frac{X}{1-X} - \kappa \nabla^2 X + \ \ldots$$



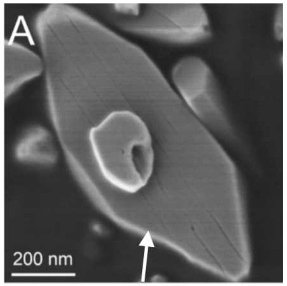
Coating



Phase boundary:
2-4% lattice mismatch
>1 GPa stress

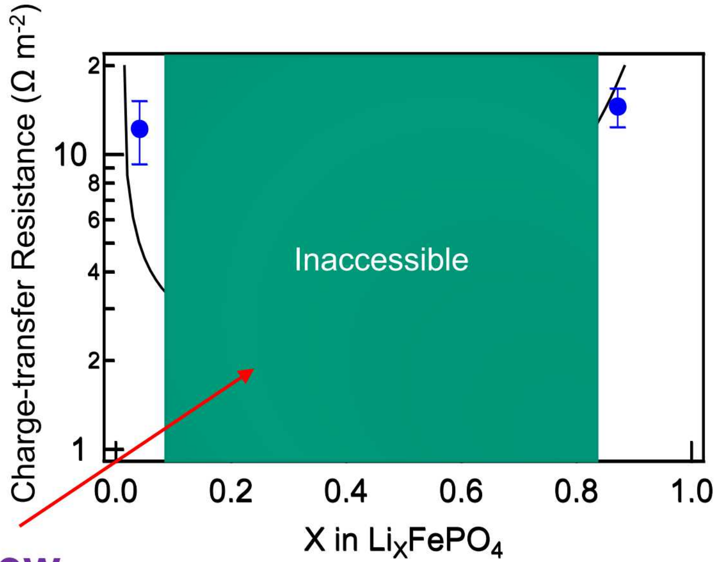


Yu et al. *Nano Lett.* (2015)

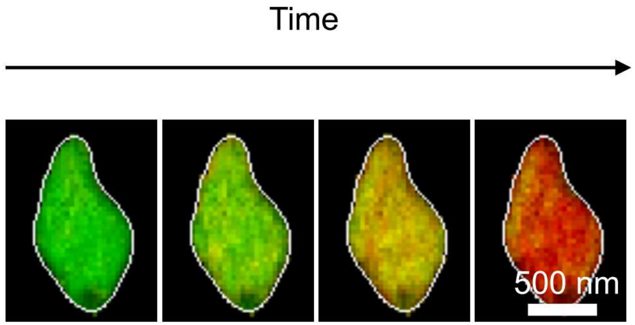


Cracks

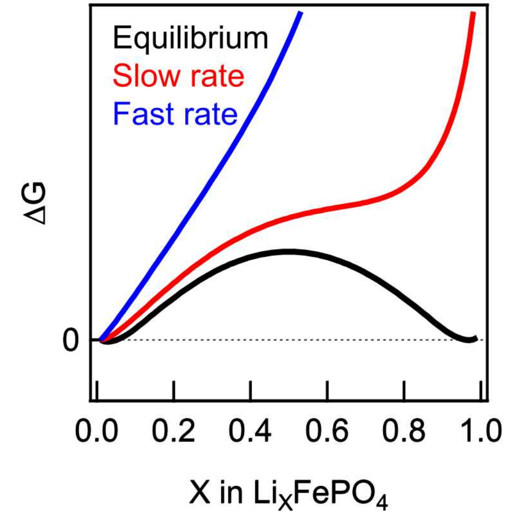
Interfacial reaction controls bulk thermodynamics

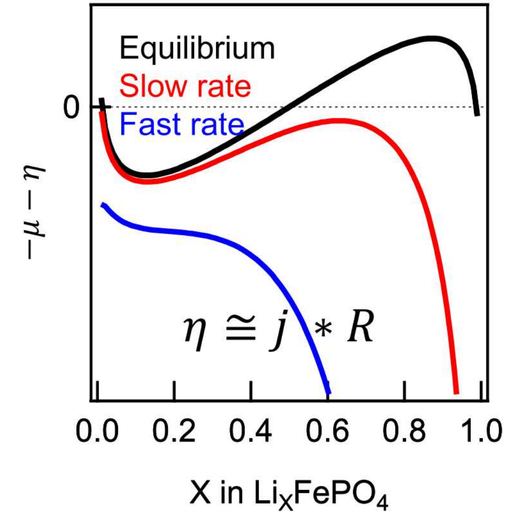


Skew



Lithium composition
Current density
Voltage





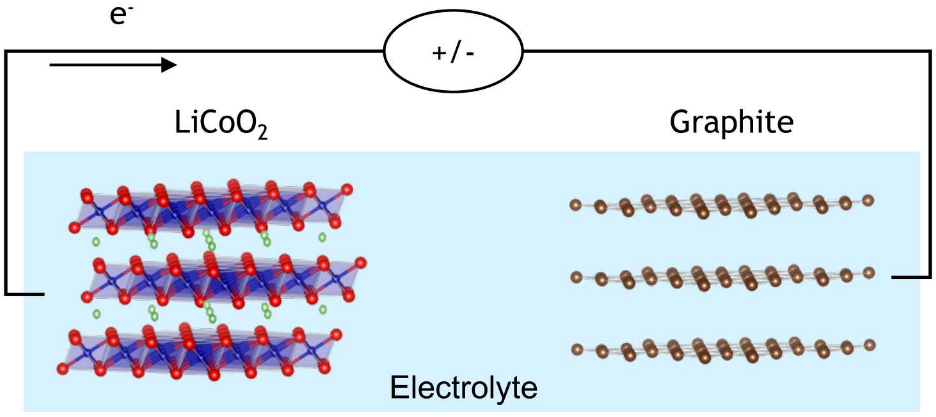
This shape of the resistance suppresses the driving force for phase separation

J. Lim*, Y. Li*, et al. *Science*, **353**, 566-571 (2016)

M. Bazant, Faraday Discussions, **199**, 423-63 (2017)

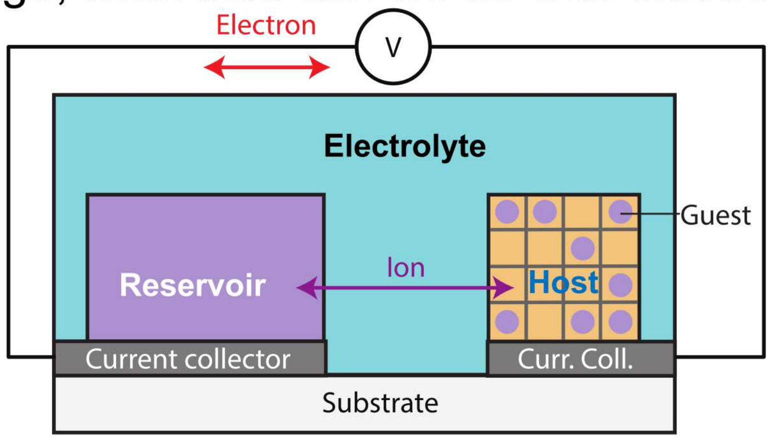
Electrochemical ion insertion

Modify chemical stoichiometry and conduct solid-state chemistry using current and voltage



$LiCoO_2 \leftrightarrow CoO_2$ $C_6 \leftrightarrow LiC_6$

Beyond energy storage, what else can we do with electrochemical ion insertion?



Ion insertion electronic device

Li, Chueh. Ann. Rev. Mater. Res. In press

Artificial neural networks and deep learning

Computers are really fast and efficient at task-specific programming

$$\frac{dx}{dt} = x^2$$

```
x=1;
dt = 0.01;
for i = 1:1000 {
    dxdt = x.^2;
    xnew = dt*dxdt;
    x = xnew; }
end
```

Computers struggle when there are no clear instructions for the task

Which one of these images is a cat?

Image recognition, online advertisement, autonomous driving

Artificial neural networks: how can a machine learn to do an operation through repeated training?

Solution: conduct matrix multiplications, while tuning the weights of the matrix

$$\begin{bmatrix} y_1 \\ \vdots \\ y_m \end{bmatrix} = \begin{bmatrix} w_{1,1} & \cdots & w_{1,n} \\ \vdots & \ddots & \vdots \\ w_{m,1} & \cdots & w_{m,n} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$$

Andrew Ng, Coursera

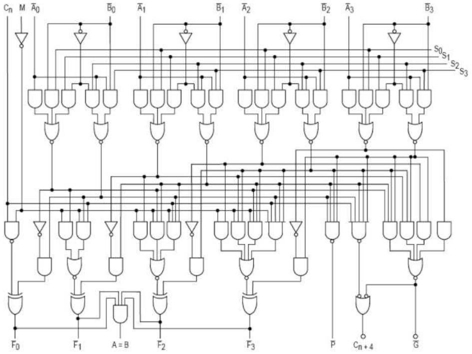
n, m > 1000

Digital vs analog computation

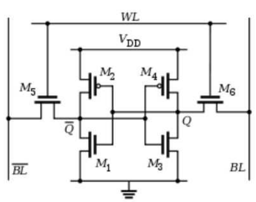
$$\begin{bmatrix} y_1 \\ \vdots \\ y_m \end{bmatrix} = \begin{bmatrix} w_{1,1} & \cdots & w_{1,n} \\ \vdots & \ddots & \vdots \\ w_{m,1} & \cdots & w_{m,n} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$$

Digital logic

Arithmetic logic unit for multiplication (read)



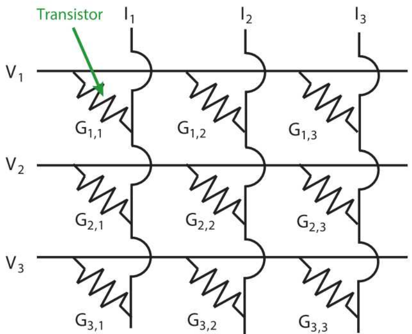
SRAM to store the weights (write)



Uses established CMOS technology

Analog logic

Crossbar for matrix multiplication

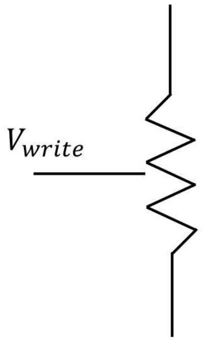


$I_1 = G_{1,1}V_1 + G_{2,1}V_2 + G_{3,1}V_3$

$I_3 = G_{1,3}V_1 + G_{2,3}V_2 + G_{3,3}V_3$

$I_2 = G_{1,2}V_1 + G_{2,2}V_2 + G_{3,2}V_3$

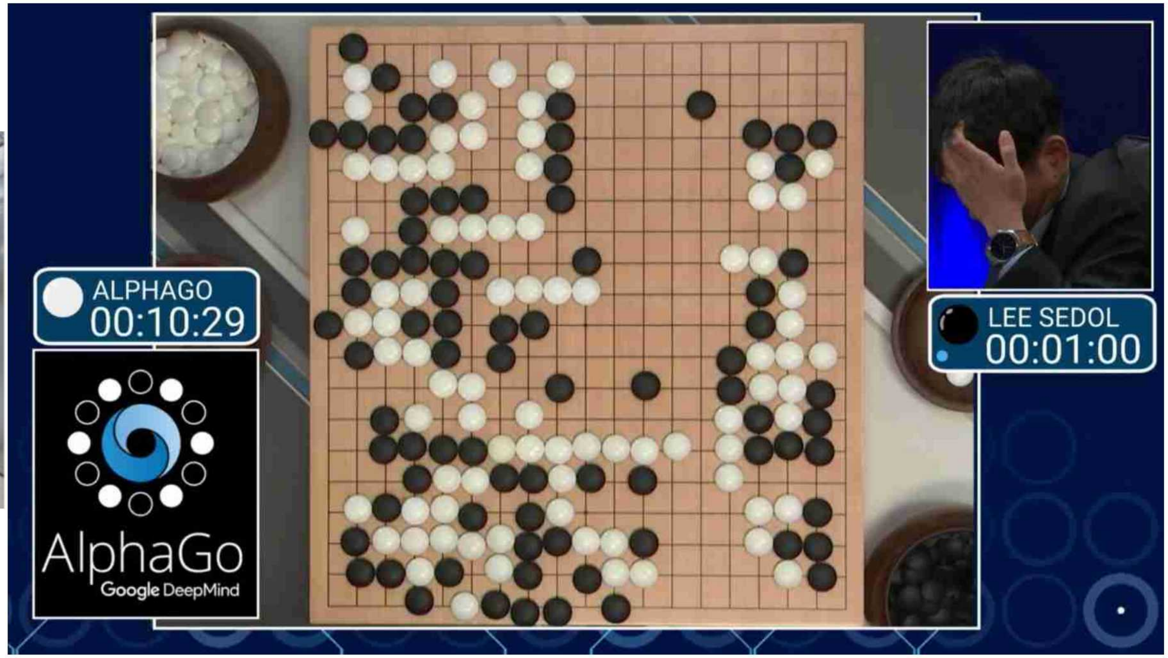
Modulate conductance during training



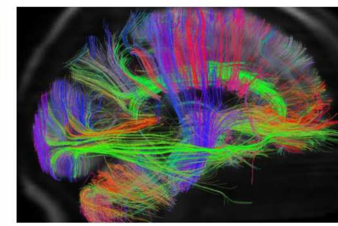
Low power
High parallelism
Simultaneous logic and memory

AlphaGo (digital) vs. Lee Sedol (analog)

64 GPU
19 CPU
4 TPU



the brain ~10 Hz



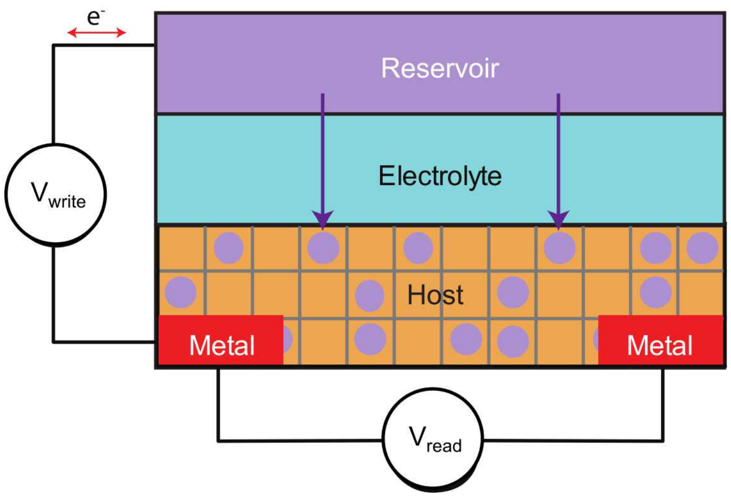
100 billion neurons
100 trillion synapses

AlphaGO: Megawatts

Human brain: 20 watt

Ion insertion, non-volatile redox transistor

Non-volatile tuning of electronic conductance (weight)



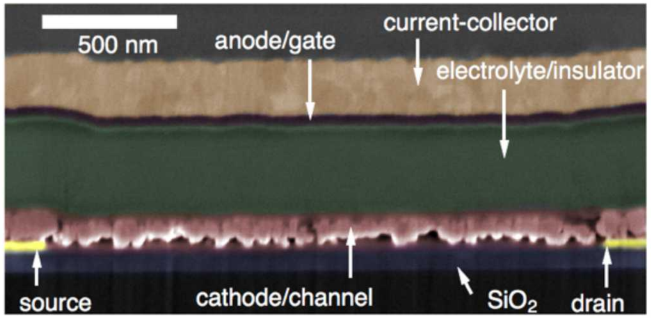
Modulating conductance via doping

n-type: $x\,Li^{+} + xe^{-} + WO_3 \leftrightarrow Li_xWO_3$

p-type: $LiCoO_2 \leftrightarrow Li_{1-x}CoO_2 + xLi^{+} + xe^{-}$

Li, Chueh. Ann. Rev. Mater. Res. In press

SEM cross section



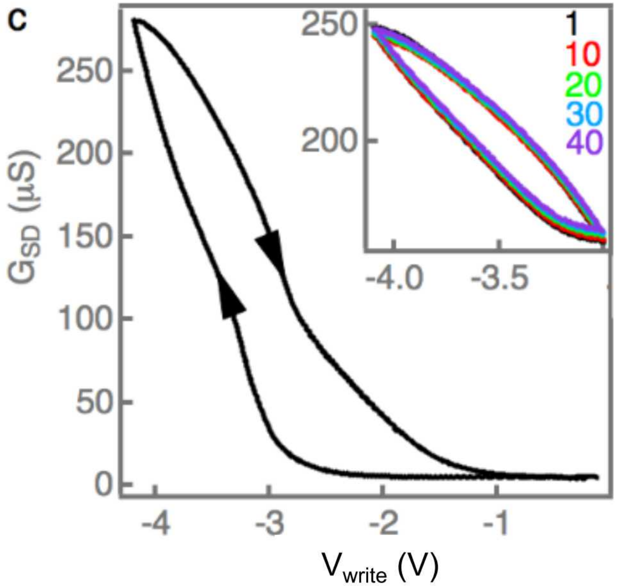
channel electrode: Li_xCoO_2

gate electrode: Li_xSi

solid electrolyte: LiPON

Nonzero open-circuit voltage

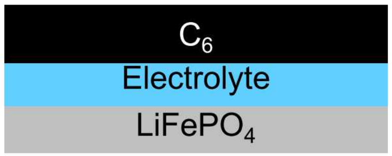
High voltage swing



Fuller et. al., *Adv. Materials*, 29, 1604310 (2017)

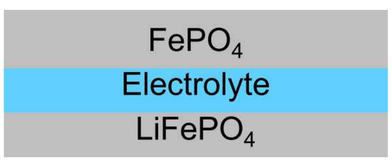
Zero-volt ion insertion transistor

Standard battery:
Different lithium hosts



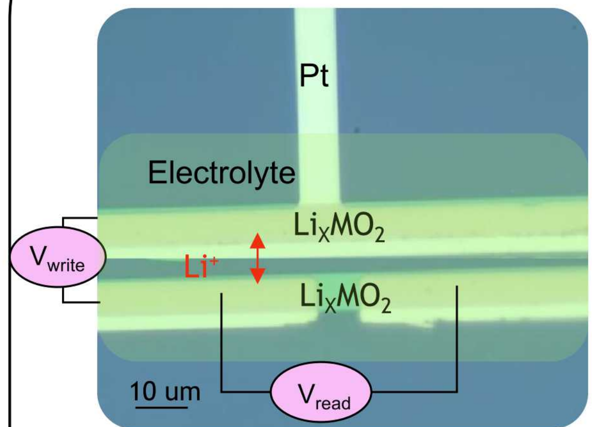
$$LiC_6 + FePO_4 \rightarrow C_6 + LiFePO_4$$
$$\Delta G = -320\,\frac{kJ}{mol}$$
$$V = -\frac{\Delta G}{nFe} = 3.4\,V$$

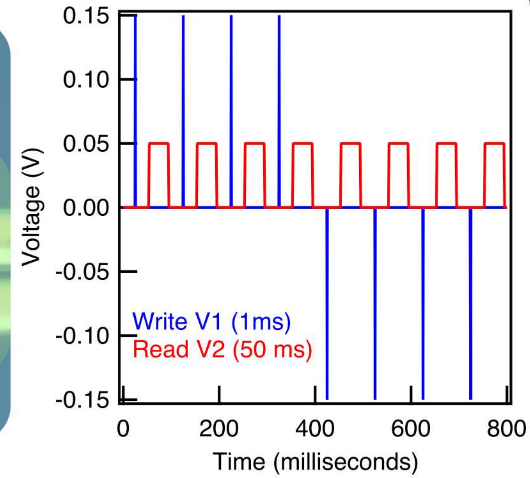
Symmetric battery:
Same lithium hosts

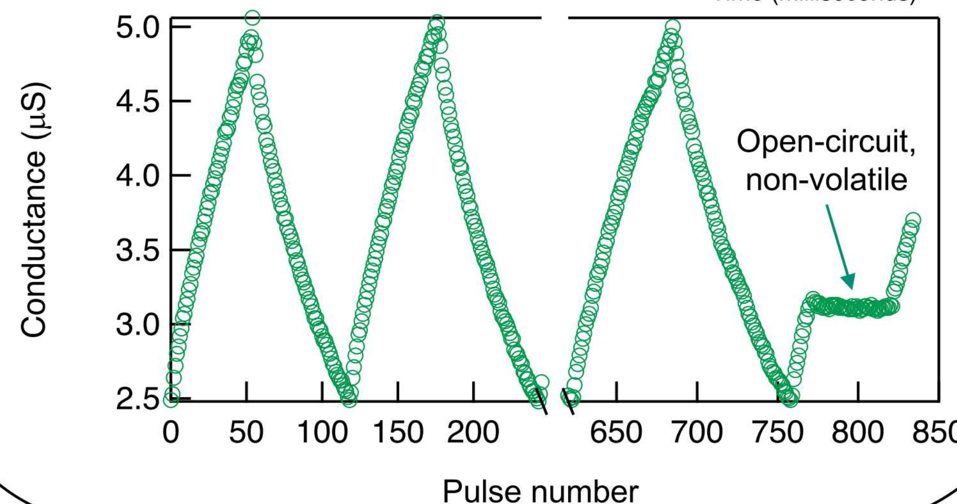


$$LiFePO_4 + FePO_4 \rightarrow FePO_4 + LiFePO_4$$
$$\Delta G \sim 0\ kJ/mol$$
$$V \sim 0\ V$$

Symmetric battery = zero-voltage transistor

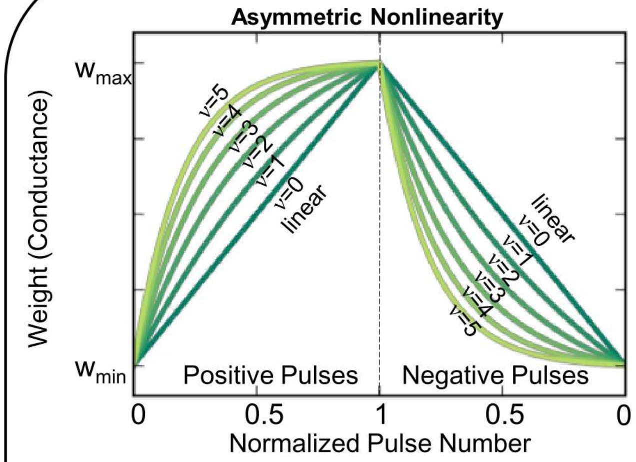


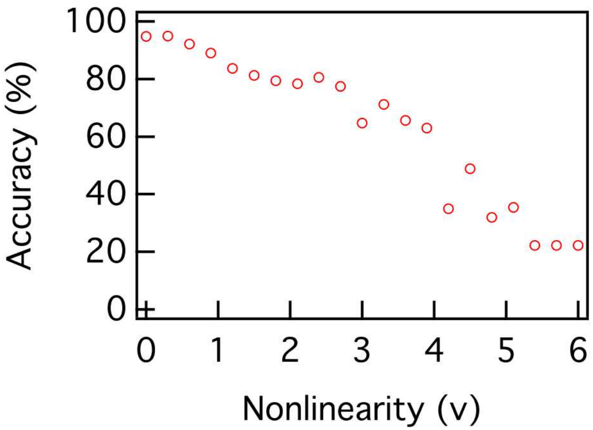




Ion insertion offers high linearity at low write voltages

Linear response allows more accurate and predictable updating of the weights





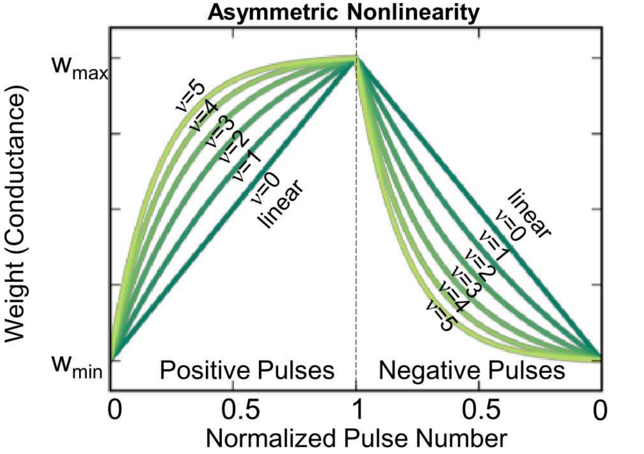
S. Agarwal et al. *IJCNN*, 2016

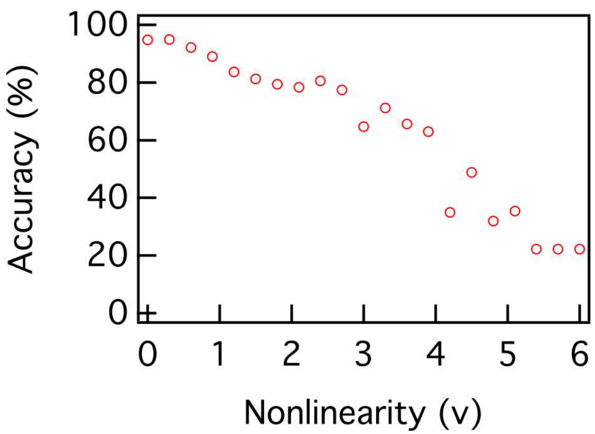
$$\begin{bmatrix} y_1 \\ \vdots \\ y_m \end{bmatrix} = \begin{bmatrix} w_{1,1} & \cdots & w_{1,n} \\ \vdots & \ddots & \vdots \\ w_{m,1} & \cdots & w_{m,n} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$$

Linearity ensures each w can be tuned by a predictable amount.

Ion insertion offers high linearity at low write voltages

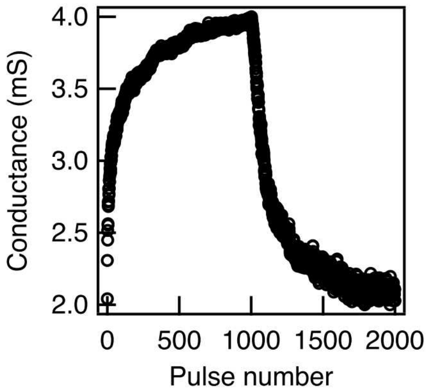
Linear response allows more accurate and predictable updating of the weights



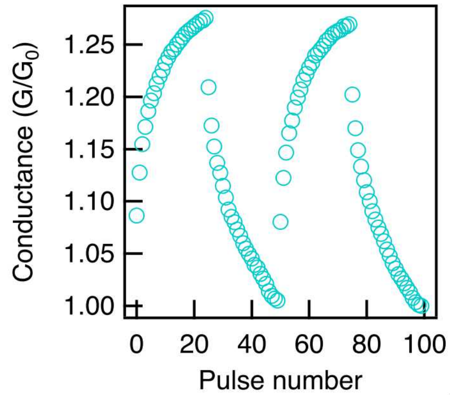


S. Agarwal et al. *IJCNN*, 2016

TaO$_x$ Memristor, ±1 V
$\nu = 4.9$
Accuracy: ~60%



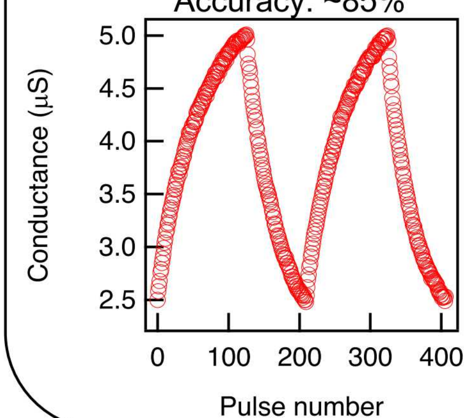
SONOS Flash, ±9 V
$\nu = 3.7$
Accuracy: ~70%



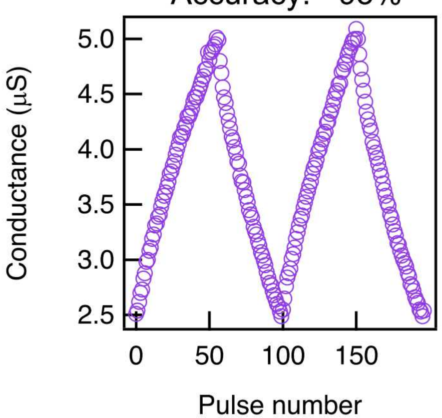
R. Jacobs-Gedrim et al. *ICRC*, 2017

Ion insertion electrode

±50 mV
$\nu = 2.27$
Accuracy: ~85%



±200 mV
$\nu = 0.67$
Accuracy: ~95%

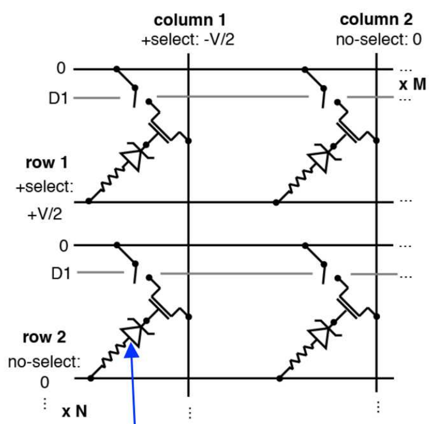


Ion insertion has much higher linearity and much lower power consumption

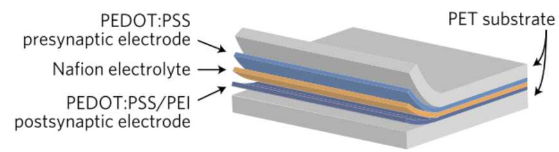
From devices to networks

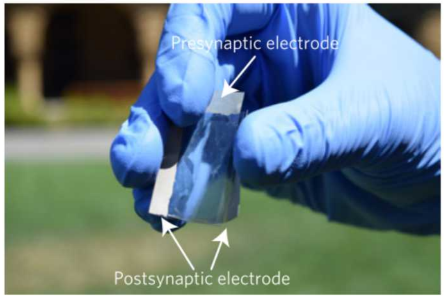
Can we build a parallel network of redox insertion transistors?

N x M Network

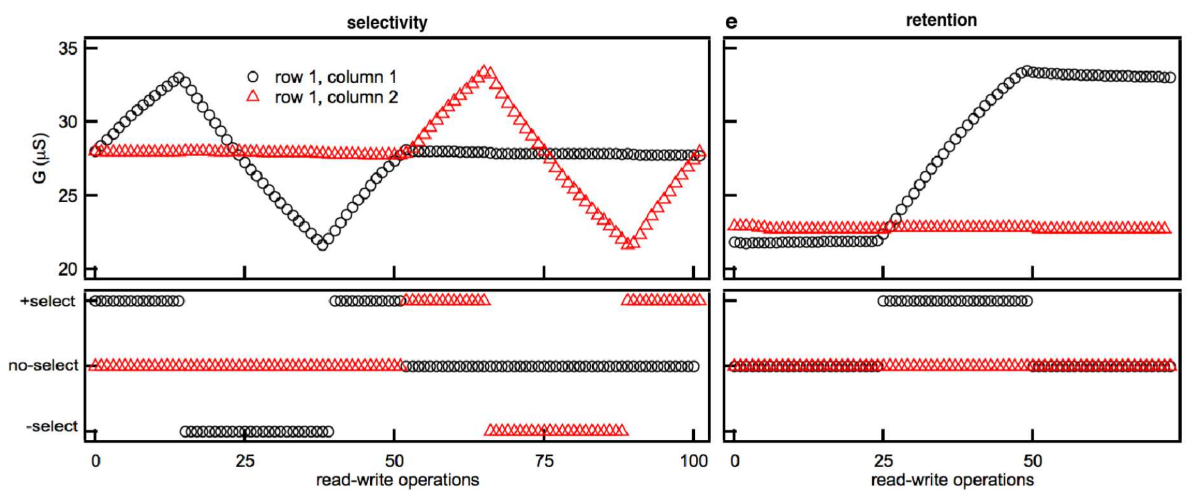


Access device selects certain transistors
to write without disturbing others





Polymer-based insertion transistors



Acknowledgements

Stanford

William Chueh
Jongwoo Lim
Will Gent
Norman Jin

Alberto Salleo
Scott Keene

Berkeley Labs

Tolek Tyliszczak
David Shapiro

MIT

Martin Bazant
Dan Cogswell

Sandia

Alec Talin
Elliot Fuller
Farid el Gabaly
Sapan Agarwal

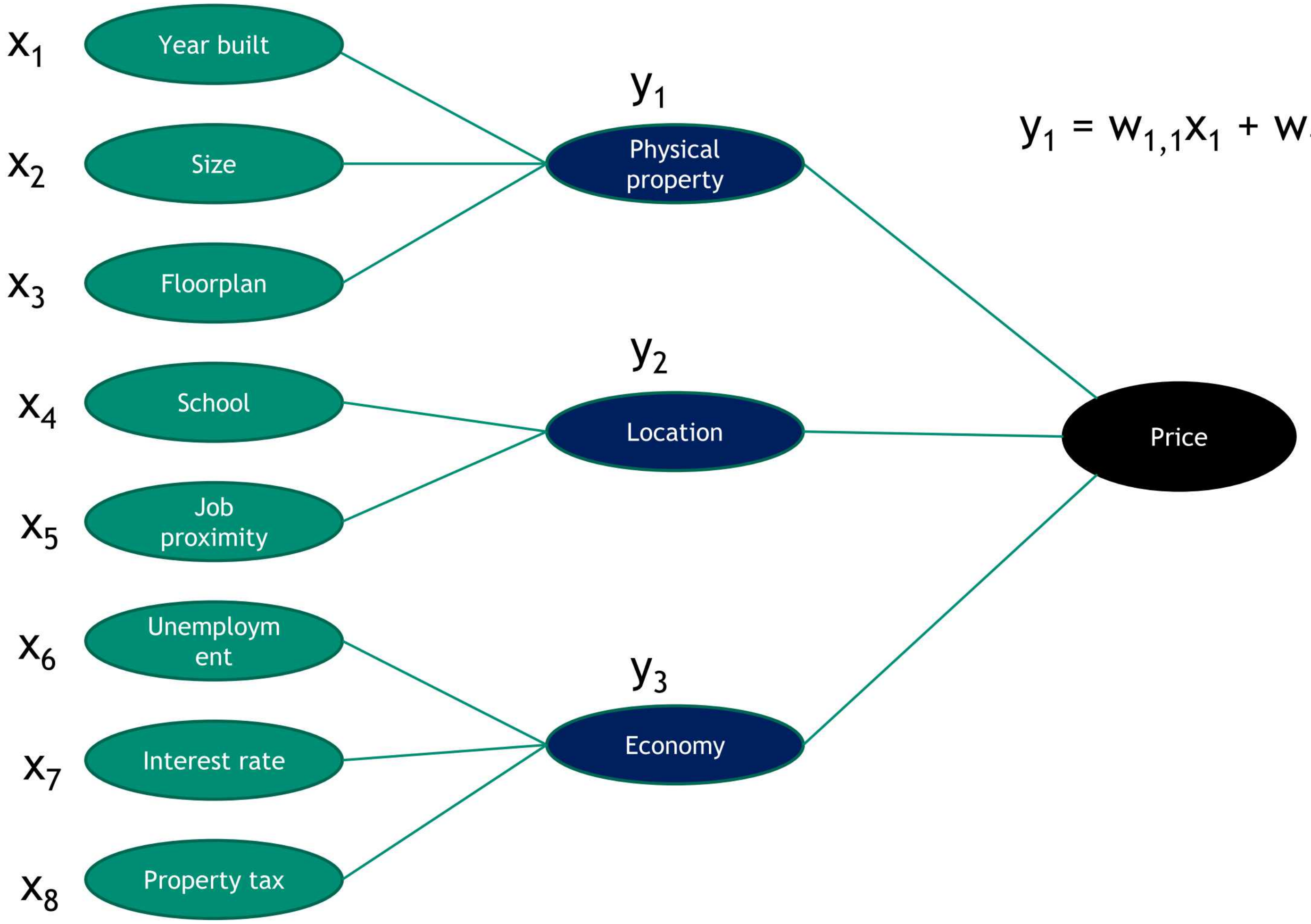
Univ of Bath

Martin Bazant
Dan Cogswell

This work is supported by the Sandia National Laboratories Truman Fellowship Program, which is funded by the Laboratory Directed Research and Development (LDRD) Program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

Matrix multiplication and artificial neural networks

How much is my home worth?

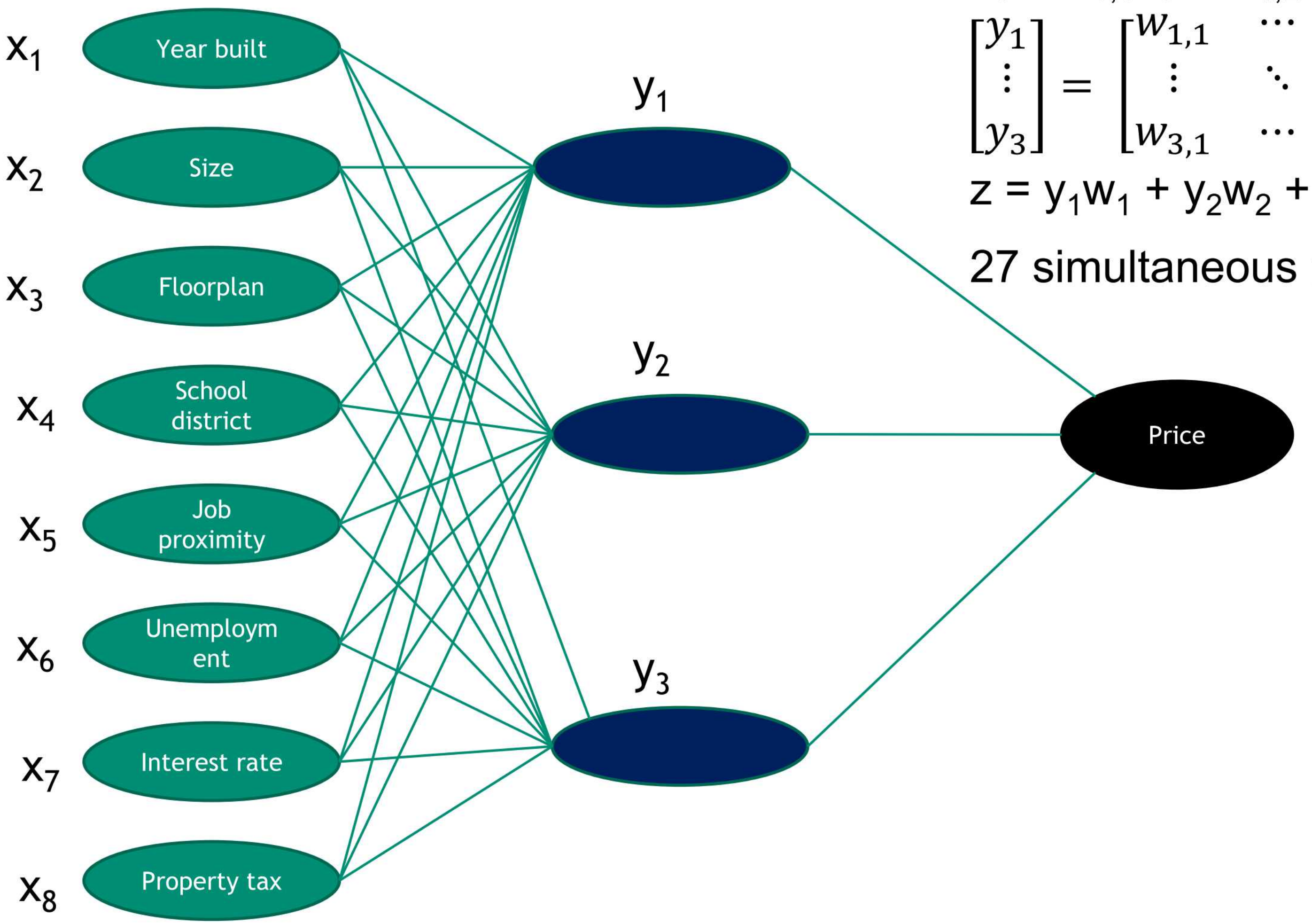


$$y_1 = w_{1,1}x_1 + w_{1,2}x_2 + w_{1,3}x_3$$

Andrew Ng, Coursera

Matrix multiplication and artificial neural networks

How much is my home worth?



$y_1 = w_{1,1}x_1 + w_{1,2}x_2 + \ldots + w_{1,8}x_8$

$$\begin{bmatrix} y_1 \\ \vdots \\ y_3 \end{bmatrix} = \begin{bmatrix} w_{1,1} & \cdots & w_{1,8} \\ \vdots & \ddots & \vdots \\ w_{3,1} & \cdots & w_{3,8} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_8 \end{bmatrix}$$

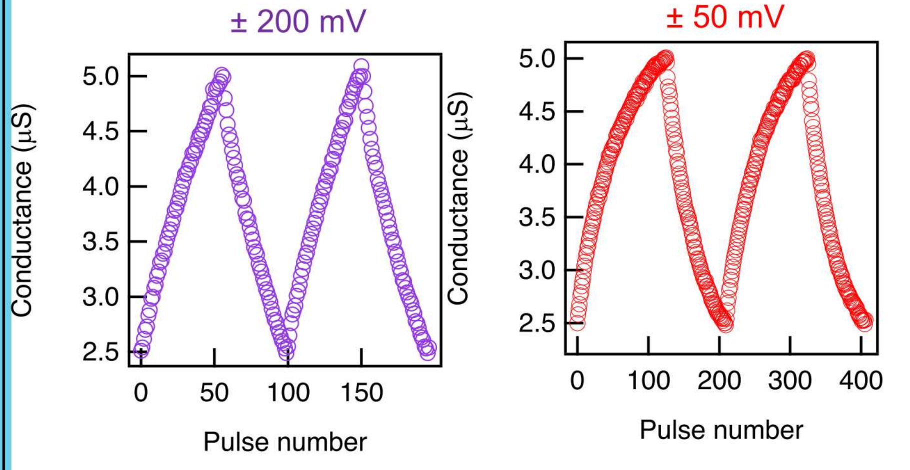
$z = y_1 w_1 + y_2 w_2 + y_3 w_3$

27 simultaneous multiplication

Neural networks often have 100 million weights
Google tensor processor unit does 65k simultaneous multiplications

Voltage pulse and linearity

Why does higher voltage pulses result in more linear response?

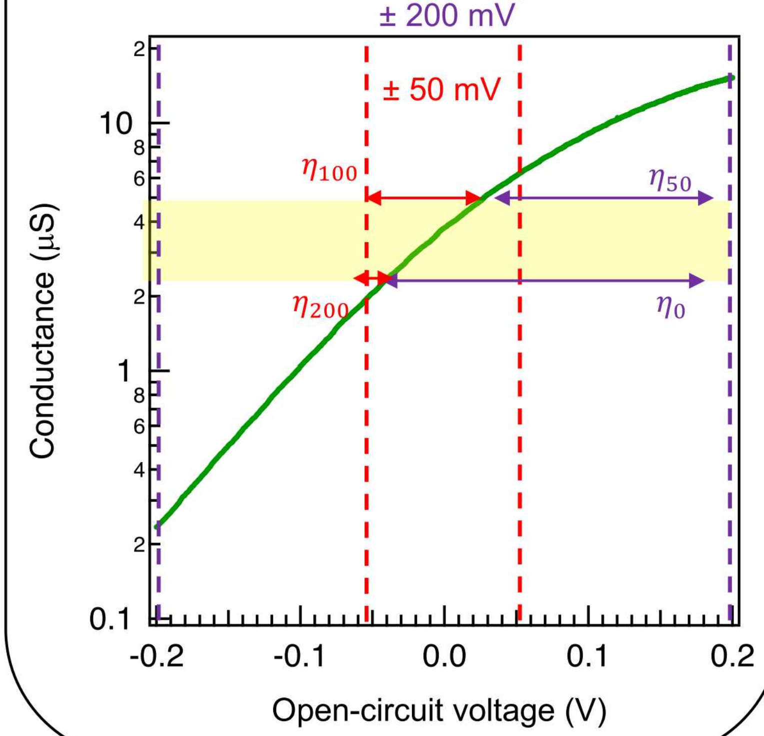


Overpotential decreases **slightly** with pulse number

Overpotential decreases **drastically** with pulse number

The open-circuit potential varies by ~100 mV due to the entropy of lithium

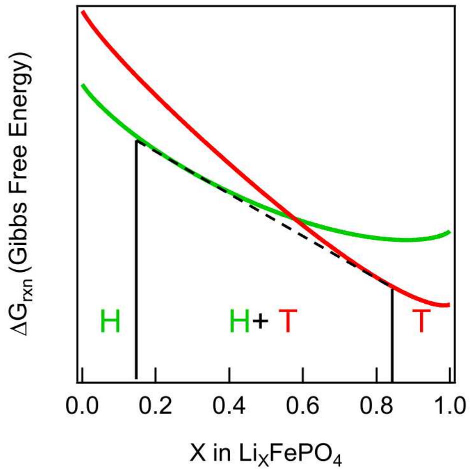
$$\mu = \mathrm{k_b T} \ln \frac{x}{1-x}$$



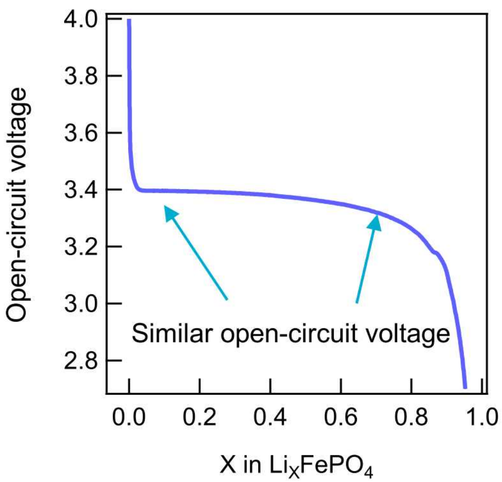
Goal: Find a material with higher dS/dV so the open-circuit voltage does not change with lithium?

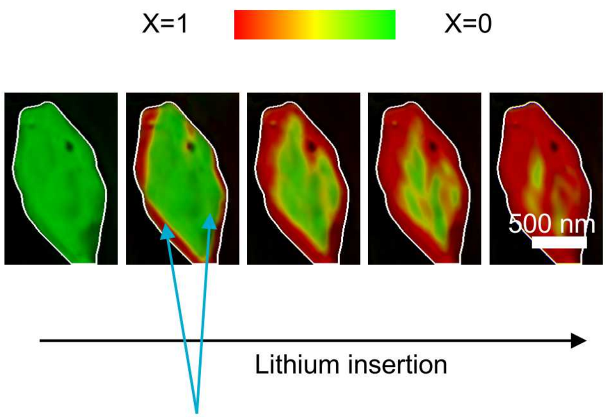
Phase-separation and voltage plateau

Phase separation

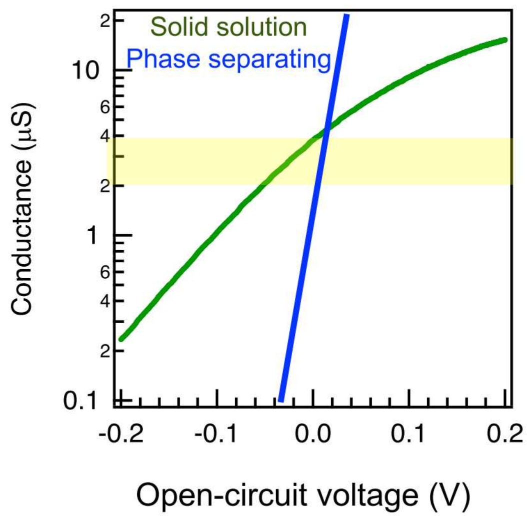


$$Li^{+} + e^{-} + FePO_4 \leftrightarrow LiFePO_4$$





Different lithium doping concentrations
Same chemical potential

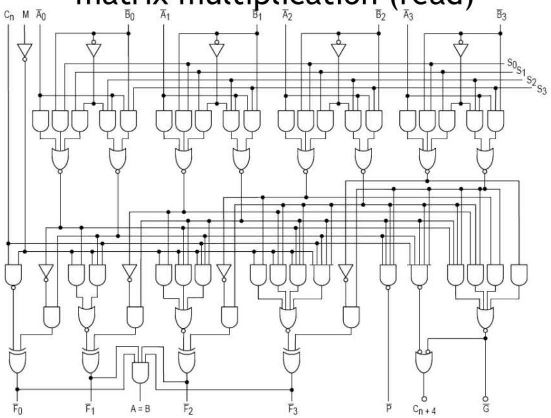


Parallel analog processing

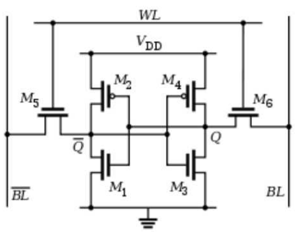
Aim: to mimic the brain and design a low-power device to conduct parallel analog matrix multiplication

Digital logic

Arithmetic logic unit for matrix multiplication (read)

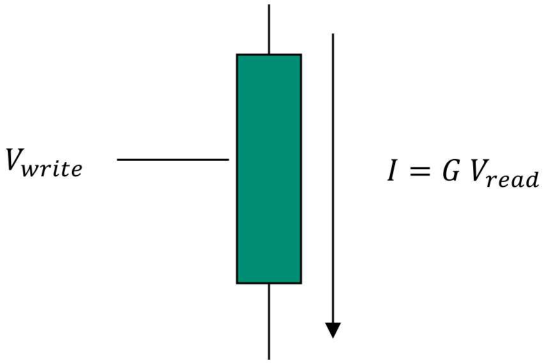


Static RAM for memory of the weights (write)



Analog logic

Computation: modulate G continuously
Memory: G should be non-volatile



$\text{Power} = CV_{write}^2$

Goal: Design devices that can linearly modulate the conductance with analog states, and retain that conductance (non-volatile)