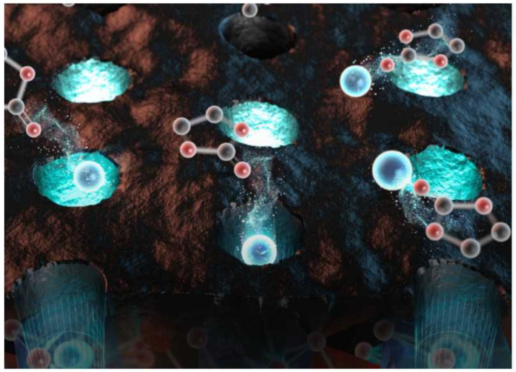
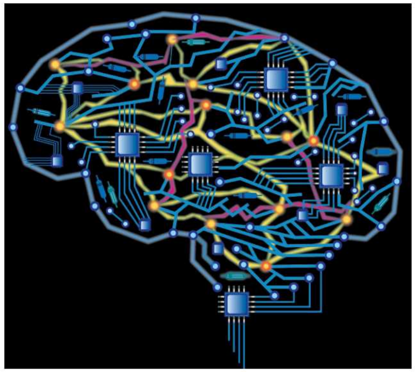
Sandia National Laboratories

SAND2018-13338C

Electrochemical ion insertion for energy storage and computing





PRESENTED BY

Yiyang Li

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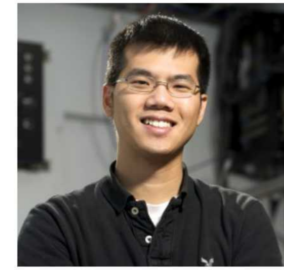

W. Chueh

J. Lim

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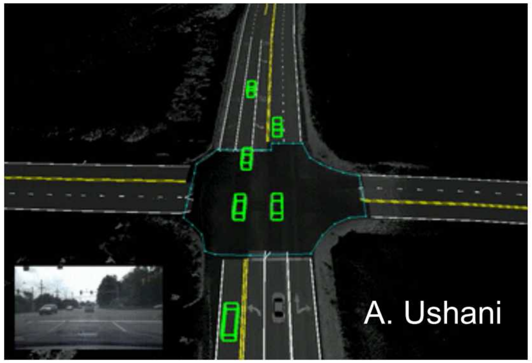
Ion insertion for energy storage and computing

Autonomous electric vehicles

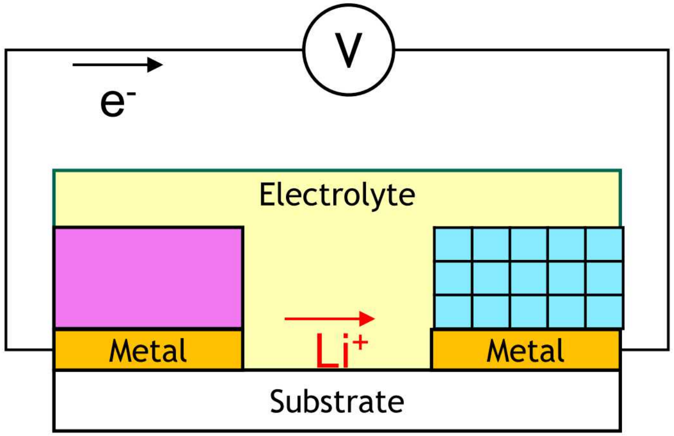
Neural Network



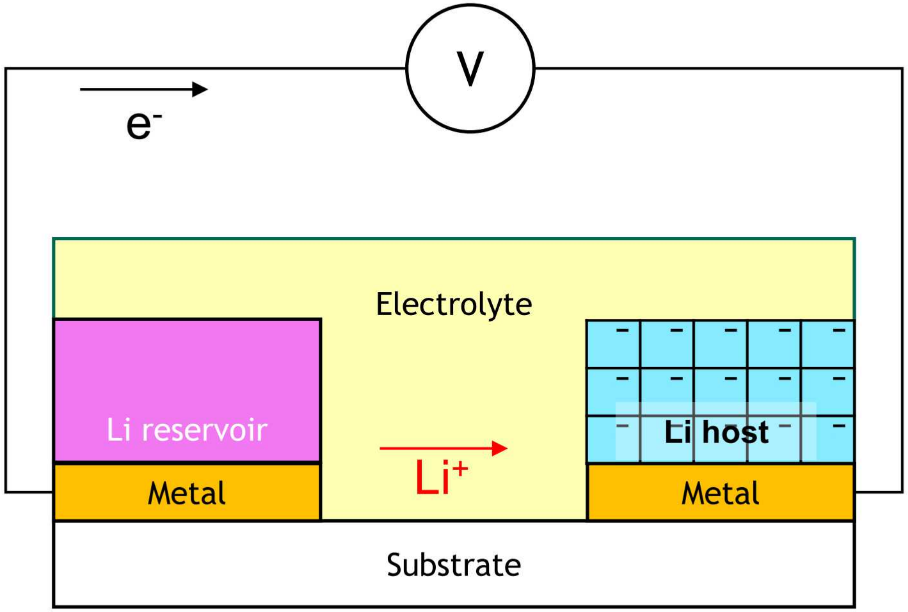
Batteries

Panasonic

Ion insertion



Electrochemical ion insertion controls materials chemistry



$C_6 \Leftrightarrow LiC_6$

$FePO_4 \Leftrightarrow LiFePO_4$

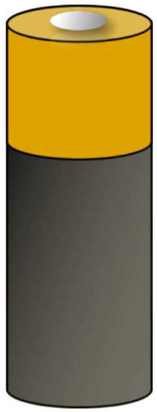
$TiO_2 \Leftrightarrow LiTiO_2$

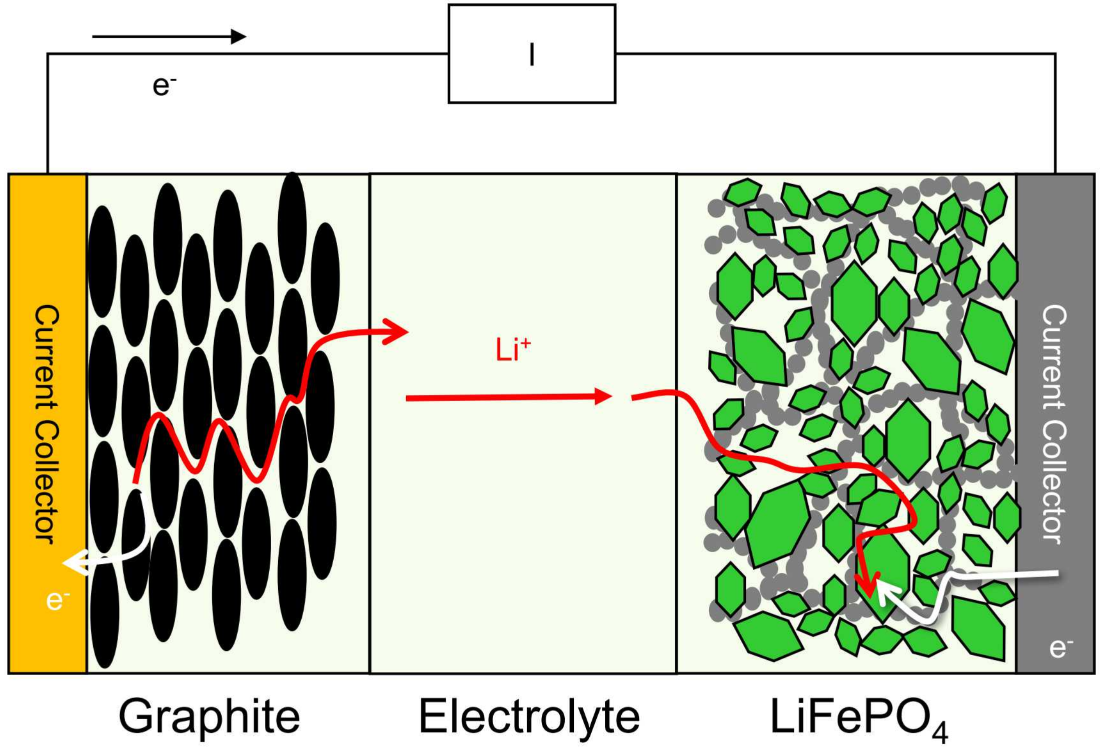
1) Using electronic controls, we alter the material composition of the Li host, conducting solid-state chemistry using current and voltage

2) The ions balance the electron charge, so a large amount of electrons can be moved without an electrostatic voltage

Y. Li, W. Chueh. Ann. Rev. Mater. Res. 48, 137 (2018)

Ion insertion in a Li-ion battery





$$LiC_6 \rightarrow Li^+ + e^- + C_6 \qquad Li^+ + e^- + FePO_4 \rightarrow LiFePO_4$$

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

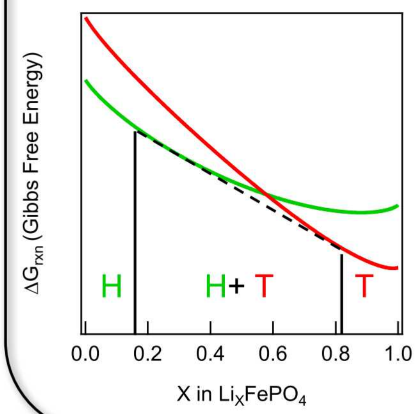
$$\Delta G = -320\,\frac{kJ}{mol}$$

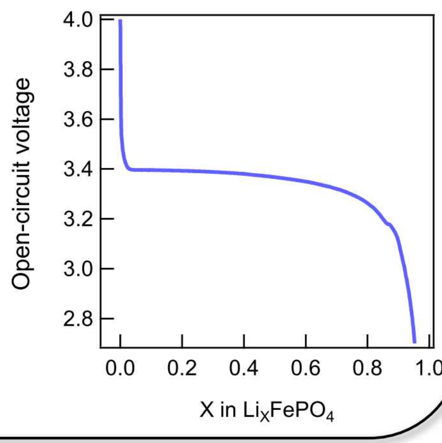
$$V = -\frac{\Delta G}{nFe} = 3.4\ V$$

Discharge: inserting Li into Li_XFePO_4
Charge: removing Li from Li_XFePO_4

Phase separation in Li_XFePO_4

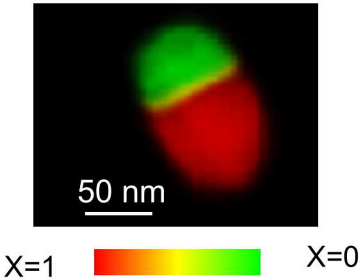
Large miscibility gap





Phase separation

Single battery particle



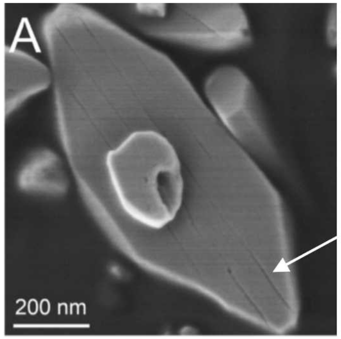
2% lattice mismatch
>1 GPa stress

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

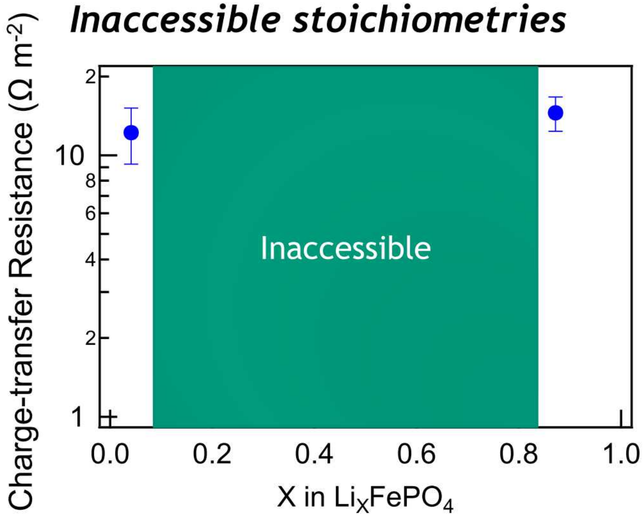
Consequences of phase separation

Mechanical strain

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



Inaccessible stoichiometries

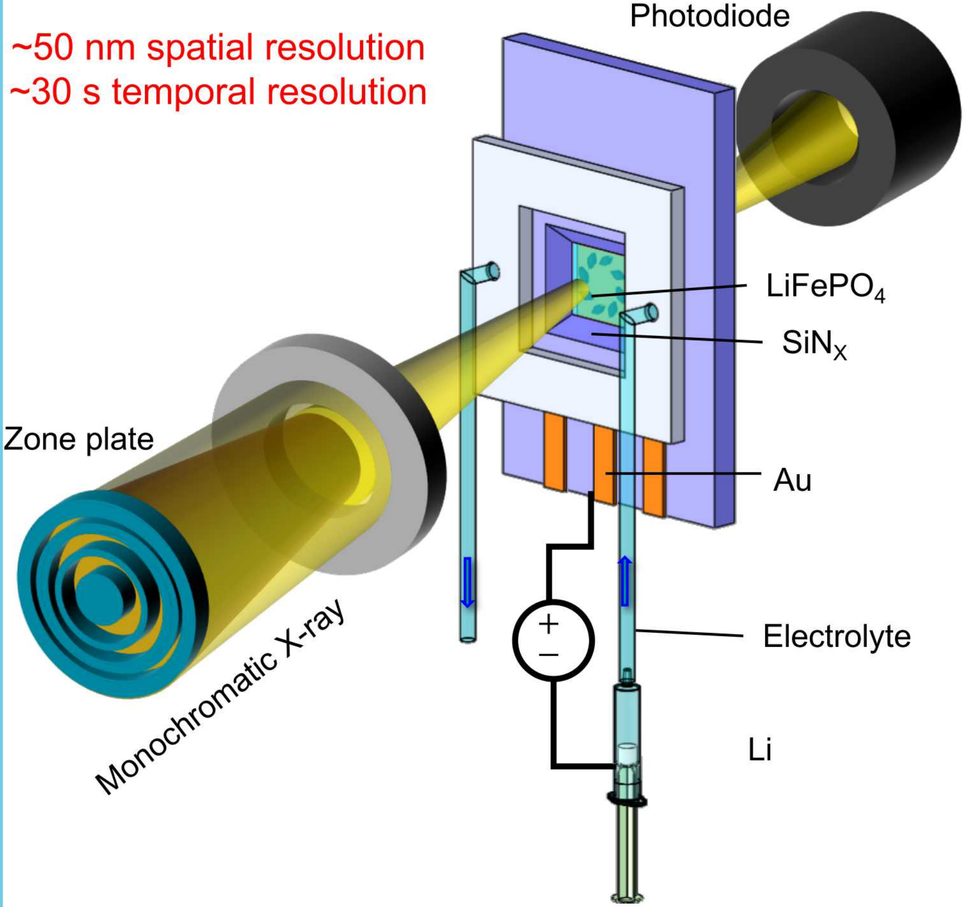


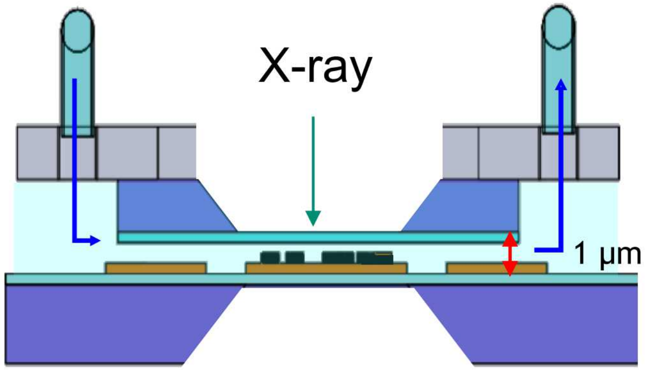
Goal: to understand the kinetics of phase separation and to suppress it

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

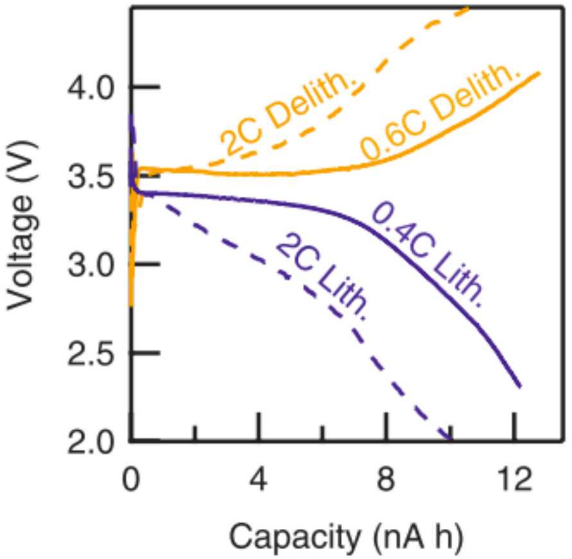
Tracking lithium insertion within individual battery particle building blocks

~50 nm spatial resolution
~30 s temporal resolution



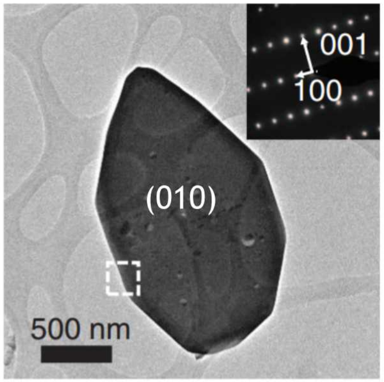


Robust electrochemical cycling

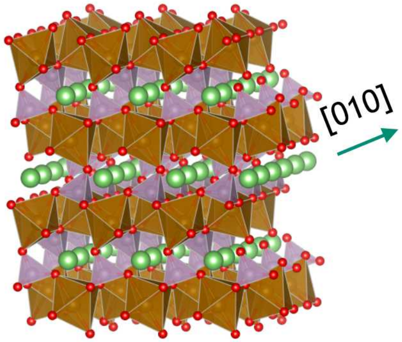


J. Lim[*], Y. Li[*], et al. *Science*, **353**, 566-571 (2016)
*equal contribution authors

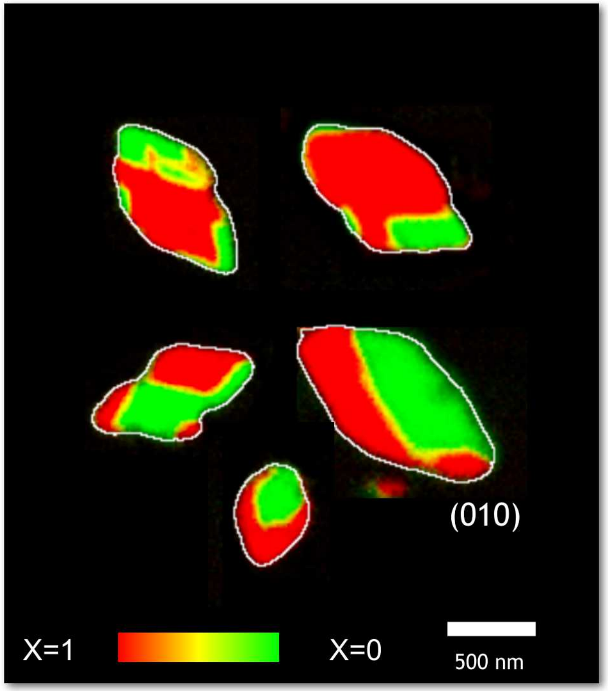
Tracking lithium insertion within particles *in situ*



100-nm thick single crystalline particles



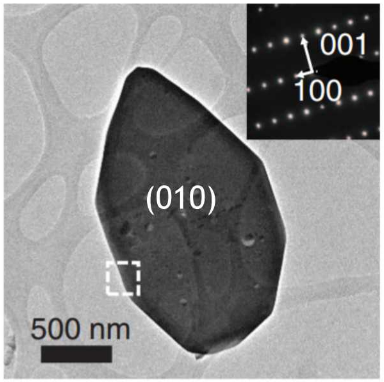
One dimensional lithium conductor



Equilibrium & slow rates

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

Tracking lithium insertion within particles *in situ*



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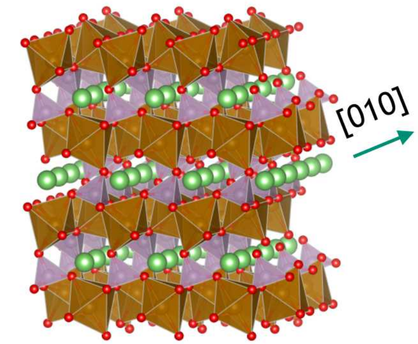

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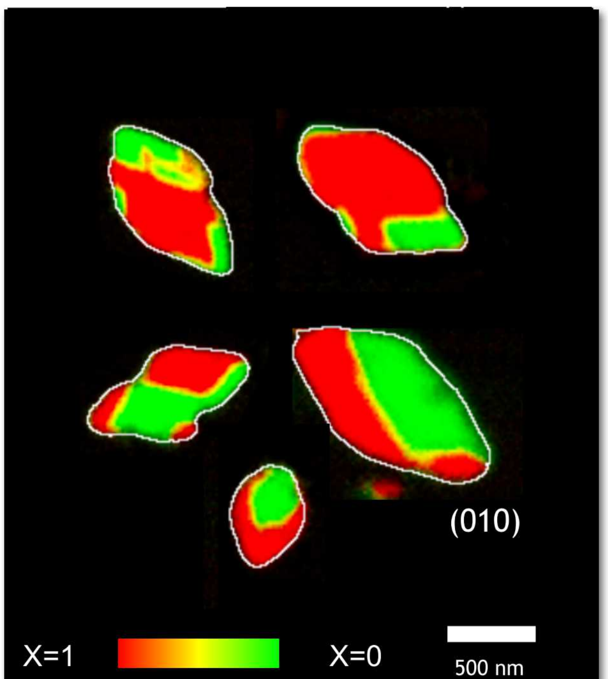

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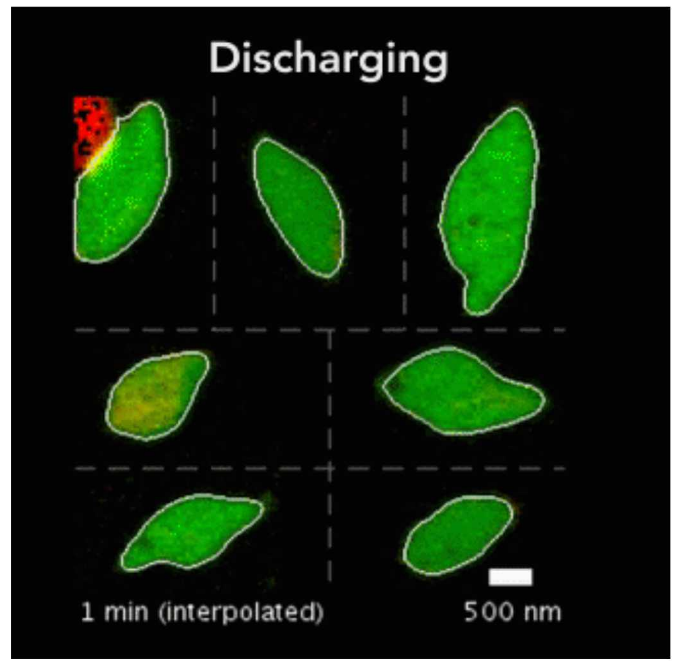
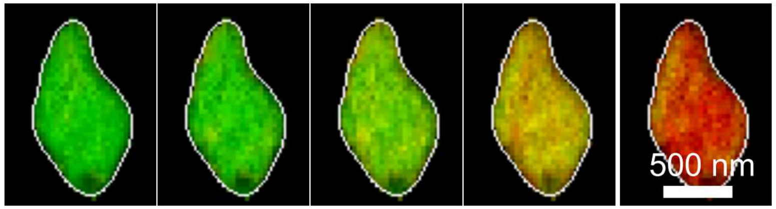
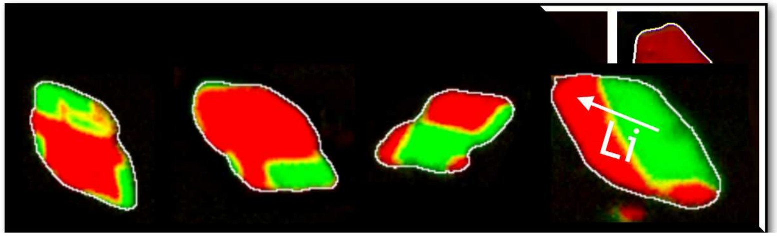


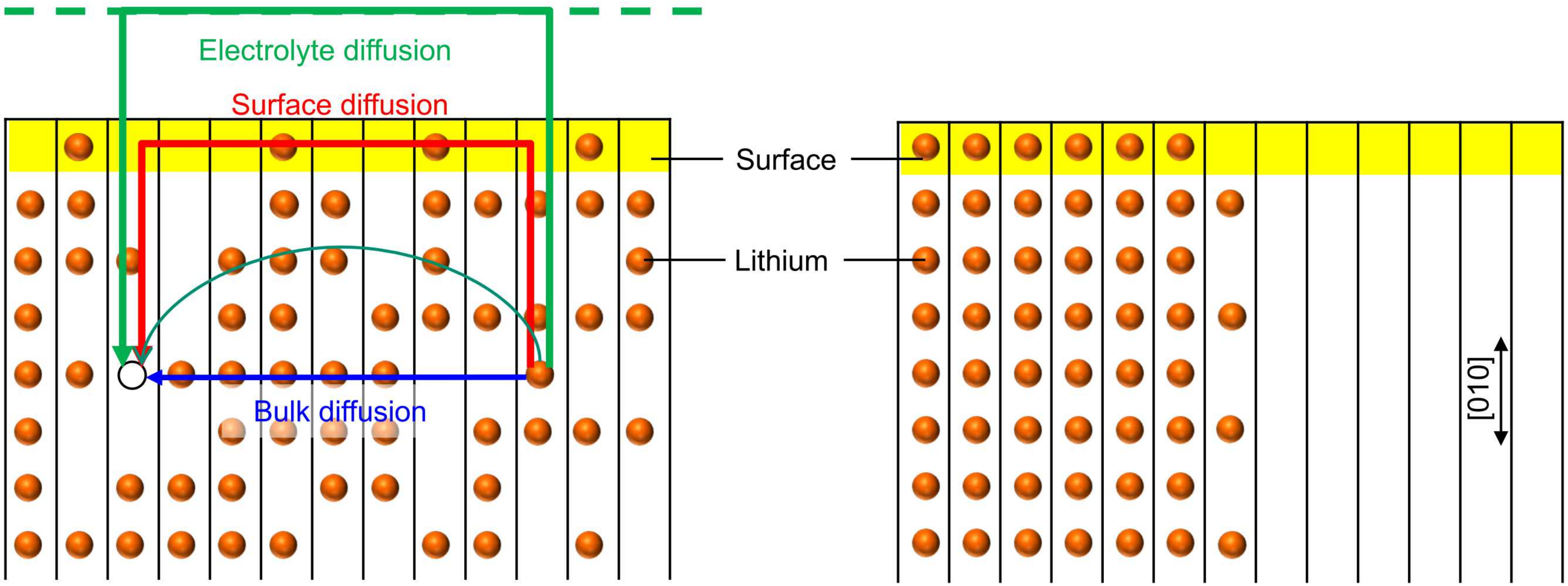
30 min lithiation

How do we prevent phase separation?





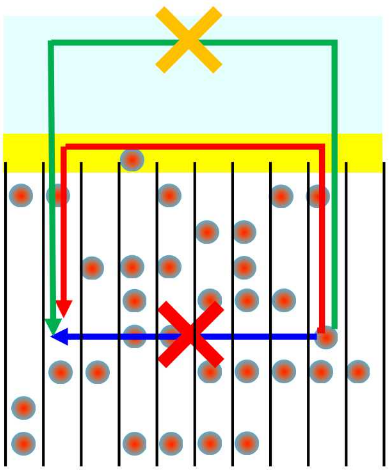
Lithium must diffuse along the non-conducting directions for phase separation

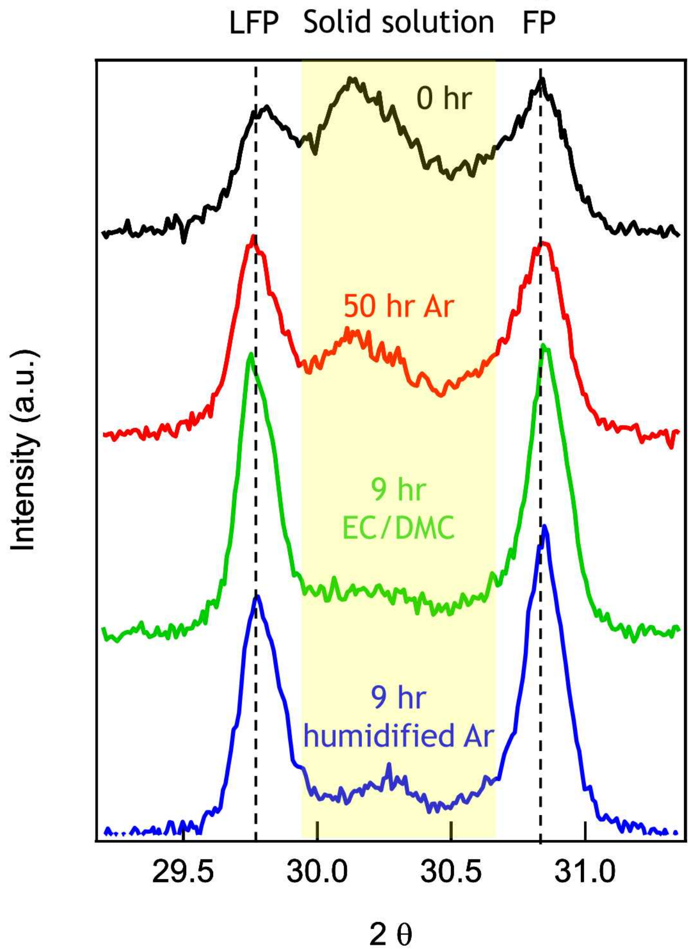


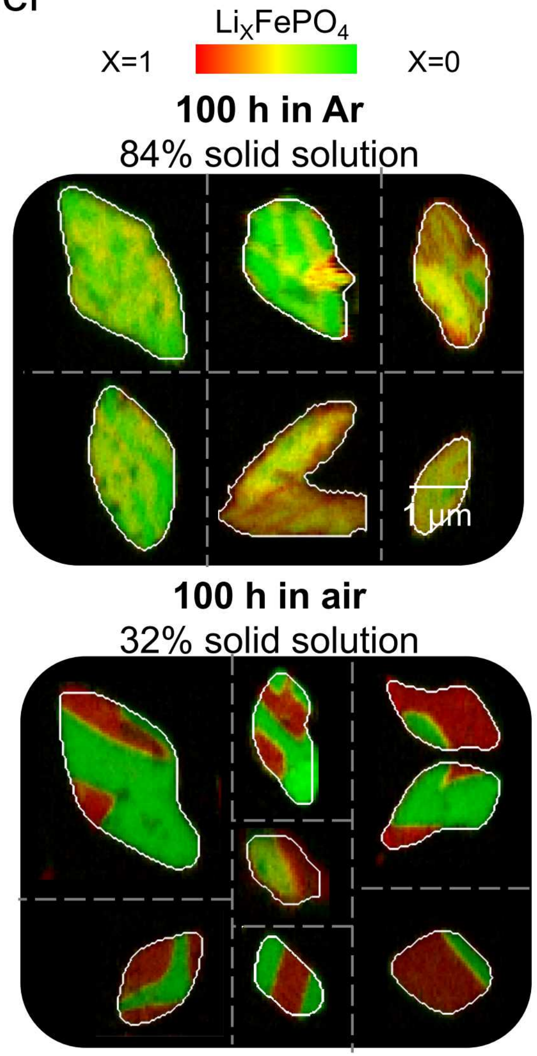
How do we prevent lithium from migrating between channels?

Phase separation without electrolyte

Solid solution $Li_{0.5}FePO_4$ prepared under 30 min discharge



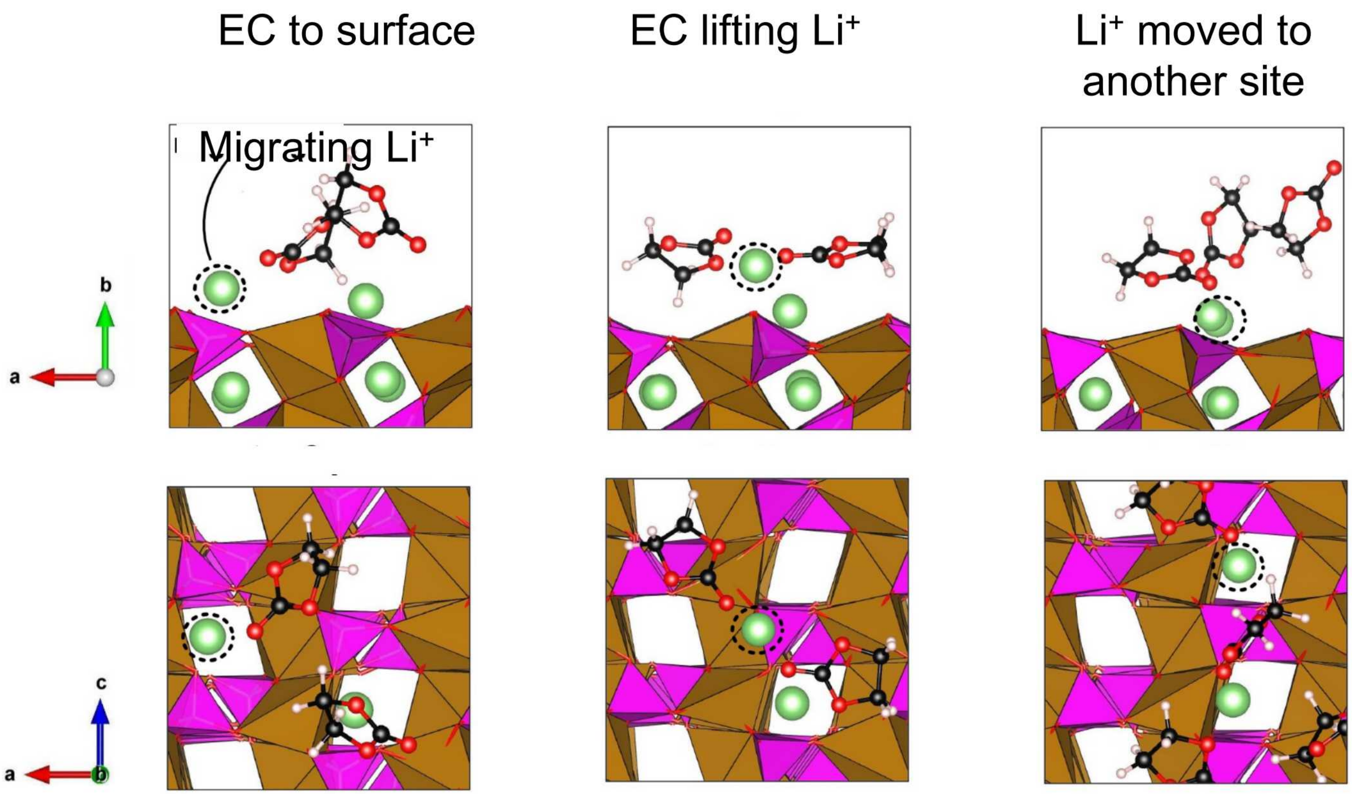




Fluid molecules enhance phase separation rate.

<u>Y. Li</u>, et al. *Nature Mater.*, **17**, 915 (2018)

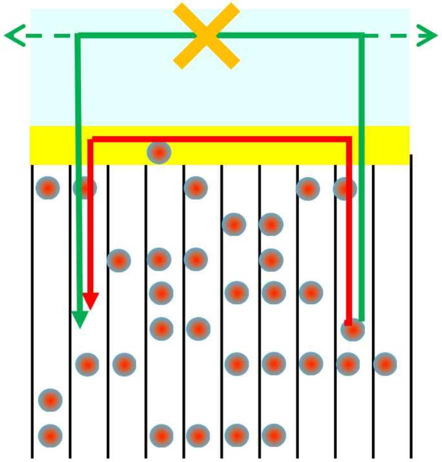
Molecular dynamics shows solvent-assisted surface diffusion

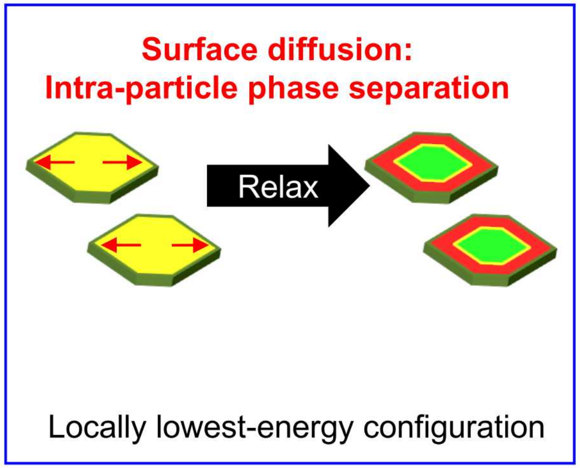


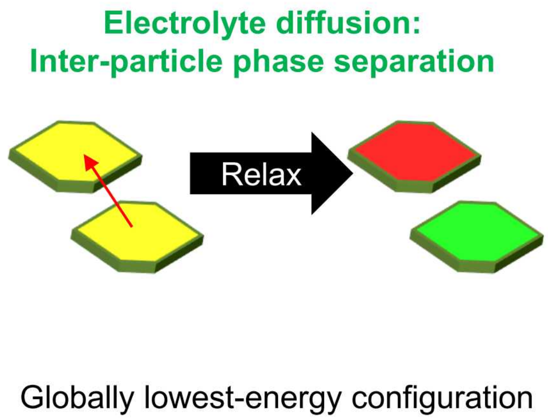
Y. Li, et al. *Nature Mater.*, **17**, 915 (2018)

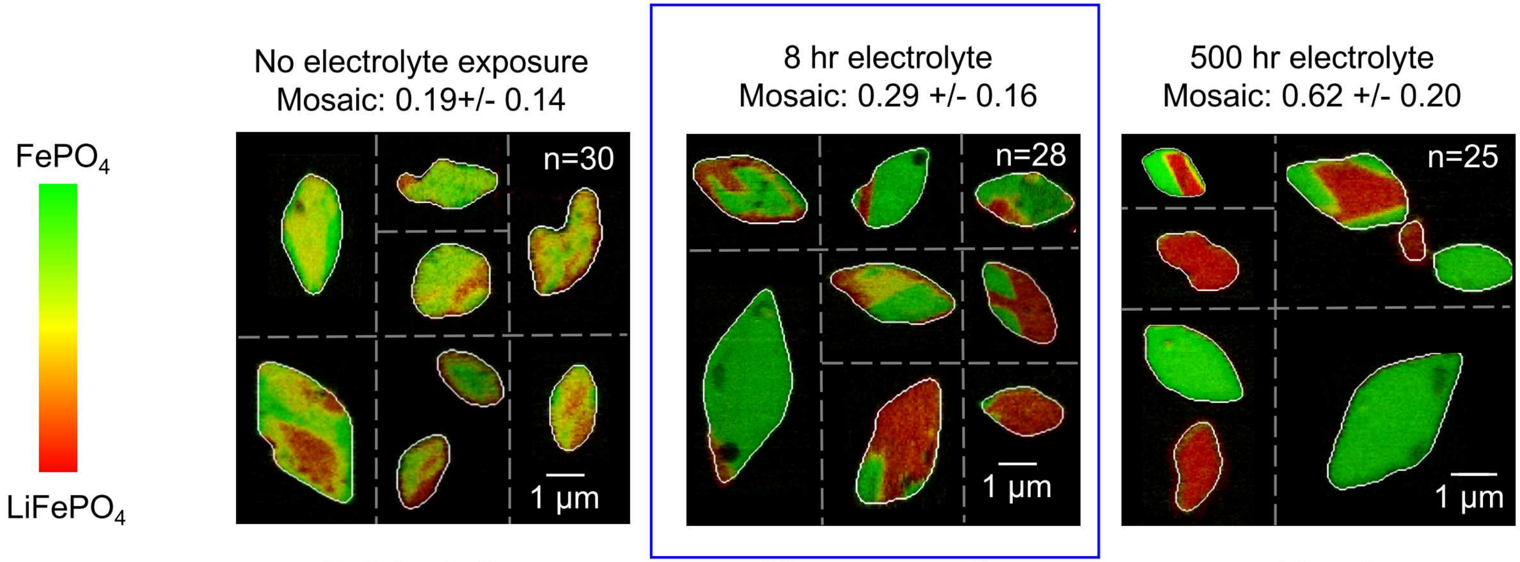
Collaboration: Hungru Chen & Saiful Islam, Univ of Bath

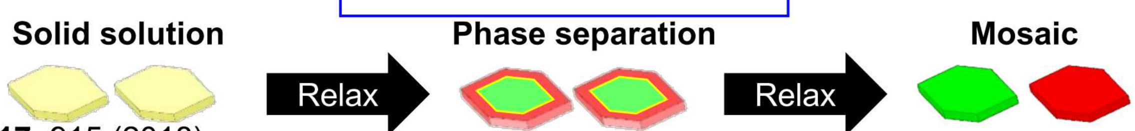
Phase separation with electrolyte







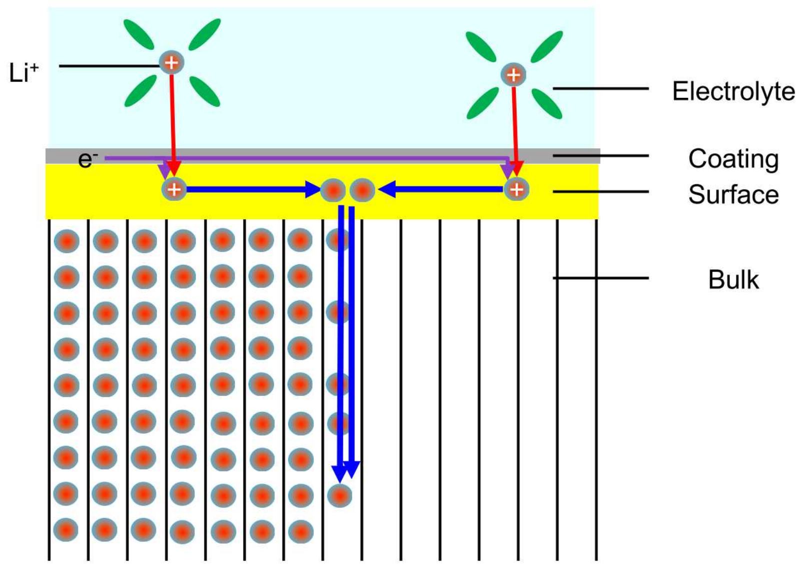




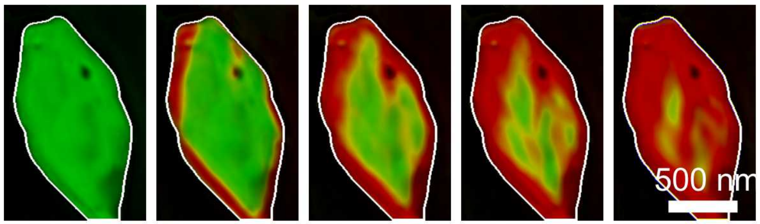
Y. Li, et al. *Nature Mater.*, **17**, 915 (2018)

Surface diffusion controls phase separation

Diffusion is faster than lithitaion



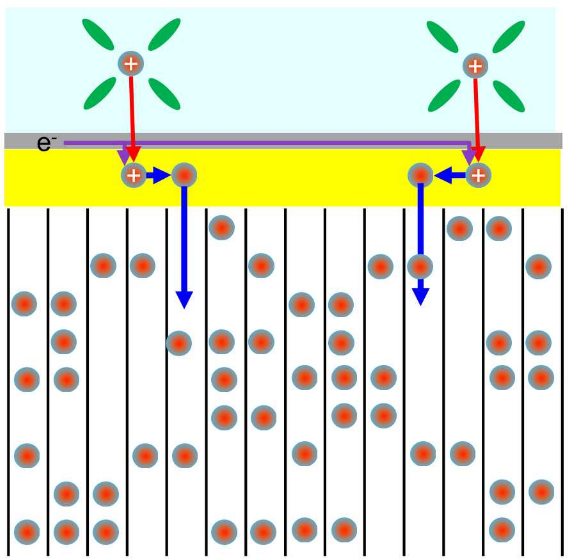
Phase separation
Da < 1



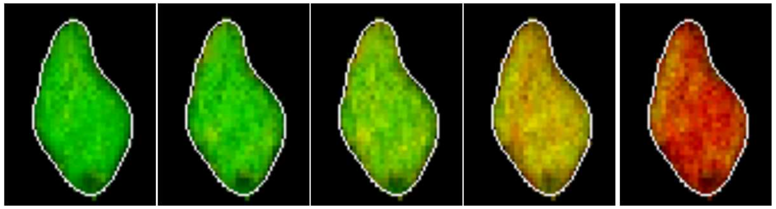
30 min lithiation

<u>Y. Li</u>, et al. *Nature Mater.*, **17**, 915 (2018)

Diffusion is slower than lithiation



Solid solution
Da > 1

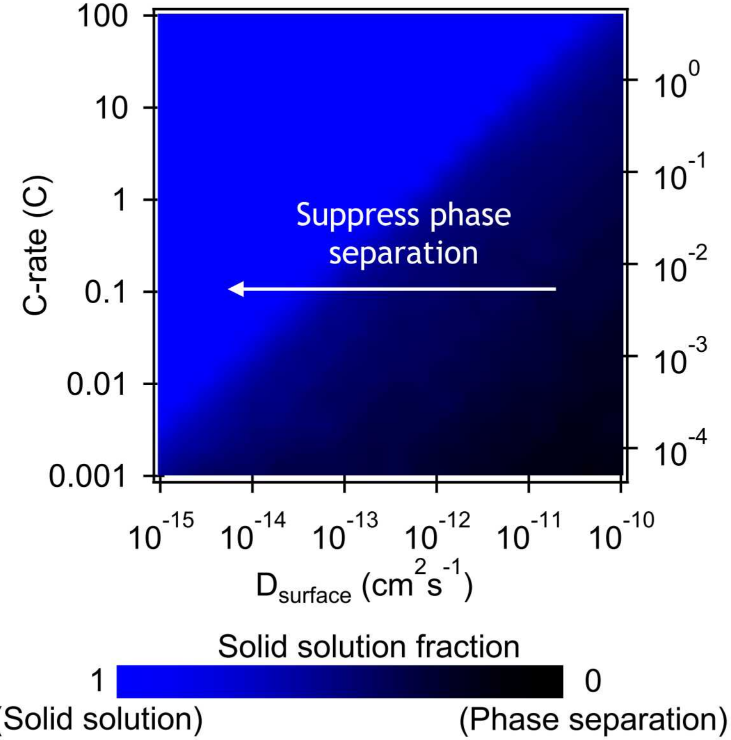


7 hr lithiation

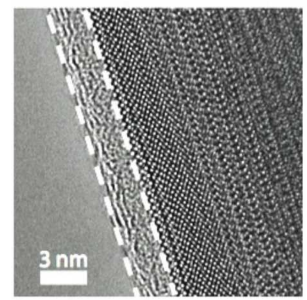
Surface diffusion controls phase separation

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

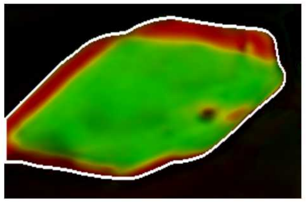
$$\mu_{Li} = \Omega(X)(1-X) + k_B T \ln \frac{X}{1-X} - \kappa \nabla^2 X + \ \ldots$$



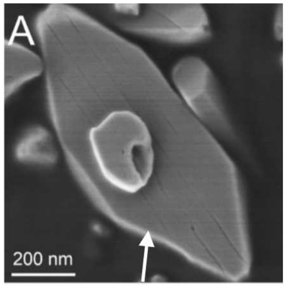
Coating



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



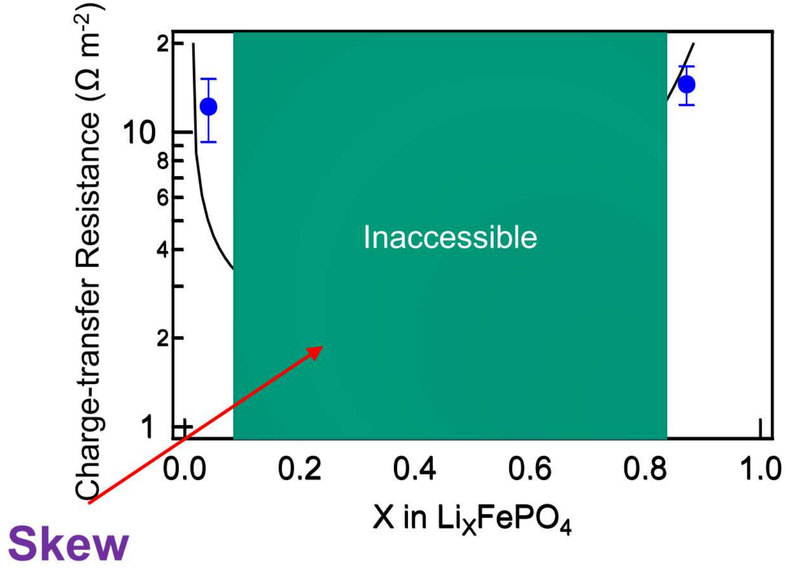
Yu et al. *Nano Lett.* (2015)



Cracks

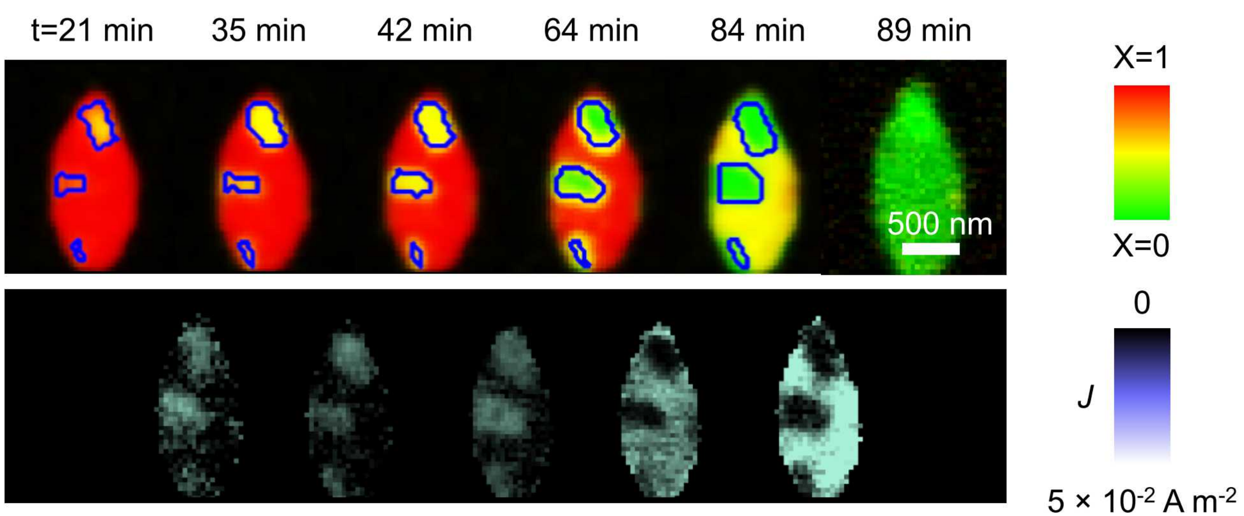
Y. Li, et al. *Nature Mater.*, **17**, 915 (2018)

Solid solution allows us to access intermediate compositions



Li concentration

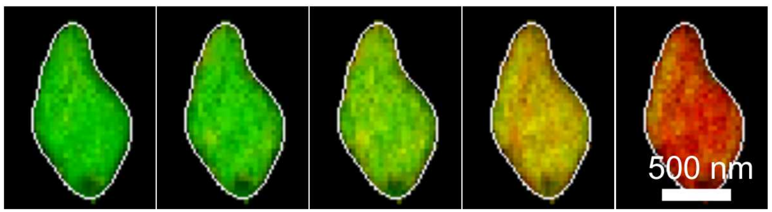
Current density



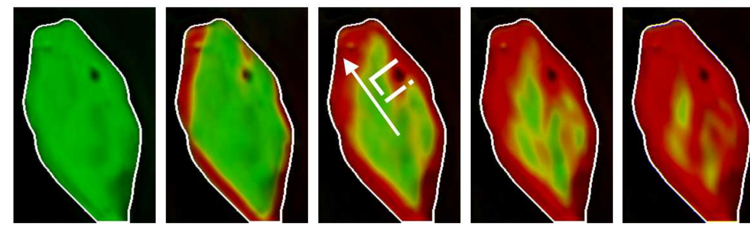
J. Lim*, Y. Li*, et al. *Science*, **353**, 566-571 (2016)

Phase separation in Li_XFePO_4

$LiFePO_4$ undergoes phase separation thermodynamically, but the phase separation is suppressed upon fast charge and discharge



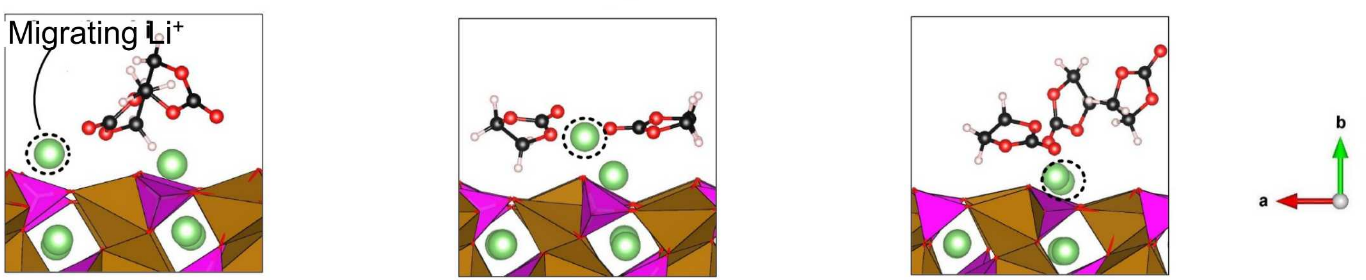
30 min lithiation



7 hour lithiation

Surface diffusion and fluid molecules facilitate phase separation

EC to surface | EC lifting Li^+ | Li^+ moved to another site



Artificial neural networks and deep learning

Computers are 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
```

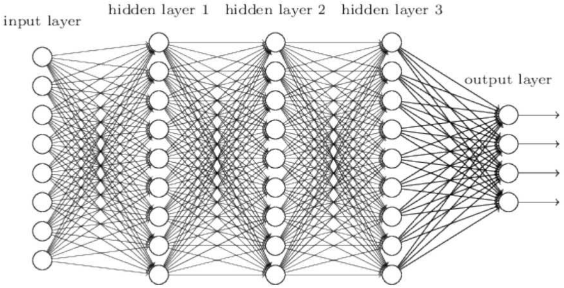
Computers struggle when there are no clear instructions for the task

Which one of these images is a cat?

Image recognition
Autonomous driving
Natural language processing

Artificial neural networks: use training examples and error backpropagation to find the matrix weights that correctly maps the input **x** onto the desired output **y**

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



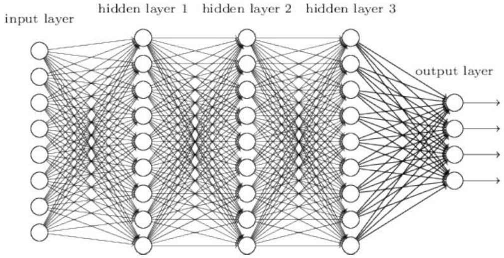
Artificial neural networks are power intensive

n, m > 1000

Andrew Ng, Coursera
Nawrocki et al. *IEEE Elec. Dev.* 2016

Implementing a neural network

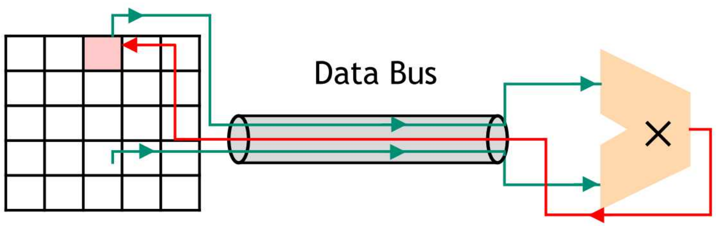
$$\begin{bmatrix} y_1 \\ \vdots \\ y_m \end{bmatrix} = \begin{bmatrix} w_{1,1} & \cdots & w_{1,n} \\ \vdots & \ddots & \vdots \\ w_{m,1} & \cdots & w_{m,n} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$$



Von Neumann Digital
Separate logic and memory structures

SRAM to store the weights

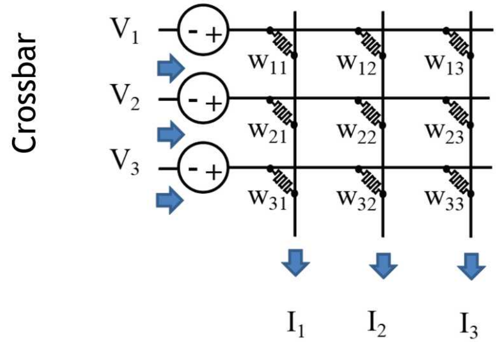
Arithmetic logic unit for multiplication



Uses established CMOS technology

Data bus results in latency and power

In-memory Analog
Use non-volatile memory



$I_1 = V_1W_{11} + V_2W_{21} + V_3W_{31}$

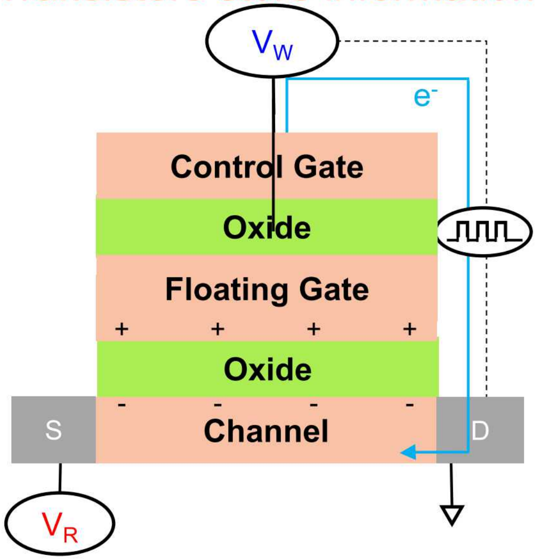
Simultaneous logic and memory
3 orders of magnitude less power

Challenge: find an appropriate non-volatile memory whose conductance can be tuned in a linear and predictable manner

M. Marinella, *IEEE Circuits and Systems*, 8, 86-101, 2018
Zidan, Strachan, & Lu, *Nat. Elec.* 1, 22, 2018

Retention time of transistor-based memory

Transistors store information by moving charge between the gate and the channel



$$\tau_{retention} = C_{gate} R_{OFF}$$

$$C_{gate} = \epsilon_0 \epsilon_r \frac{A}{t_{ox}} \approx 10^{-6}\ \mathrm{F\ cm^{-2}} = 10^{-16}\ \mathrm{F}\ \ (A = 100\ \mathrm{nm}^2)$$

Option 1: transistor switch: $R_{OFF} \sim 10^{15}\ \Omega$

$\tau_{retention} < 1$ s (Dynamic RAM)

S. Ambrogio, G. Burr, et al. Nature, **558**, 60 (2018)

Option 2: floating gate oxide switch, $R_{OFF} \sim \infty$

$\tau_{retention} > 10$ yr (Flash memory)

10V, high power, limited endurance (10^5)

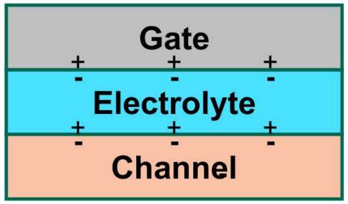
Improving retention by increasing C_{gate}? $C = \frac{\Delta Q}{\Delta V}$

Electrochemical double-layer transistors

Electrons stored at the **interface**

$C_{gate} \sim 10^{-4}\ \mathrm{F\ cm^{-2}}$

$t_{"ox"} < 1\ nm$



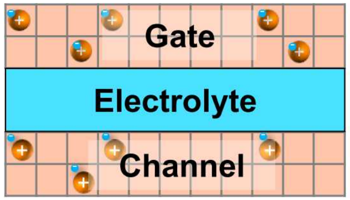
P. Gkoupidenis, G. Malliaras, Adv Mater, 27, 7176 (2015)

Ion insertion transistors

Electrons (and ions) are stored in the **bulk** of the material (pseudo-capacitor)

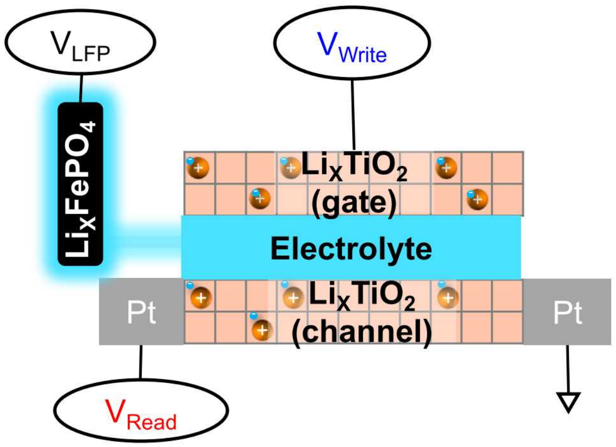
Electron/ion neutral ambipolar pair enables ΔQ without electrostatic charging

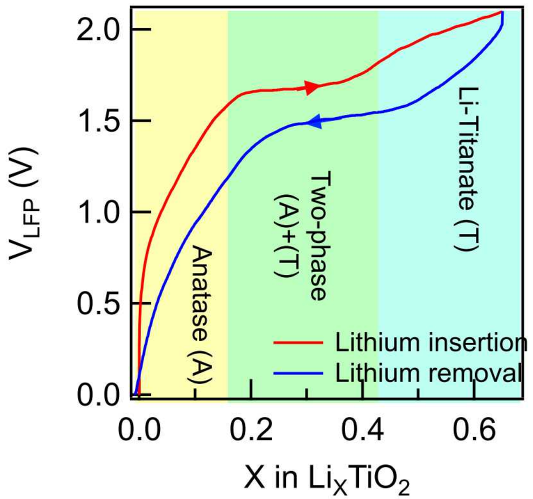
$C_{gate} \sim 10^{-1}\ \mathrm{F\ cm^{-2}}$ (100-nm film)



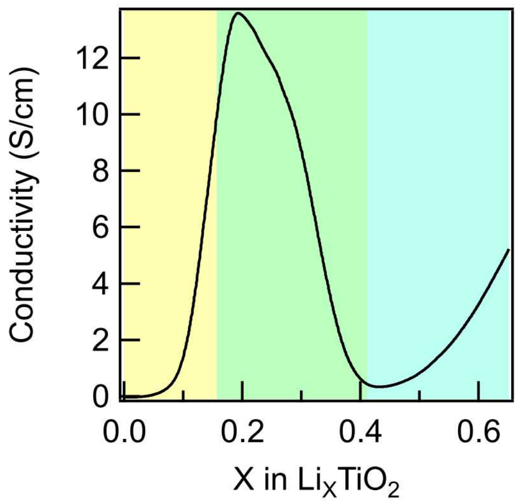
E. Fuller, Adv Mater. 29, 1604310 (2017)
Y. van de Burgt, Nat. Mater., 16, 414 (2017)

Lithium insertion into Li_xTiO_2 (anatase)



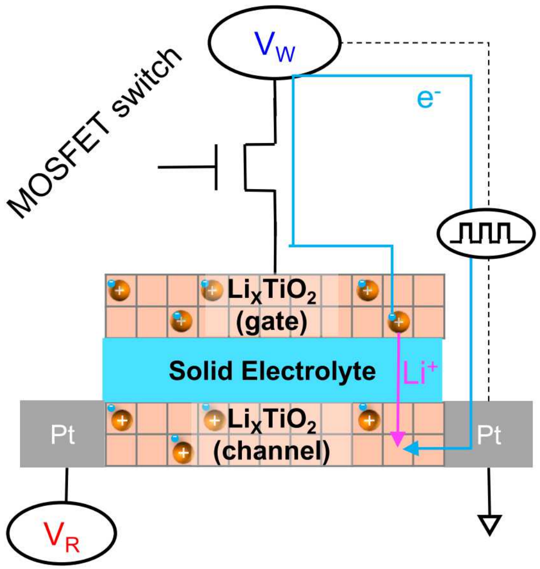


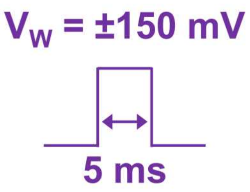
$$Li^{+} + e^{-} + Ti_{Ti}^{X} \rightarrow Li_{i}^{\circ} + \boldsymbol{Ti'_{Ti}}$$

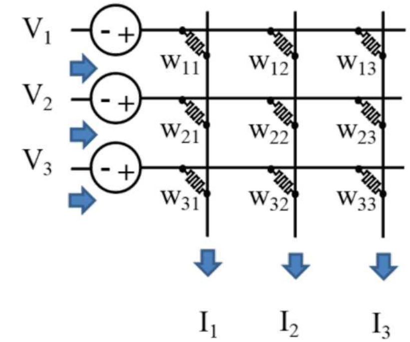


Small polarons increase the electronic conductivity

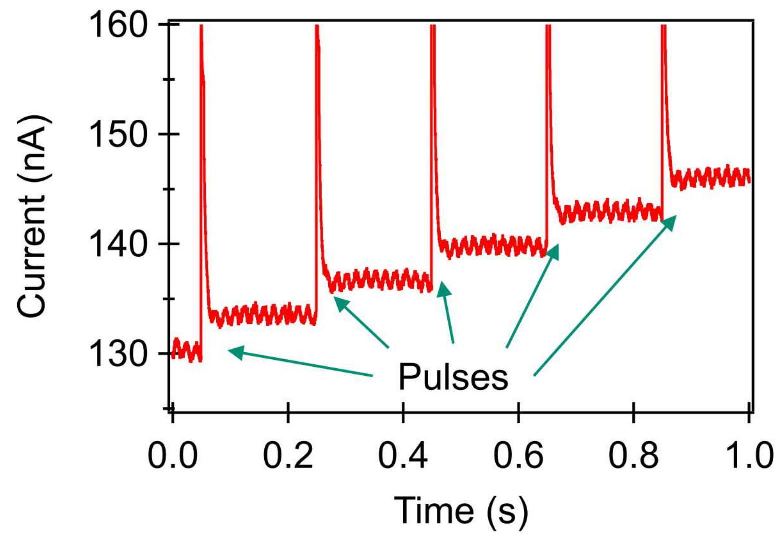
Ion insertion transistor using Li_xTiO_2 (anatase)



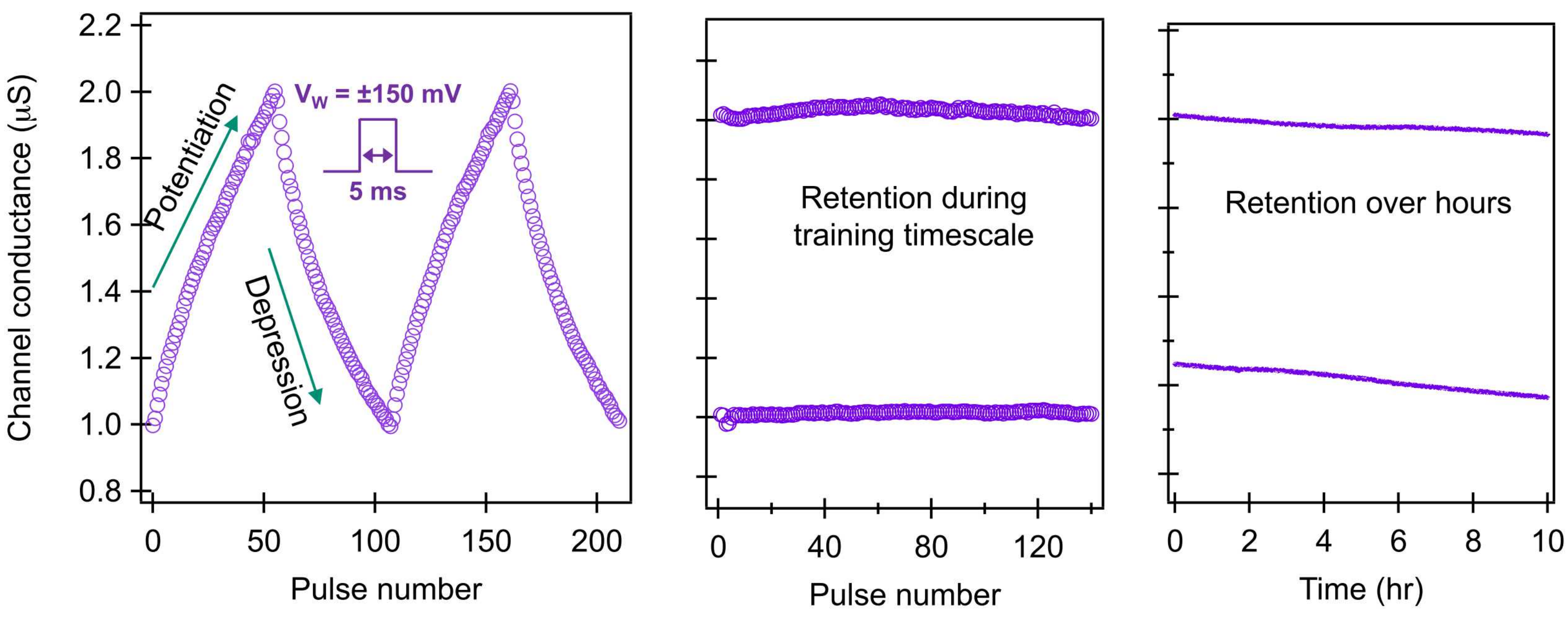




- Analog, non-volatile states
- Linear and symmetric programming
- 150-mV write pulses

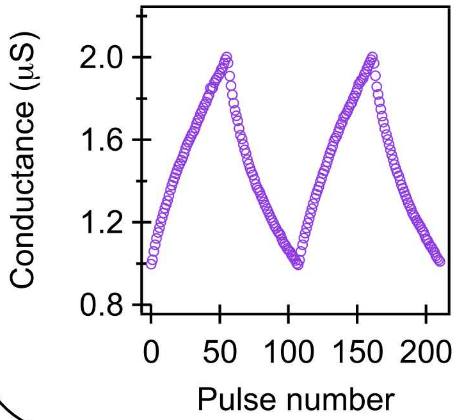


Ion insertion transistor using Li_XTiO_2 (anatase)

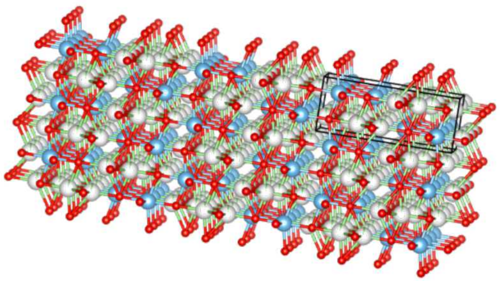


Linear programming and high accuracy

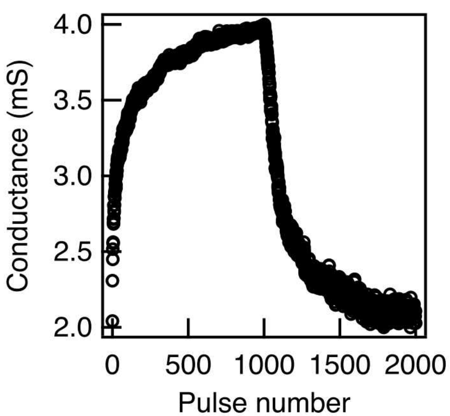
Li_XTiO_2 transistor
Voltage: ± 0.15 V



Ion insertion: stores information continuously as dopants in a crystal

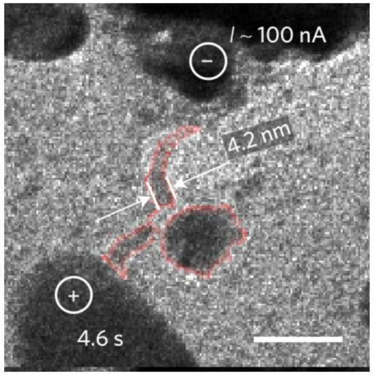


TaO_x Memristor
Voltage: ±1 V



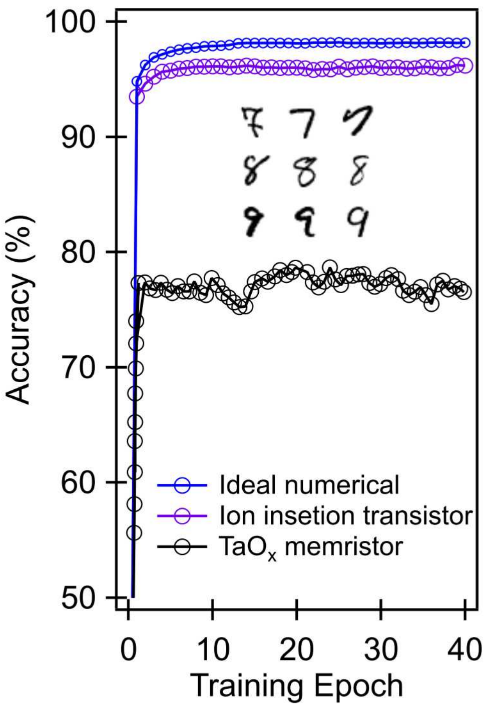
R. Jacobs-Gedrim et al. *ICRC*, 2017

Memristors: stores information at filaments



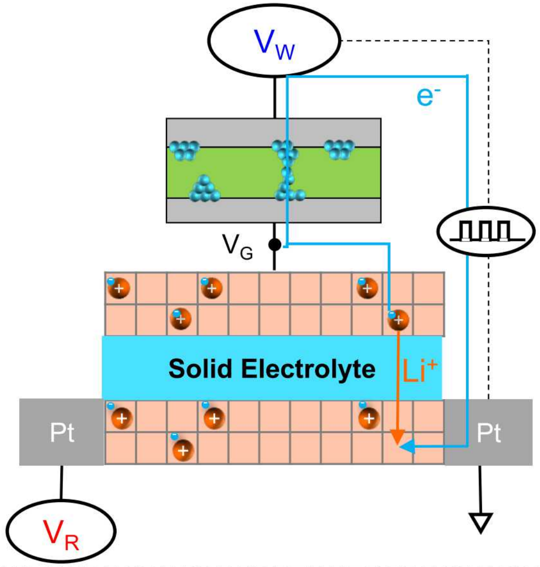
Wang et al. *Nat Mater.* 2017

Linearity is essential to train an accurate neural network



Crossbar Simulator

Low-voltage, Si-free electrochemical memory



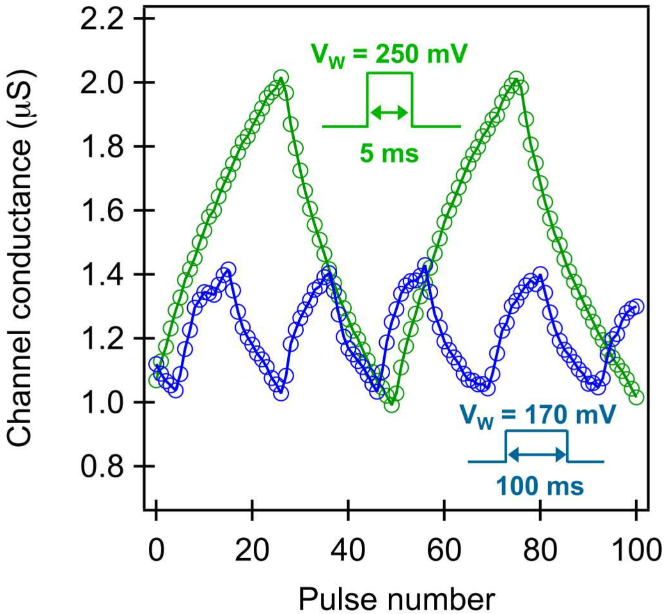
Diffusive memristor (Ag in SiO_X): high ON/OFF ratio

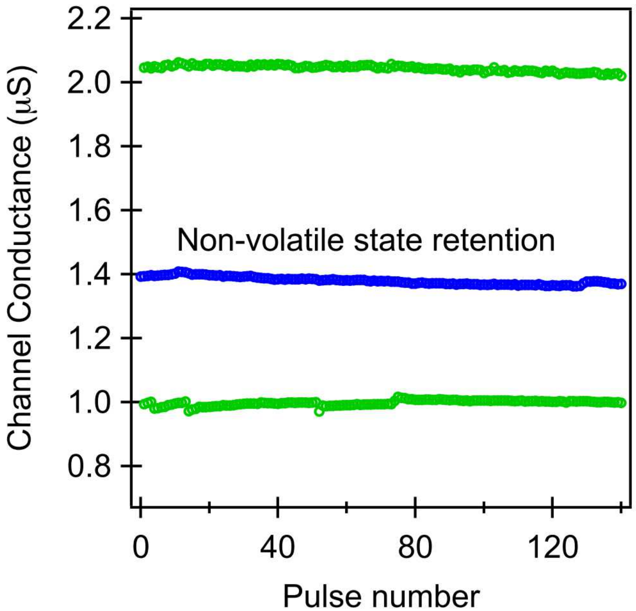
Ion insertion transistor: high charge density via bulk storage

Both: Low switching voltages

Wang et al. Nat. Mater. 2017

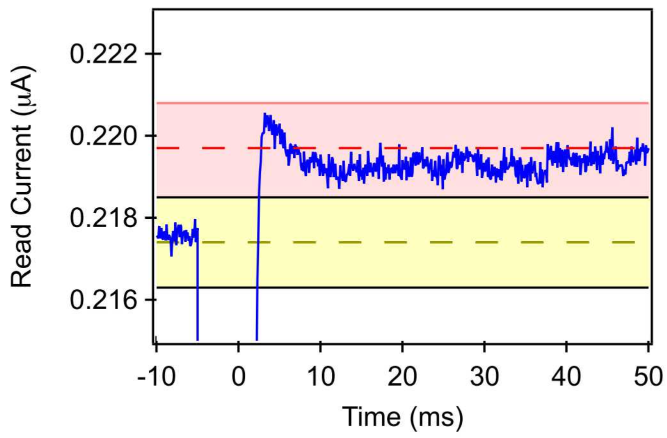
Non-volatile memory that switches at just 6 times the thermal voltage

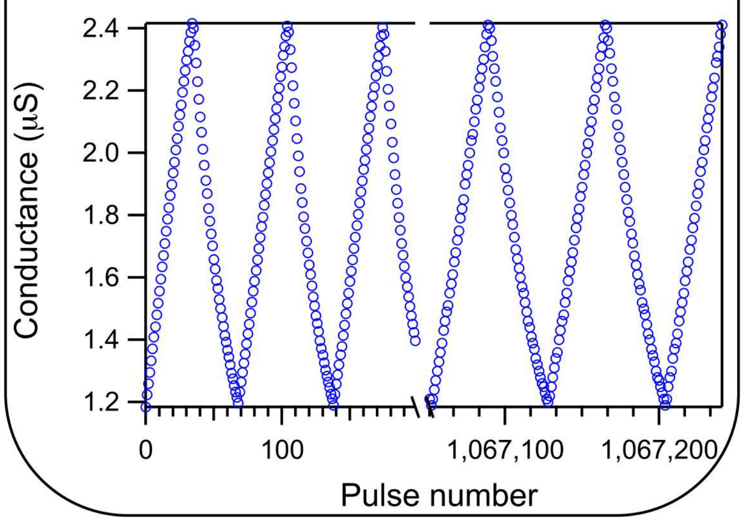




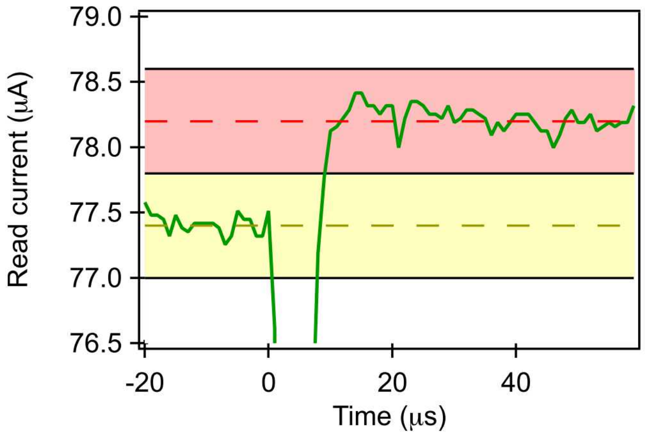
Switching speed and endurance

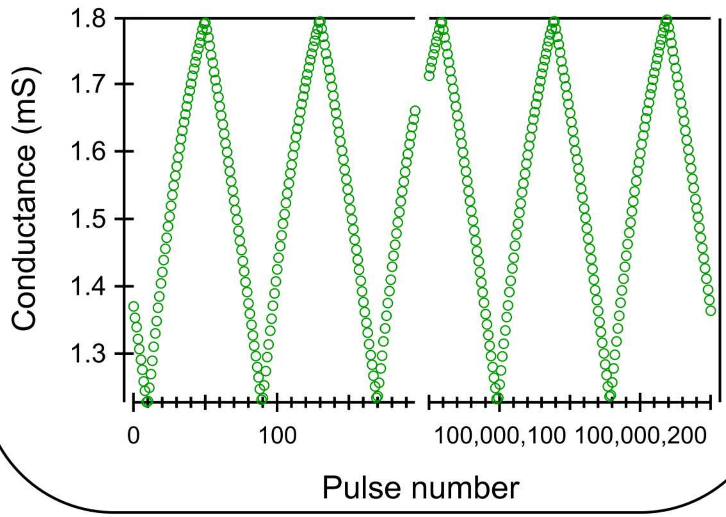
Inorganic (Li_XTiO_2) ~5 ms, 10^6 read/write cycles





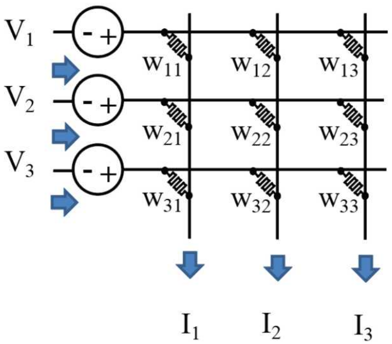
Organic (PEDOT/PSS) ~10 μs 10^8 read/write cycles



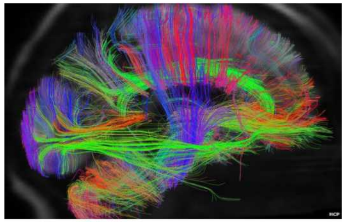


Ion insertion transistors for neuromorphic computing

Analog neuromorphic computing provides lower energy and more parallelism compared to digital computing.

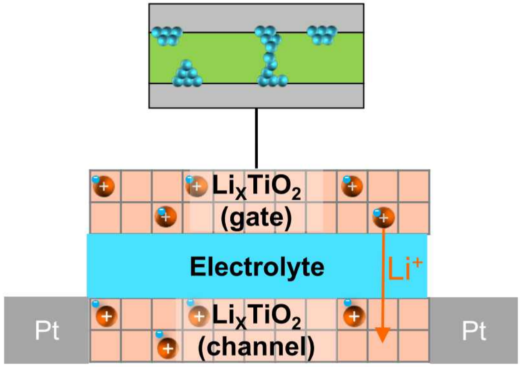


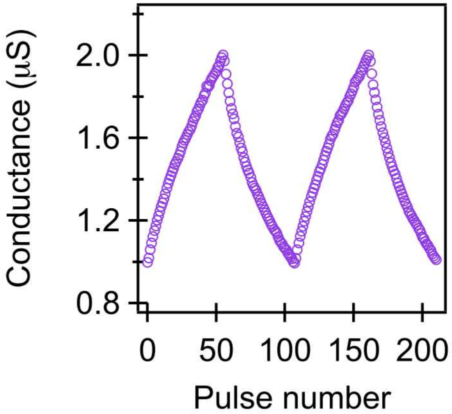
the brain ~10 Hz



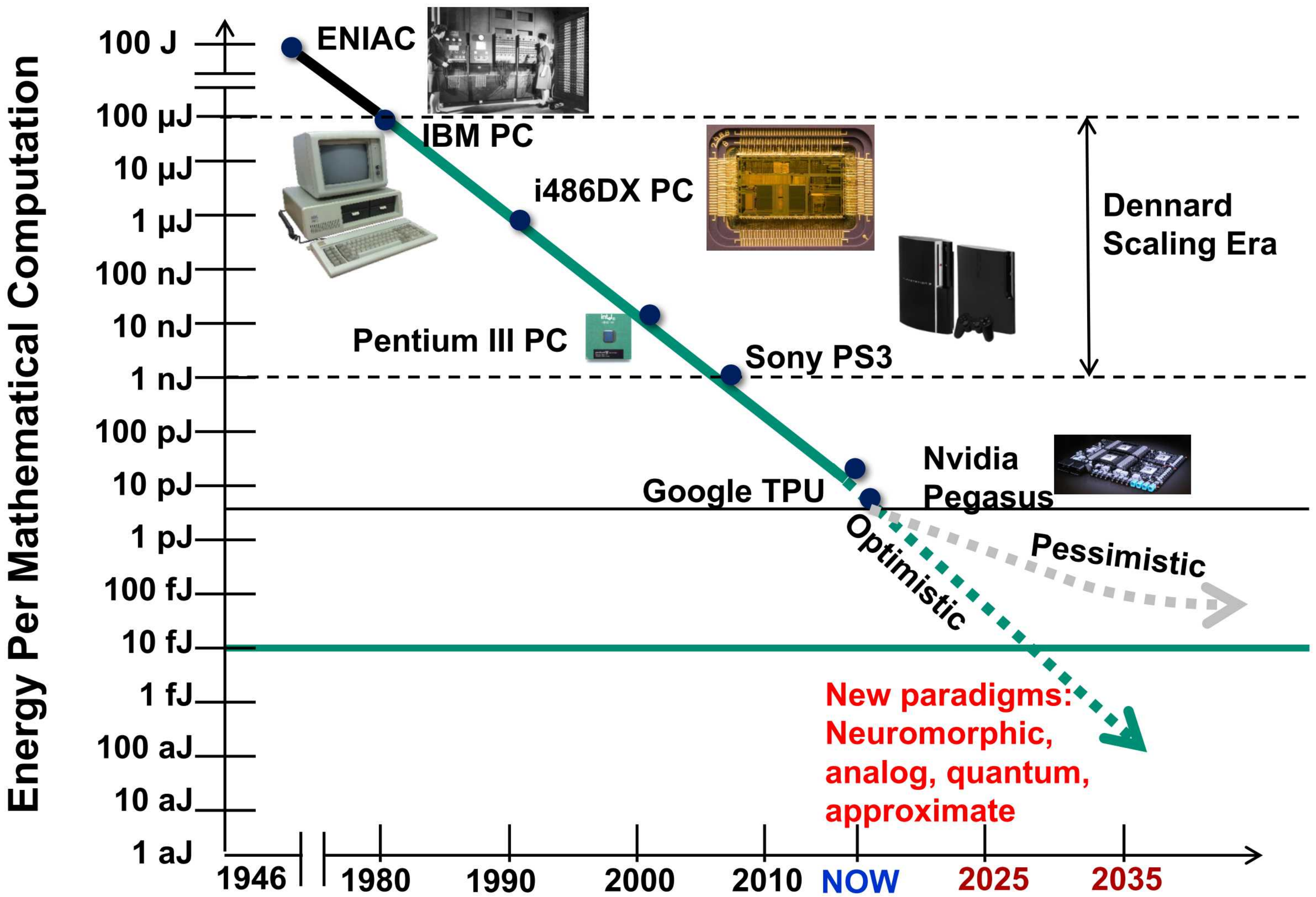
100 billion neurons
100 trillion synapses

Electrochemical ion insertion can be used to create highly linear, low voltage non-volatile analog transistors





Evolution of Computing Machinery



28

Sandia Careers

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Three-year Postdoc Fellowships (you are your own PI):

Harry S. Truman Fellowship
Jill Hruby Fellowship

Our team: Materials Physics, Livermore. Intern and postdoc positions available. Contact yiyli@sandia.gov or aatalin@sandia.gov

Acknowledgements

Sandia

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Univ of Bath

Saiful Islam

Hungru Chen

Stanford

William Chueh

Jongwoo Lim

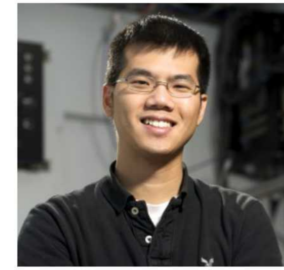
Will Gent

Norman Jin

MIT

Martin Bazant

Dan Cogswell



W. Chueh

J. Lim

M. Bazant

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Hourly AQI (Combined PM and O3)
Friday, November 16, 2018 12:20 AM PST
Santa Rosa
Vacaville
San Rafael
Antioch
Oakland
San Francisco
Livermore
San Jose
101
80
580
1
280
5
505


Sfgate.com

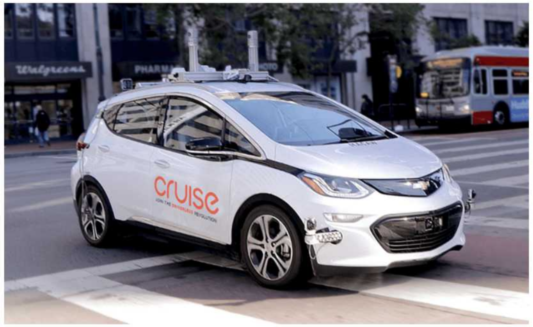

BUTTE COLLEGE
3536 BUTTE CAMPUS DRIVE

Energy and computing

2000: Why is my computer so slow?

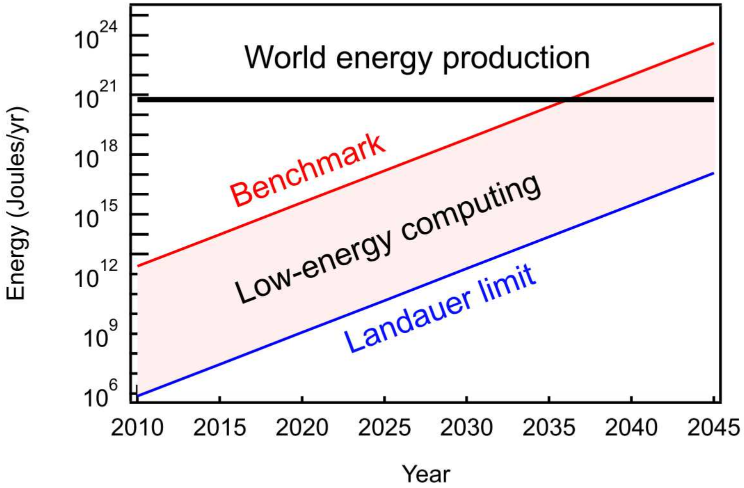
2018: Why is my phone's battery dead?

Autonomous Chevy Bolt (Electric)
Propulsion at 20mph: 5 kW
Computers & sensors: 2 kW



J. Gawron, *Env. Sci.Tech.* 2018

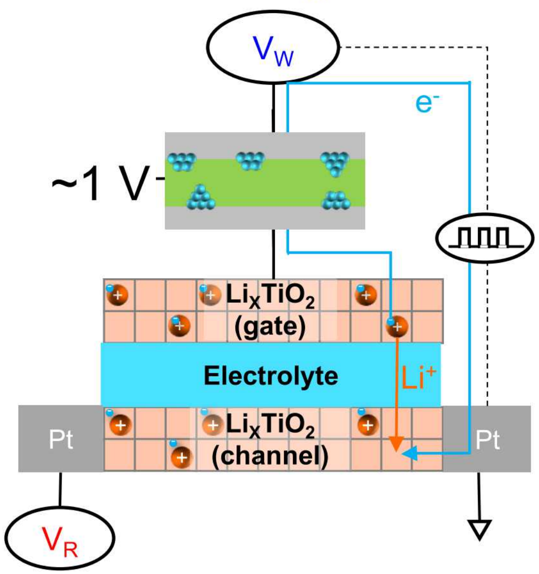
Computing already consumes over 10% of global electricity



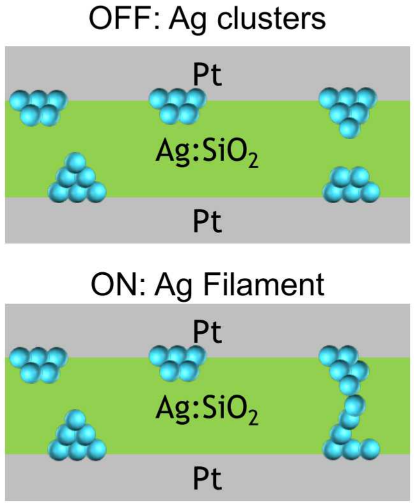
Semiconductor industry association 2015

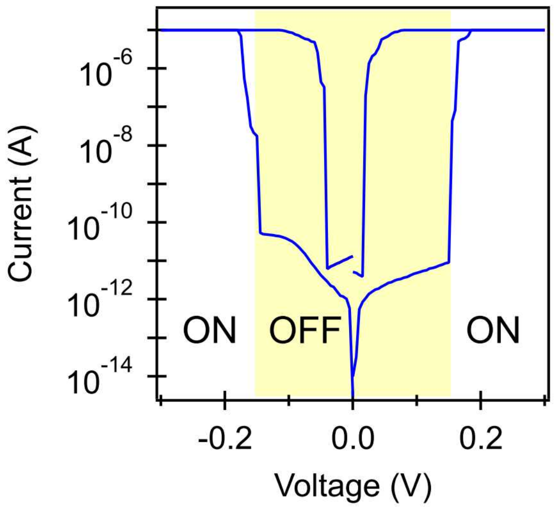
Non-volatile memory at the thermal limit

What is the minimum switching voltage for non-volatile memory?



Diffusive memristor

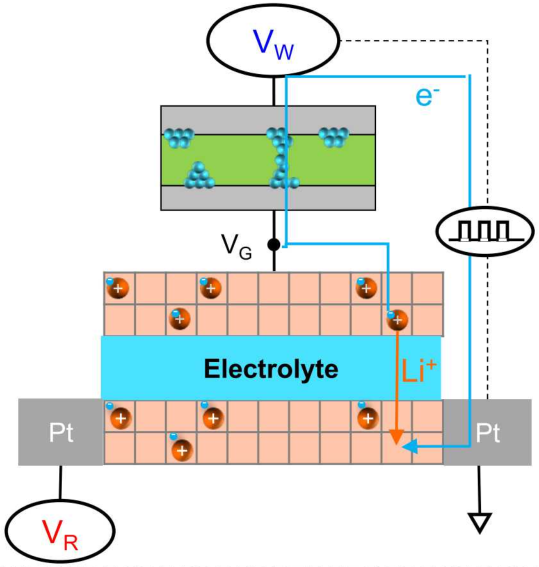




Diffusive memristor has an extremely sharp ON/OFF ratio at just 150mV threshold

Collaboration: Joshua Yang, U-Mass
Wang et al. *Nat Mater.* 2017

Non-volatile memory at the thermal limit

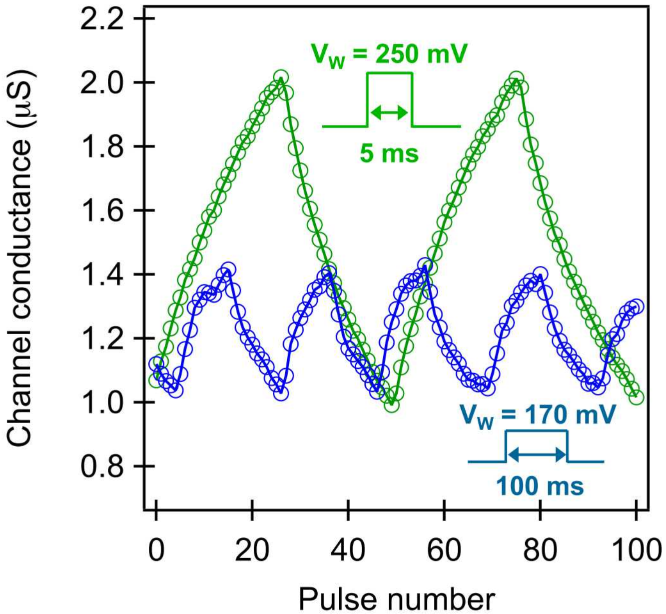


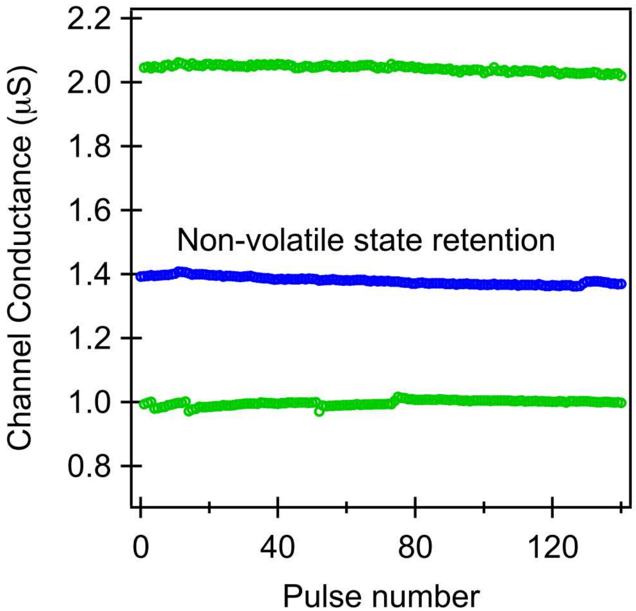
Diffusive memristor: high ON/OFF ratio

Ion insertion transistor: high charge density via bulk storage

Both: Low switching voltages

Non-volatile memory that switches at just 6 times the thermal voltage

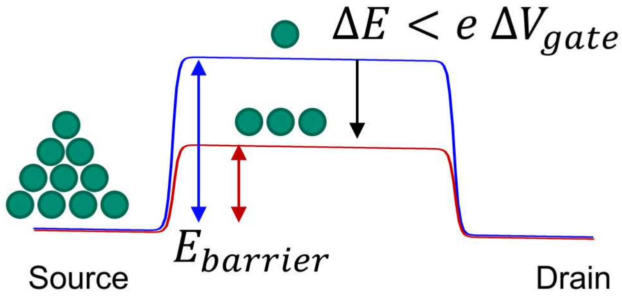




How is non-volatility attained at low switching voltages

High ON/OFF ratios with low

Field-effect transistor

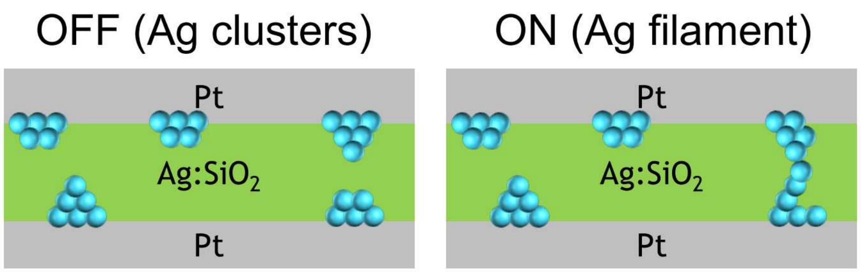


$$n \sim \exp\left(-\frac{E_{barrier}}{k_B T}\right)$$

The gate voltage lowers the energy barrier

Transistor gain cannot exceed 60 mV/decade due to the Boltzmann electron energy distribution

Diffusive memristor



$$E_{barrier} \sim n_{Ag}\,(\mu_{Ag,filament} - \mu_{Ag,clusters})$$

Voltage modifies $\Delta\mu_{Ag}$

$\Delta E_{barrier} > e\Delta V$

Switching slope ~ 2 mV/decade, allowing for ~150 mV switching thresholds

Materials technologies for energy and climate challenges

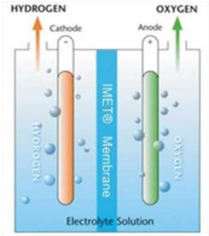
Energy generation

Solar

Wind

Energy storage

Batteries



Chemical fuels

Negative carbon emission

Energy efficiency

Solid-state LED Lighting

Low-energy computing

Resource management

Mining

Recycling

Phase separation with electrolyte