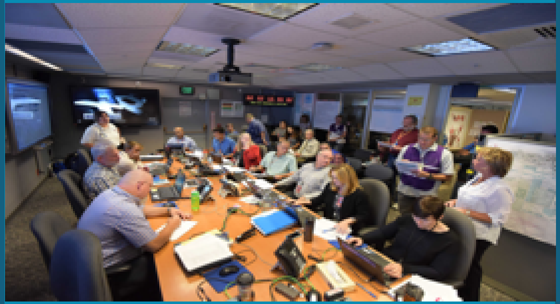
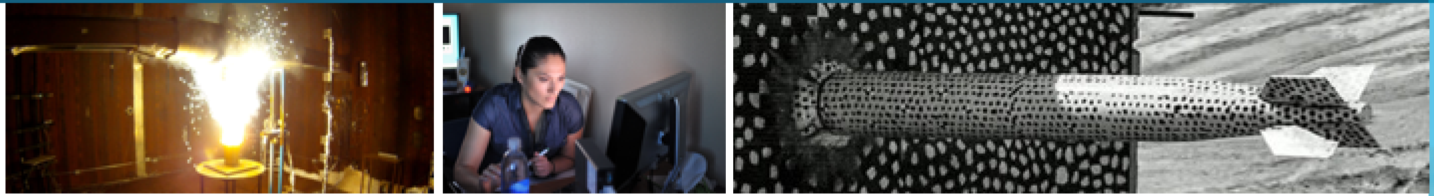
SAND2022-9763C

Imaging phase segregation in nanoscale Li_xCoO_2 single crystal particles

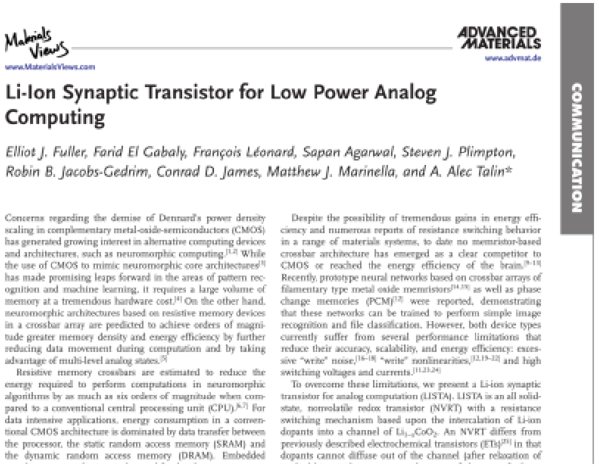




Elliot J. Fuller

LABORATORY DIRECTED RESEARCH & DEVELOPMENT
WHERE INNOVATION BEGINS

$LiCoO_2$ from batteries to electrochemical random access memory



Materials Views
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COMMUNICATION

Li-Ion Synaptic Transistor for Low Power Analog Computing

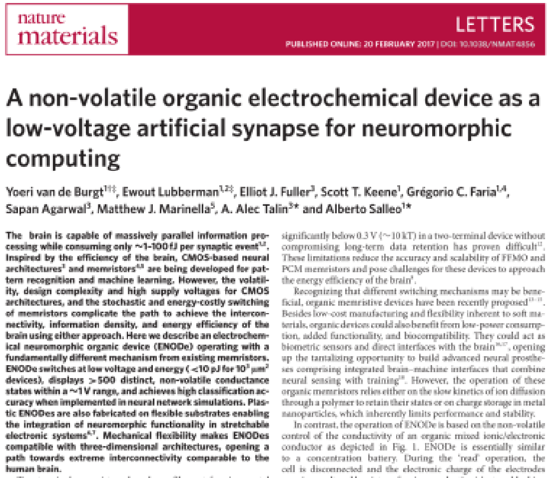
*Elliot J. Fuller, Farid El Gabaly, François Léonard, Sapan Agarwal, Steven J. Plimpton, Robin B. Jacobs-Gedrim, Conrad D. James, Matthew J. Marinella, and A. Alec Talin**

Concerns regarding the demise of Dennard's power density scaling in complementary metal-oxide-semiconductors (CMOS) has generated growing interest in alternative computing devices and architectures, such as neuromorphic computing.[1,2] While the use of CMOS to mimic neuromorphic core architectures[3] has made promising leaps forward in the areas of pattern recognition and machine learning, it requires a large volume of memory at a tremendous hardware cost.[4] On the other hand, neuromorphic architectures based on resistive memory devices in a crossbar array are predicted to achieve orders of magnitude greater memory density and energy efficiency by further reducing data movement during computation and by taking advantage of multi-level analog states.[5]

Resistive memory crossbars are estimated to reduce the energy required to perform computations in neuromorphic algorithms by as much as six orders of magnitude when compared to a conventional central processing unit (CPU).[6,7] For data intensive applications, energy consumption in a conventional CMOS architecture is dominated by data transfer between the processor, the static random access memory (SRAM) and the dynamic random access memory (DRAM). Embedded

Despite the possibility of tremendous gains in energy efficiency and numerous reports of resistance switching behavior in a range of materials systems, to date no memristor-based crossbar architecture has emerged as a clear competitor to CMOS or reached the energy efficiency of the brain.[9–13] Recently, prototype neural networks based on crossbar arrays of filamentary type metal oxide memristors[14,15] as well as phase change memories (PCM)[12] were reported, demonstrating that these networks can be trained to perform simple image recognition and file classification. However, both device types currently suffer from several performance limitations that reduce their accuracy, scalability, and energy efficiency: excessive "write" noise,[16–18] "write" nonlinearities,[12,19–22] and high switching voltages and currents.[11,23,24]

To overcome these limitations, we present a Li-ion synaptic transistor for analog computation (LISTA). LISTA is an all solid-state, nonvolatile redox transistor (NVRT) with a resistance switching mechanism based upon the intercalation of Li-ion dopants into a channel of $Li_{1-x}CoO_2$. An NVRT differs from previously described electrochemical transistors (ETs)[25] in that dopants cannot diffuse out of the channel (after relaxation of



nature materials
LETTERS
PUBLISHED ONLINE: 20 FEBRUARY 2017 | DOI: 10.1038/NMAT4856

A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing

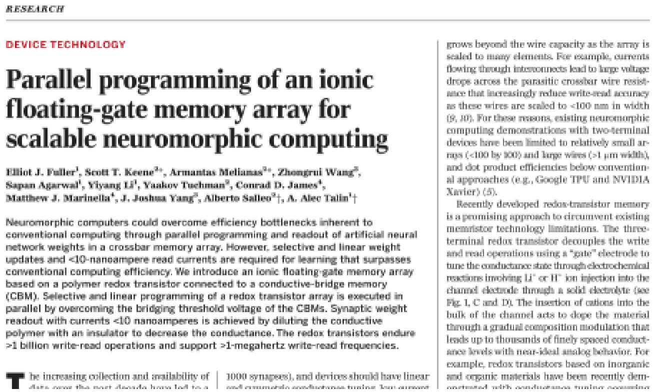
Yoeri van de Burgt[1†‡], Ewout Lubberman[1,2‡], Elliot J. Fuller[3], Scott T. Keene[1], Grégorio C. Faria[1,4], Sapan Agarwal[3], Matthew J. Marinella[3], A. Alec Talin[3*] and Alberto Salleo[1*]

The brain is capable of massively parallel information processing while consuming only ~1–100 fJ per synaptic event[1,2]. Inspired by the efficiency of the brain, CMOS-based neural architectures[3] and memristors[4,5] are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. Here we describe an electrochemical neuromorphic organic device (ENODe) operating with a fundamentally different mechanism from existing memristors. ENODe switches at low voltage and energy (<10 pJ for $10^3\ \mu m^2$ devices), displays >500 distinct, non-volatile conductance states within a ~1 V range, and achieves high classification accuracy when implemented in neural network simulations. Plastic ENODes are also fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems[6,7]. Mechanical flexibility makes ENODes compatible with three-dimensional architectures, opening a path towards extreme interconnectivity comparable to the human brain.

significantly below 0.3 V (~10 kT) in a two-terminal device without compromising long-term data retention has proven difficult[12]. These limitations reduce the accuracy and scalability of FFMO and PCM memristors and pose challenges for these devices to approach the energy efficiency of the brain[1].

Recognizing that different switching mechanisms may be beneficial, organic memristive devices have been recently proposed[13–15]. Besides low-cost manufacturing and flexibility inherent to soft materials, organic devices could also benefit from low-power consumption, added functionality, and biocompatibility. They could act as biometric sensors and direct interfaces with the brain[16,17], opening up the tantalizing opportunity to build advanced neural prostheses comprising integrated brain–machine interfaces that combine neural sensing with training[18]. However, the operation of these organic memristors relies either on the slow kinetics of ion diffusion through a polymer to retain their states or on charge storage in metal nanoparticles, which inherently limits performance and stability.

In contrast, the operation of ENODe is based on the non-volatile control of the conductivity of an organic mixed ionic/electronic conductor as depicted in Fig. 1. ENODe is essentially similar to a concentration battery. During the 'read' operation, the cell is disconnected and the electronic charge of the electrodes



DEVICE TECHNOLOGY

Parallel programming of an ionic floating-gate memory array for scalable neuromorphic computing

Elliot J. Fuller[1], Scott T. Keene[2*], Armantas Melianas[2*], Zhongrui Wang[3], Sapan Agarwal[1], Yiyang Li[1], Yaakov Tuchman[2], Conrad D. James[4], Matthew J. Marinella[4], J. Joshua Yang[3], Alberto Salleo[2]†, A. Alec Talin[1]†

Neuromorphic computers could overcome efficiency bottlenecks inherent to conventional computing through parallel programming and readout of artificial neural network weights in a crossbar memory array. However, selective and linear weight updates and <10-nanoampere read currents are required for learning that surpasses conventional computing efficiency. We introduce an ionic floating-gate memory array based on a polymer redox transistor connected to a conductive-bridge memory (CBM). Selective and linear programming of a redox transistor array is executed in parallel by overcoming the bridging threshold voltage of the CBMs. Synaptic weight readout with currents <10 nanoamperes is achieved by diluting the conductive polymer with an insulator to decrease the conductance. The redox transistors endure >1 billion write-read operations and support >1-megahertz write-read frequencies.

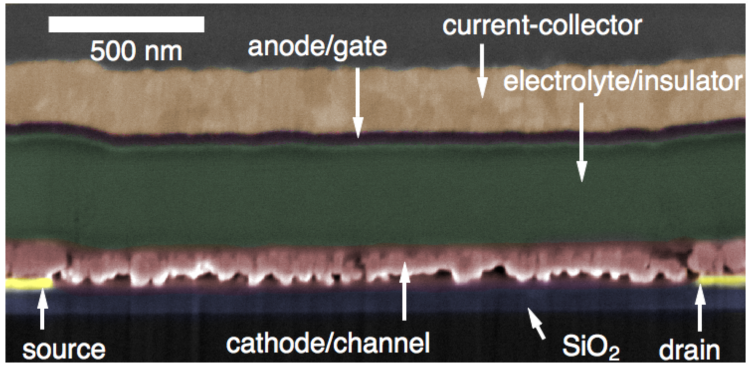
The increasing collection and availability of

1000 synapses), and devices should have linear

grows beyond the wire capacity as the array is scaled to many elements. For example, currents flowing through interconnects lead to large voltage drops across the parasitic crossbar wire resistance that increasingly reduce write-read accuracy as these wires are scaled to <100 nm in width (*9*, *10*). For these reasons, existing neuromorphic computing demonstrations with two-terminal devices have been limited to relatively small arrays (<100 by 100) and large wires (>1 μm width), and dot product efficiencies below conventional approaches (e.g., Google TPU and NVIDIA Xavier) (*5*).

Recently developed redox-transistor memory is a promising approach to circumvent existing memristor technology limitations. The three-terminal redox transistor decouples the write and read operations using a "gate" electrode to tune the conductance state through electrochemical reactions involving Li^+ or H^+ ion injection into the channel electrode through a solid electrolyte (see Fig. 1, C and D). The insertion of cations into the bulk of the channel acts to dope the material through a gradual composition modulation that leads up to thousands of finely spaced conductance levels with near-ideal analog behavior. For example, redox transistors based on inorganic and organic materials have been recently dem-

SEM cross section



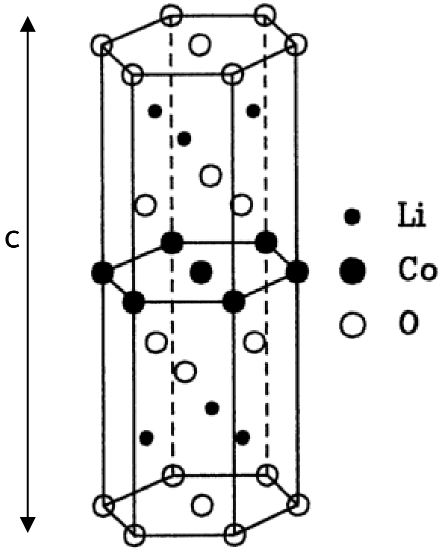
channel electrode: Li_xCoO_2
gate electrode: Li_xSi
solid electrolyte: LiPON

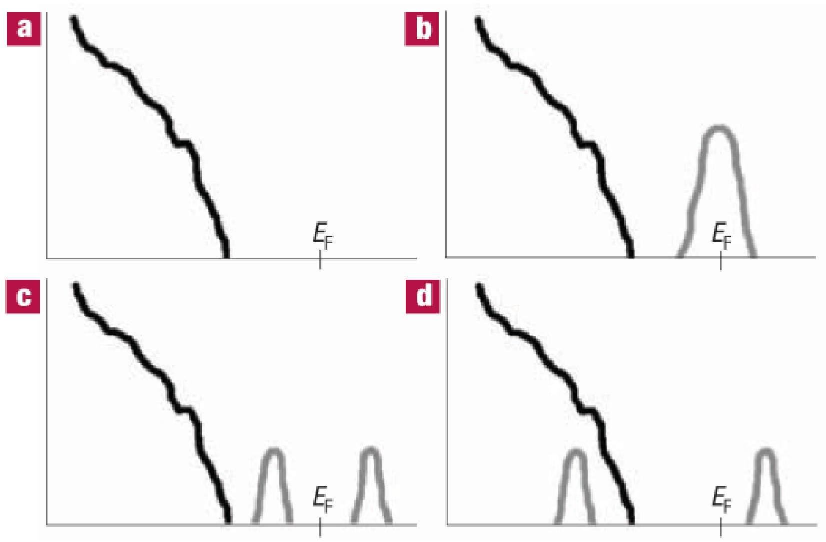
Can ion-insertion devices operate with speed, scale and stability required to compete with traditional semiconductor devices?

- **<100 nm dimensions?**
- **previous work: 100 μm features, polycrystalline with defects, grain boundaries etc. that adversely affect performance.**

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

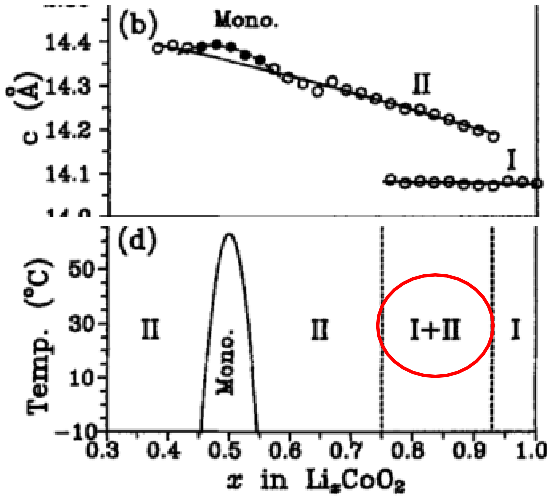
LiCoO$_2$ – electron correlation effects





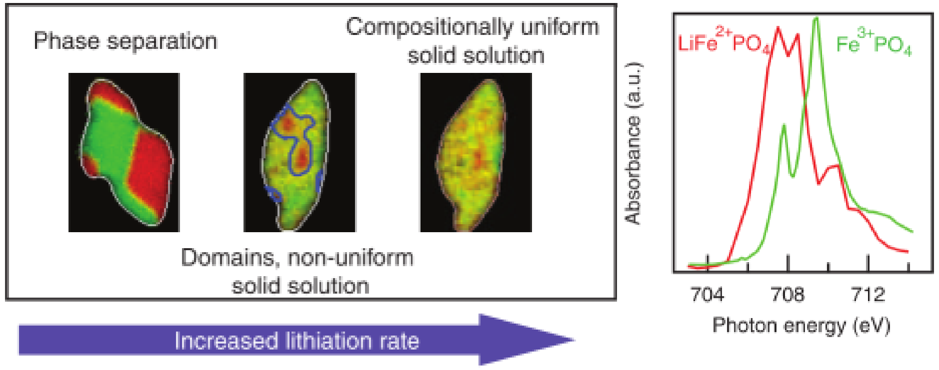
Marianeti et. al. *Nature Materials* 2004

X-ray diffraction

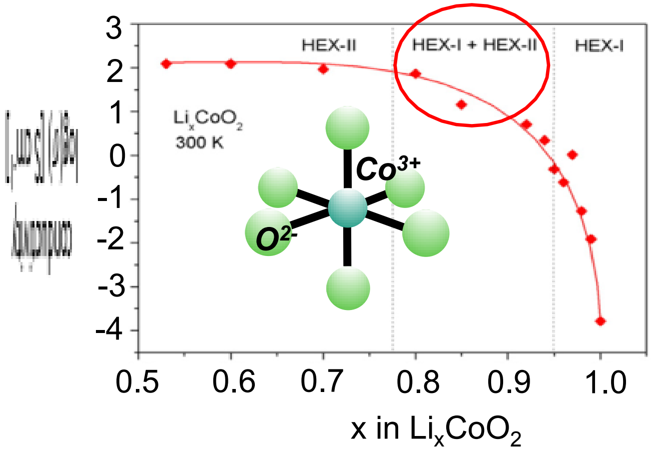


Reimers et. al. *J. Elec. Soc.* 1992

STXM of Li$_x$FePO$_4$ single crystal platelets

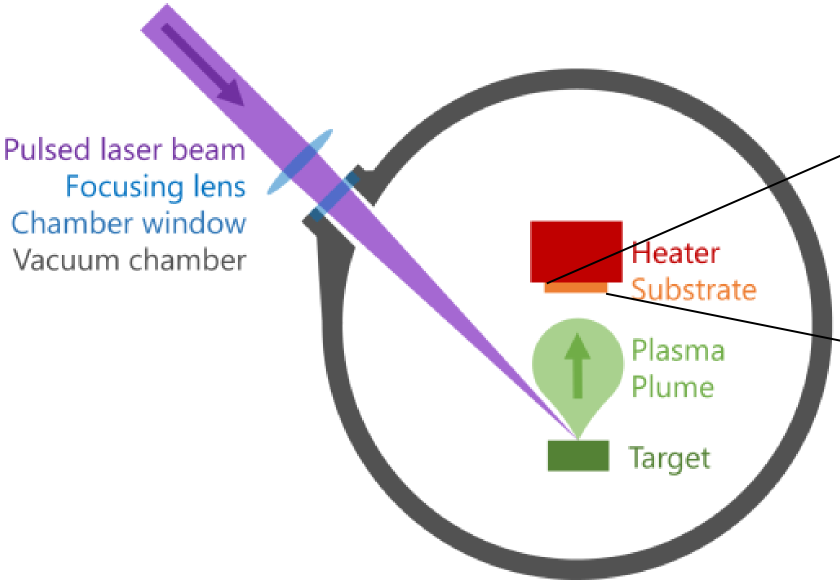


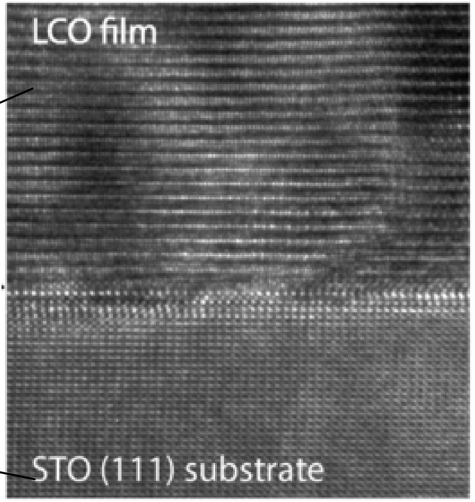
J. Lim, Y. Li et. al. *Science* 2016

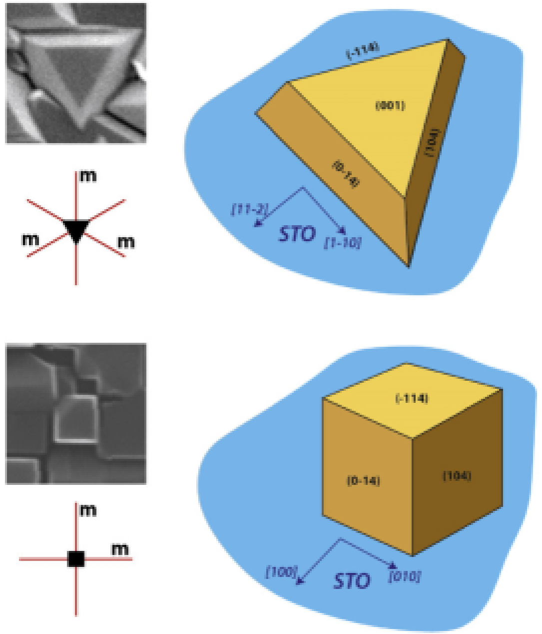


Milewska et. al. *Solid State Ionics* 2014

Pulsed laser deposition to create model systems





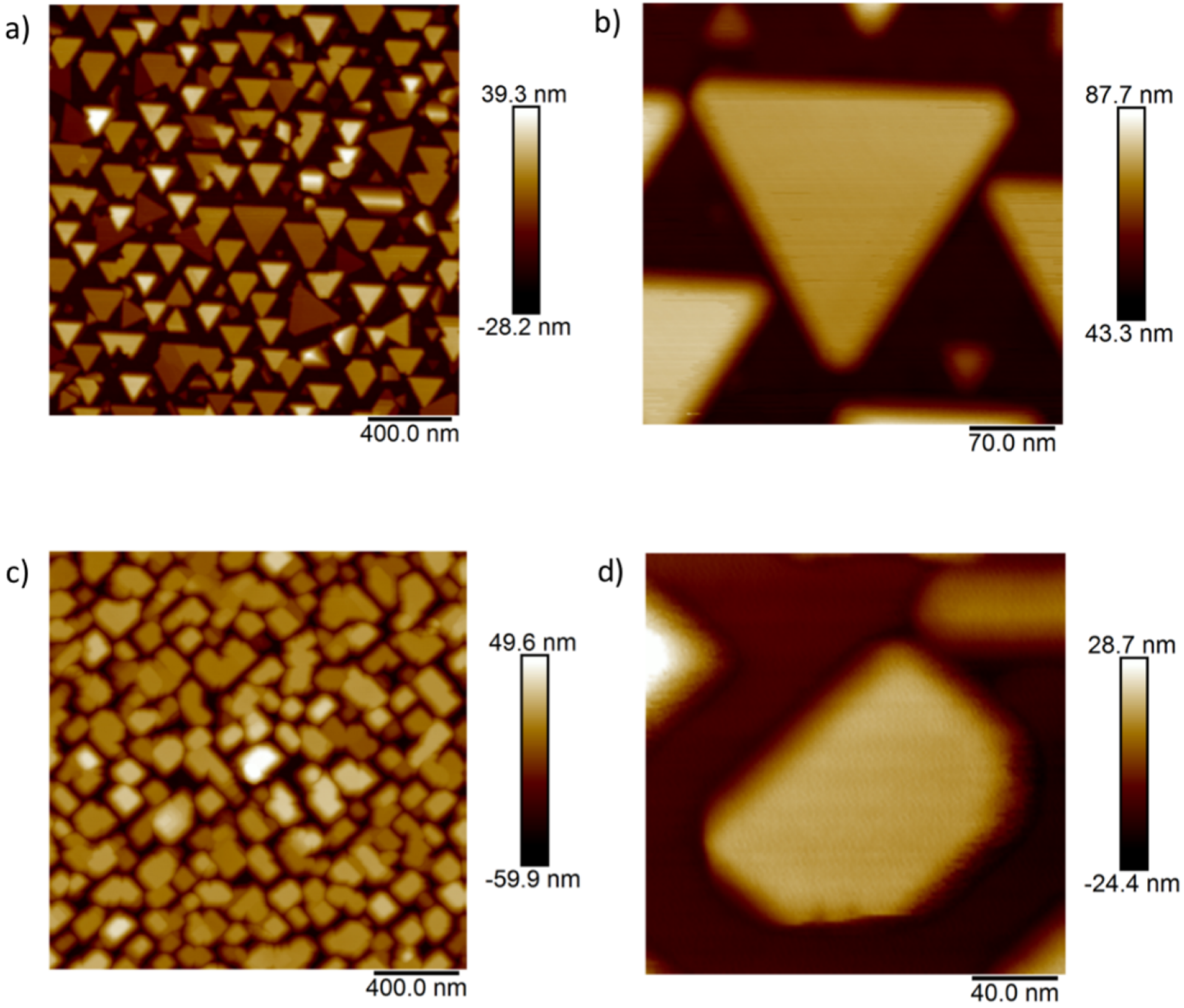


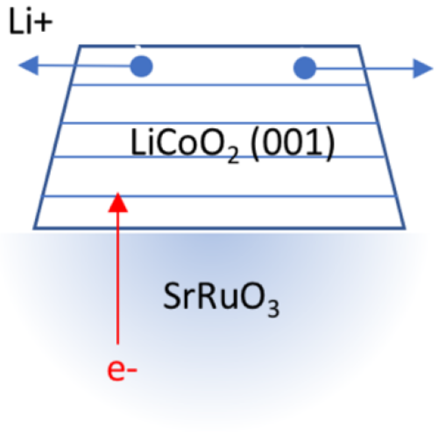
Can we create **ideal material** systems for fundamental studies?

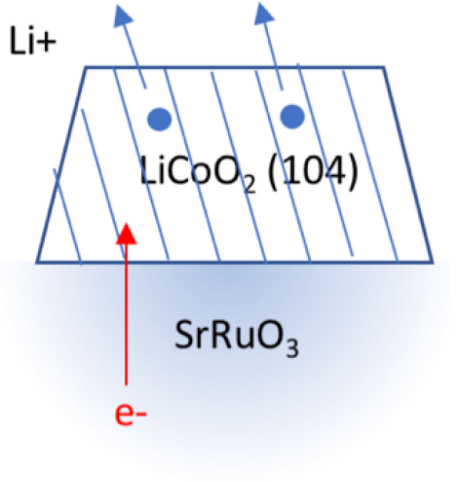
1) fewer defects, no grain boundaries
2) well-defined interfaces
3) highly-scaled geometries <100 nm
4) Large, isolated single crystals >1 micron

Z. Li et al. *Thin Solid Films*, *612*, 472–482 (2016)

Two orientations of $LiCoO_2$ epitaxial islands

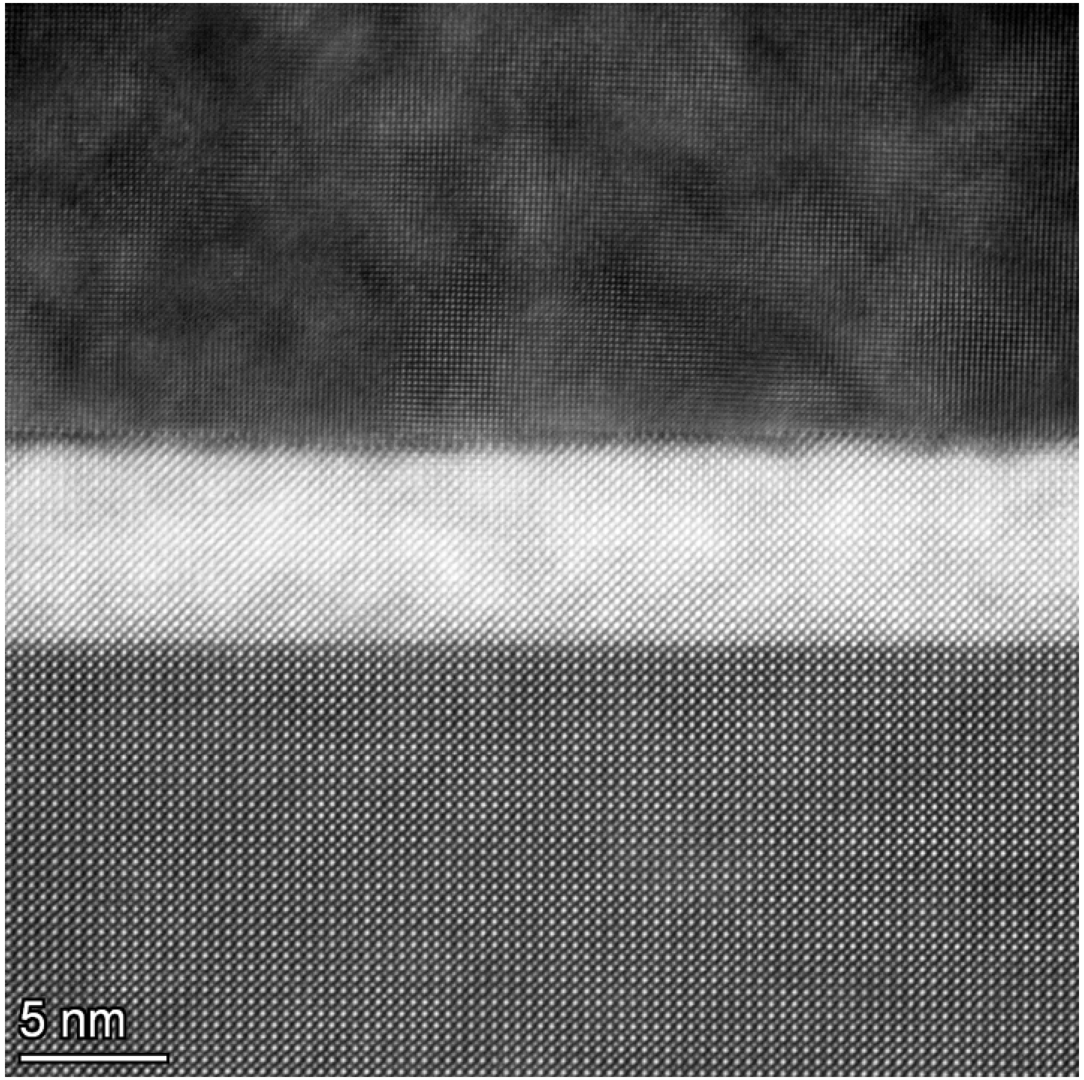




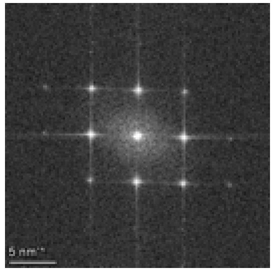


HRTEM epitaxial islands

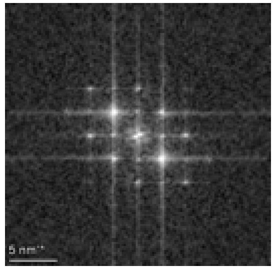
HR-TEM



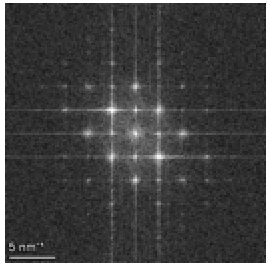
SAED



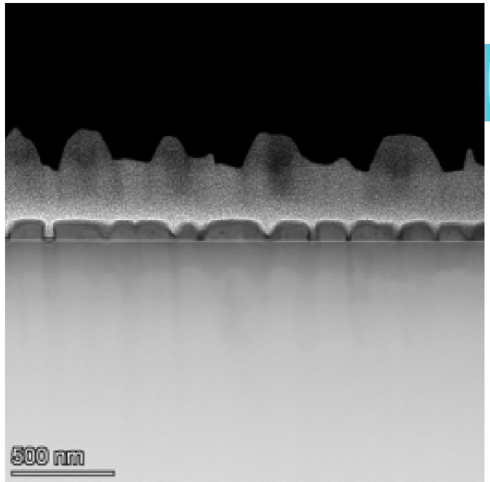
$LiCoO_2$



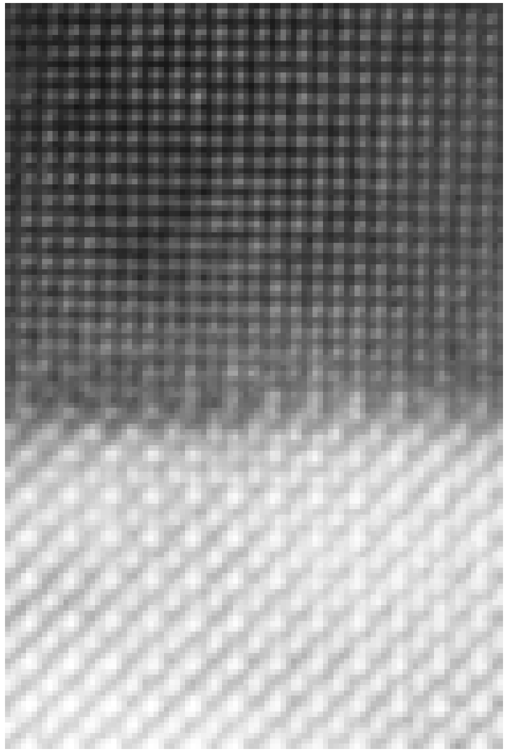
$SrRuO_3$



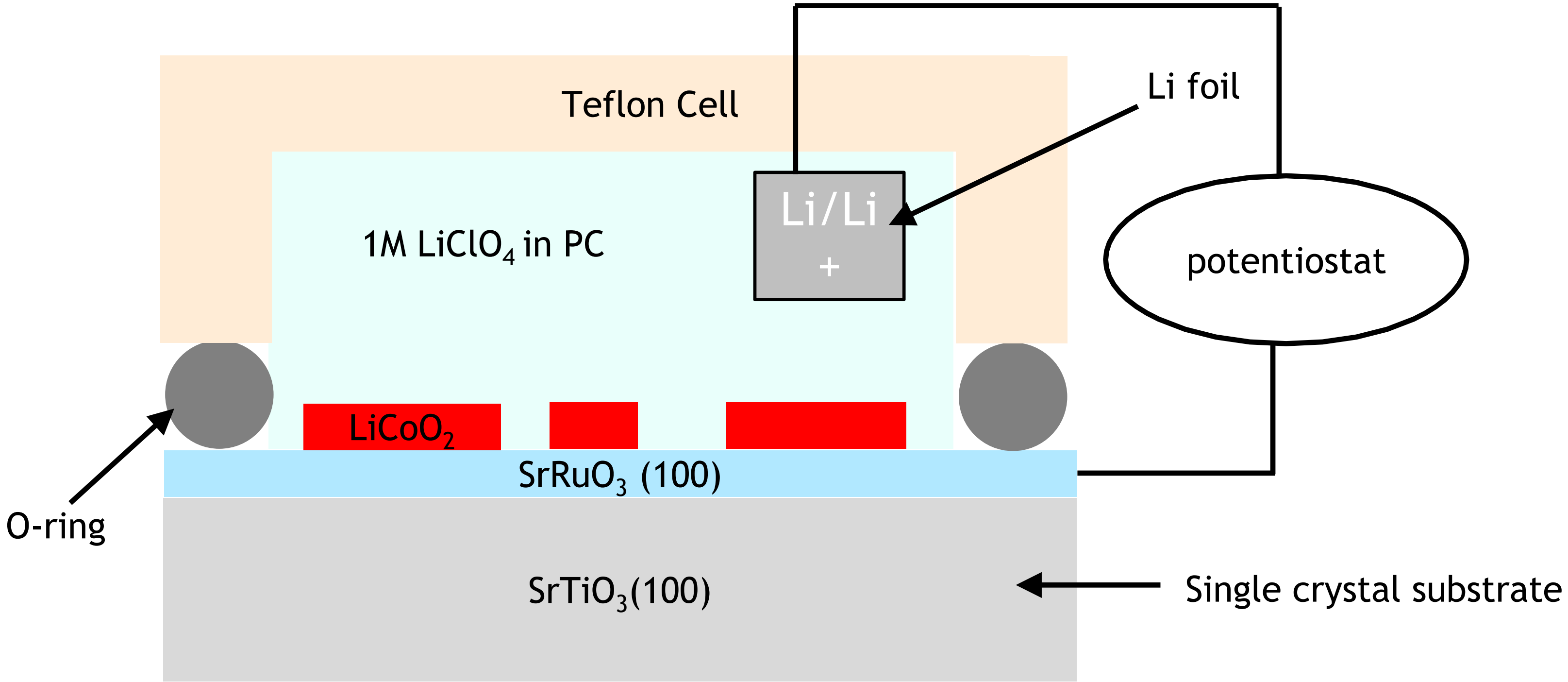
$SrTiO_3$



$LiCoO_2$ / $SrRuO_3$



Electrochemical cycling



Teflon Cell

1M $LiClO_4$ in PC

Li/Li^+

Li foil

potentiostat

$LiCoO_2$

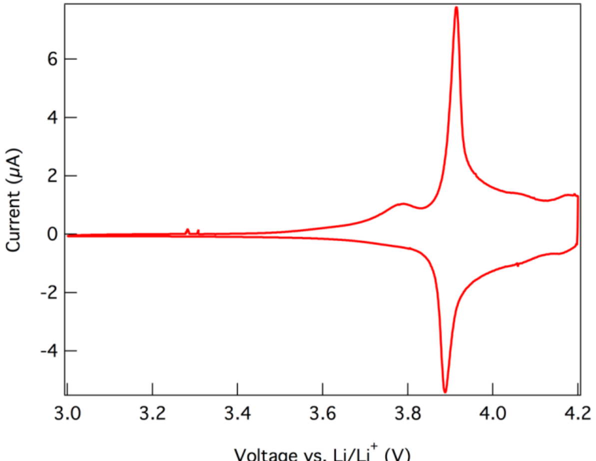
$SrRuO_3$ (100)

O-ring

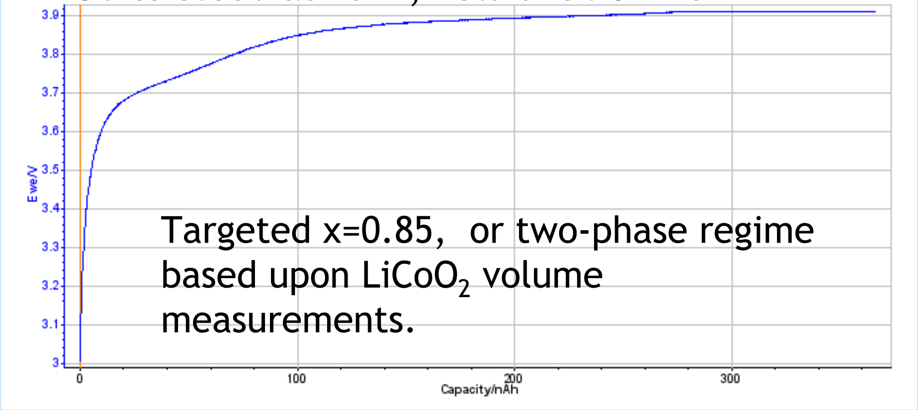
$SrTiO_3$(100)

Single crystal substrate

Cyclic voltammetry



GV to 3.88V at 40nA, held until C=120nAh

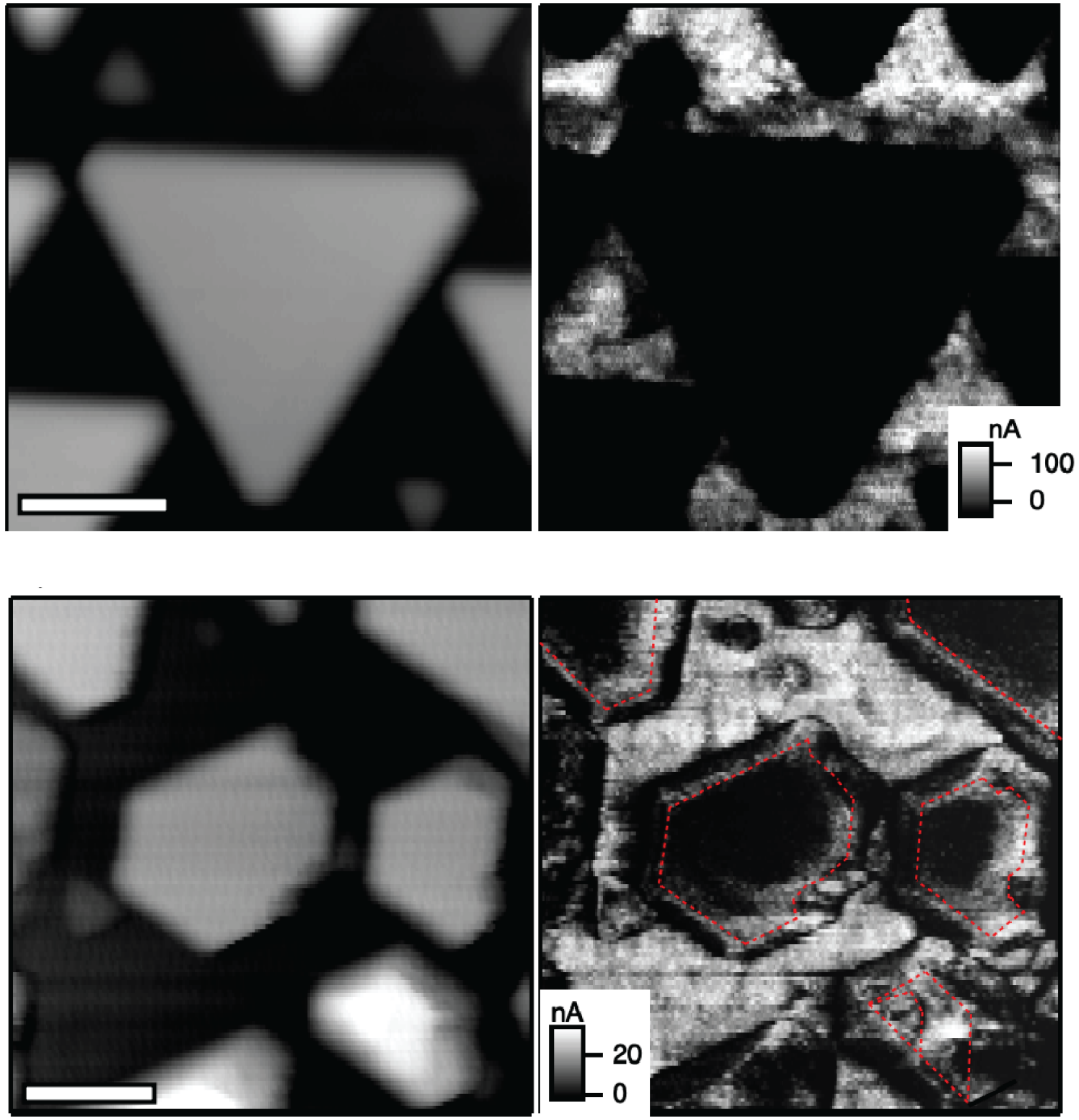


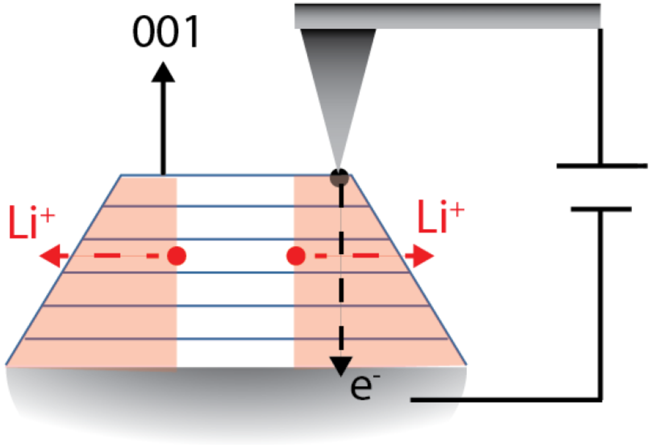
Targeted x=0.85, or two-phase regime based upon $LiCoO_2$ volume measurements.

Anisotropic diffusion – c-axis oriented islands

Before cycling

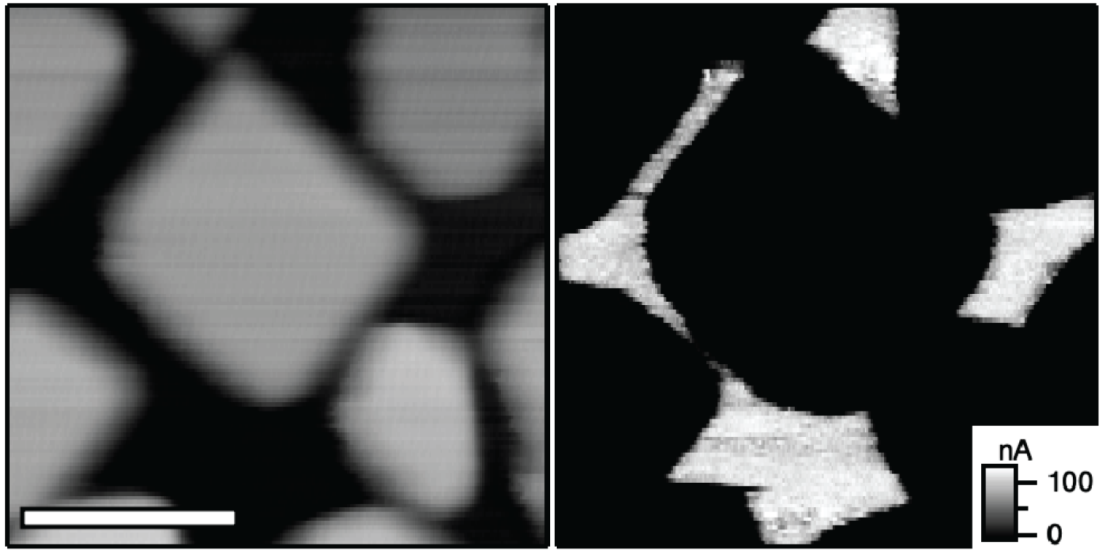
After cycling



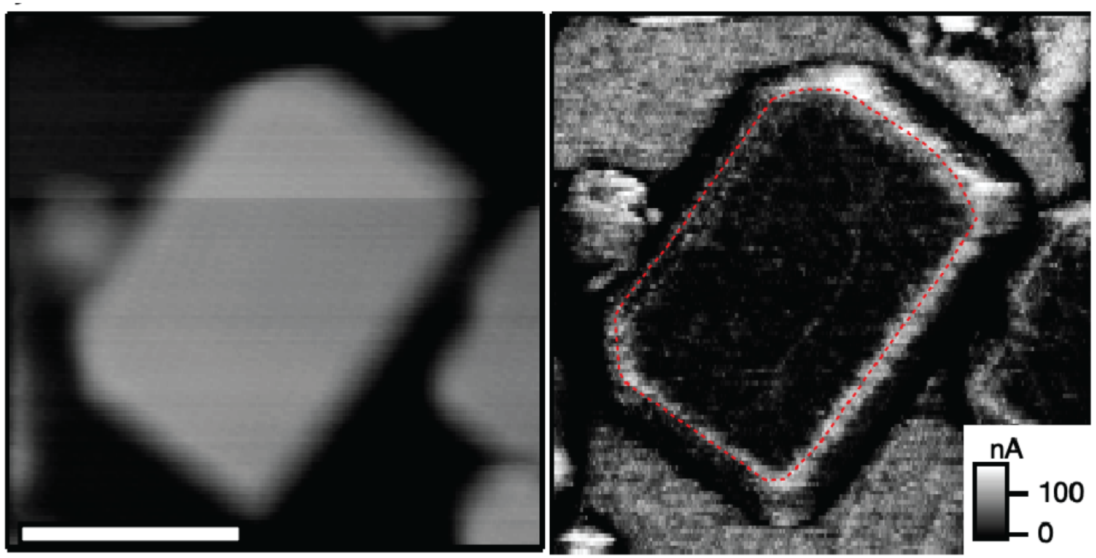


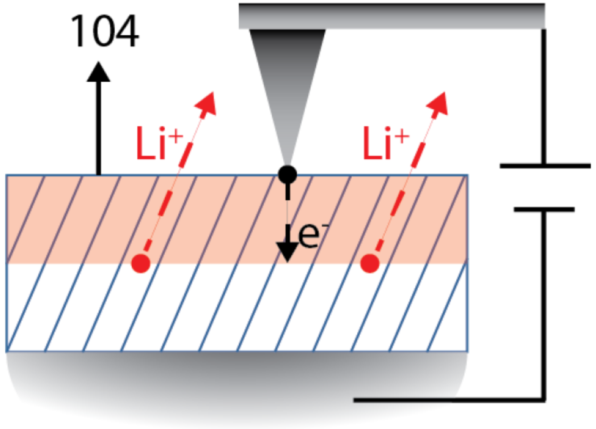
Anisotropic diffusion – planes oriented normal to surface

Before cycling

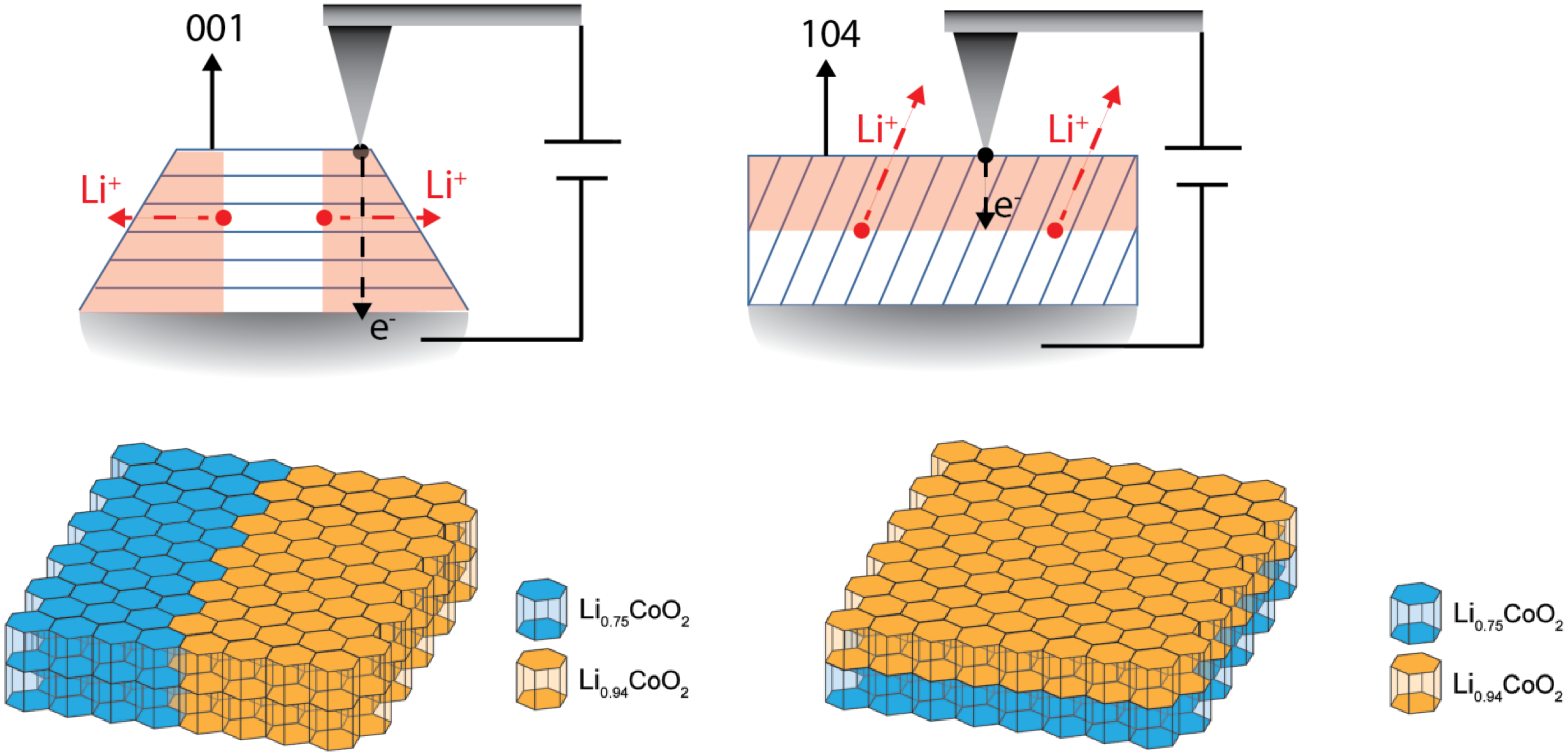


After cycling





Conclusion – diffusion constrains islands to kinetically arrested state



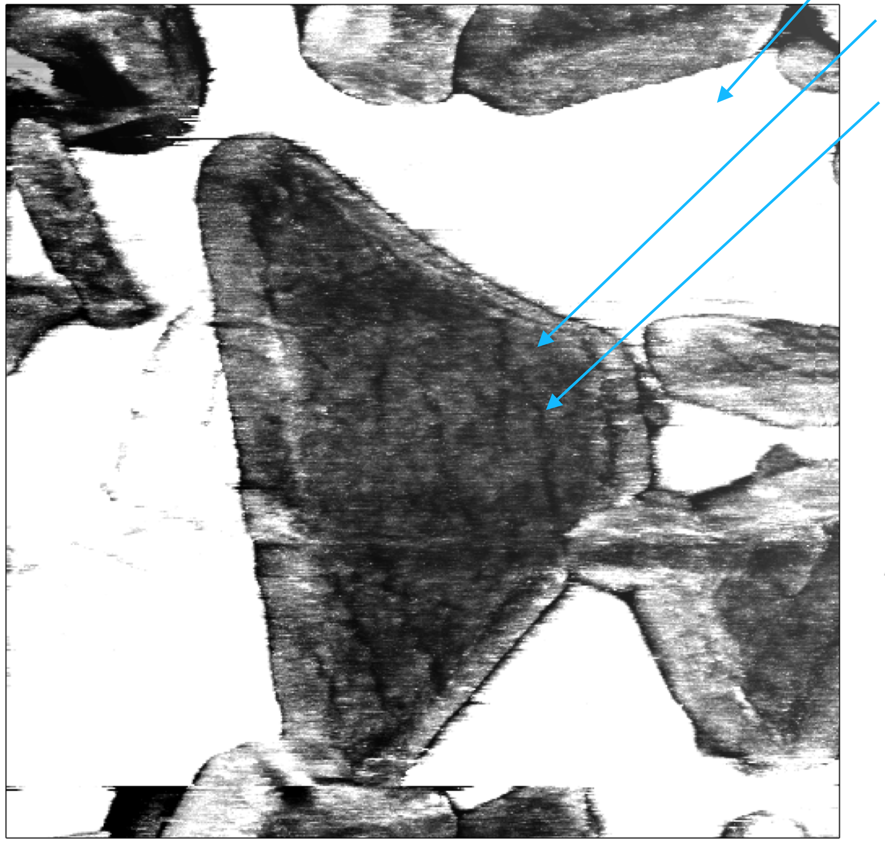
(C) kinetically arrested state
(no vertical diffusion)

(D) strain energy minimum
(vertical diffusion activated)

Nadkarni et. al. Adv. Func. Mat. 2019

Below a critical thickness films exhibit striping effect

AFM current map



white: conductive $SrRuO_3$

light : lithium poor

dark : lithium rich

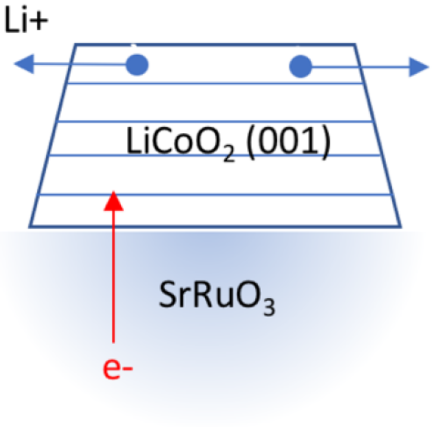
- fringes appear with about ~35 nm spacing
- We can relate to coherency strain

$$\lambda = \sqrt{\frac{2\gamma L_C}{\Delta f}}$$

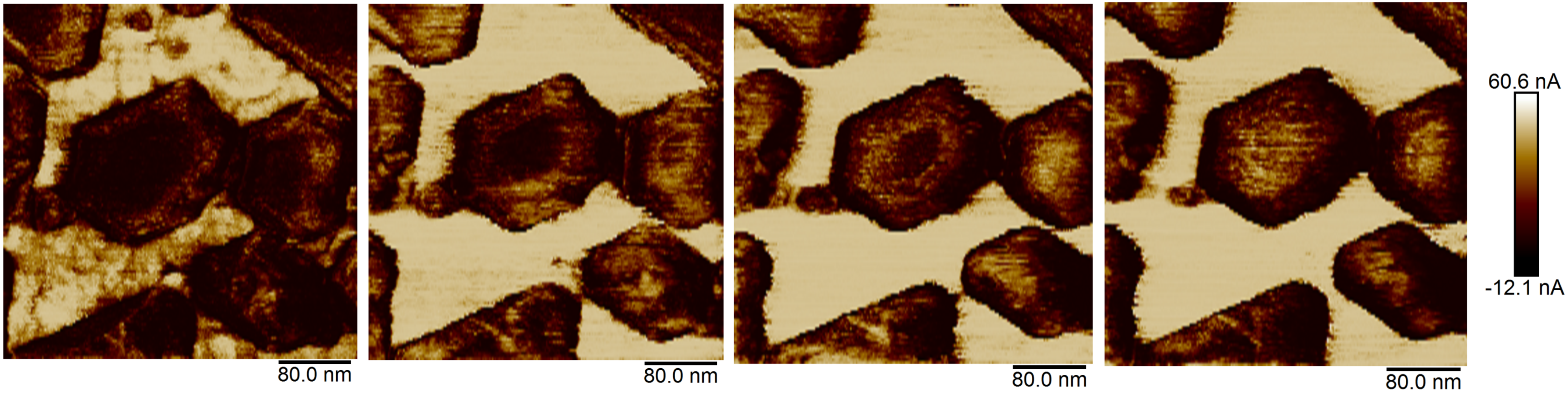
γ: interfacial energy
L_C: width of particle
Δf: difference in free energy

Assume L_C= ~30 nm or crystal thickness

Force induced metallization

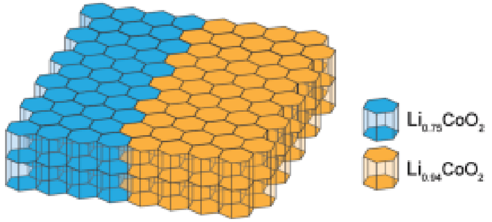


20 nN → 180 nN

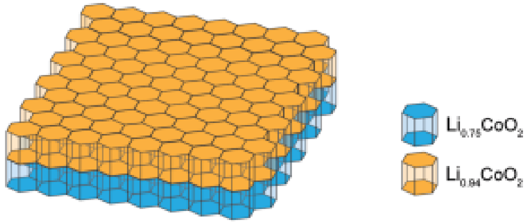


Conclusions

$LiCoO_2$ particles/islands sit in a kinetically arrested state due to diffusional anisotropy

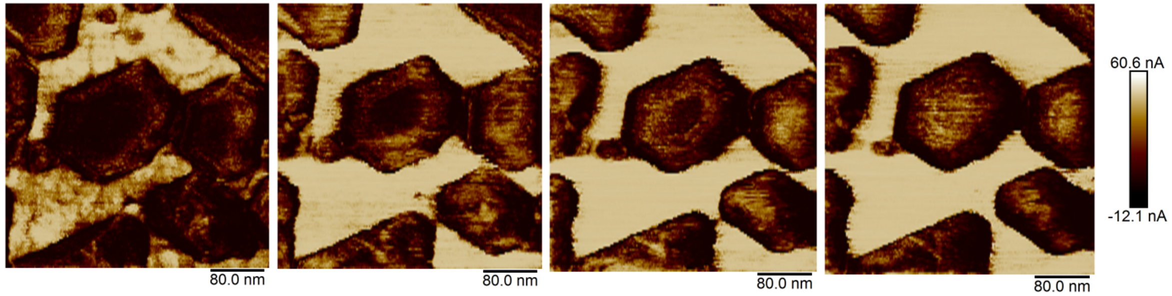


(C) kinetically arrested state
(no vertical diffusion)

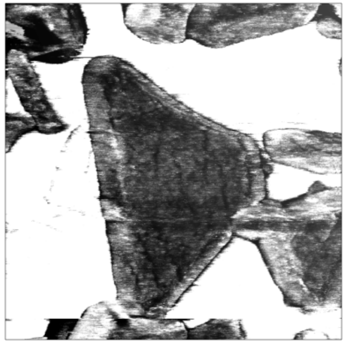


(D) strain energy minimum
(vertical diffusion activated)

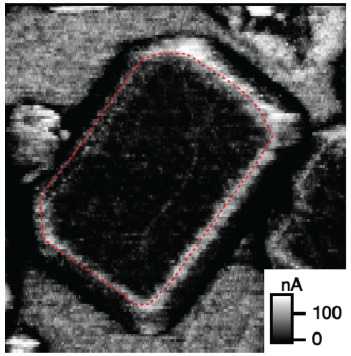
Strain from cycling, solid overlayers can play a critical role.



Scaled particles can exhibit other segregation effects when surface energy dominates



Where facets meet, the low surface area to volume ratio may ratio may lead to phases that different than bulk.



- All effects will play a critical role in ECRAM synaptic/neuronal properties
- Results may inform single-particle level battery charging models

Thank you

Sandia National Laboratories

Elliot J. Fuller

David S. Ashby

A. Alec Talin

Universidad Autónoma de Madrid

Celia Polop

Instituto de Ciencia de Materiales de Madrid

Enrique Vasco

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