Oak Ridge National Laboratory

Department of Energy
Early Career Research Award

Spatially Resolved Ionic Diffusion and Electrochemical Reactions in Solids: A Biased View at Lithium Ion Batteries

Nina Balke

Oak Ridge National Laboratory

Center for Nanophase Materials Sciences

Outlook

Introduction

- Why Li-ion batteries?
- Why scanning probe microscopy?
- Principles of Electrochemical Strain Microscopy (ESM)

Science

- New information available through ESM
  - Description of ionic transport
  - Coupling of ionic transport and microstructure
  - Ionic transport through a battery

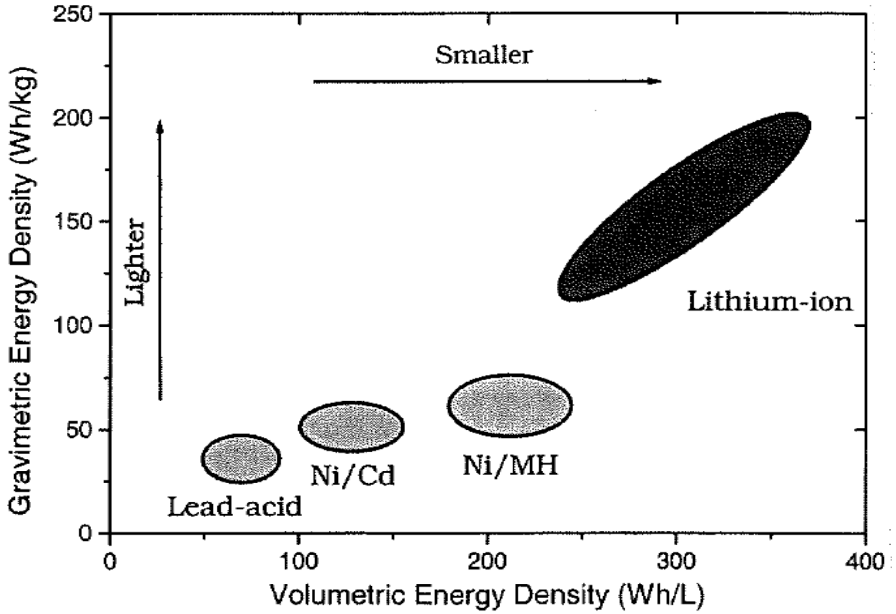
Early Career Award

- ESM in the big picture

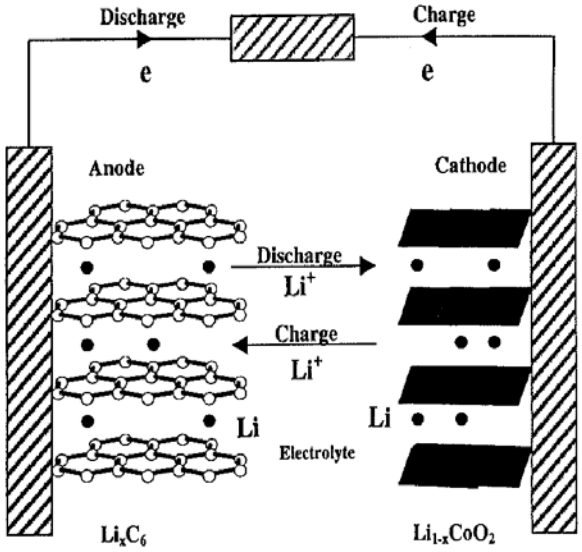
Why Li-Ion Batteries?

Secondary (rechargeable) batteries for portable electronic devices

Li-ion batteries are considered to be the most promising technology



Li-ion intercalation batteries

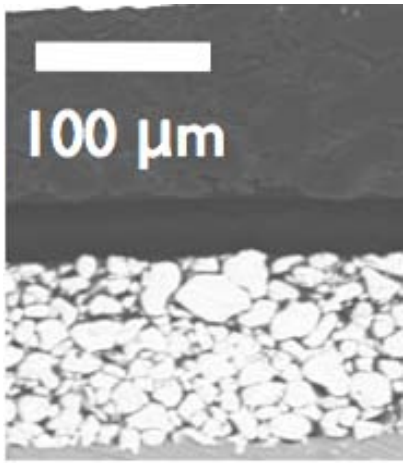


Nazri, Lithium batteries 2009

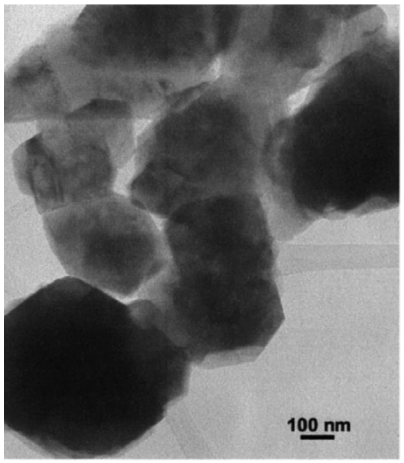
Li-Ion Batteries - From Ideal to Real

Li-ion batteries

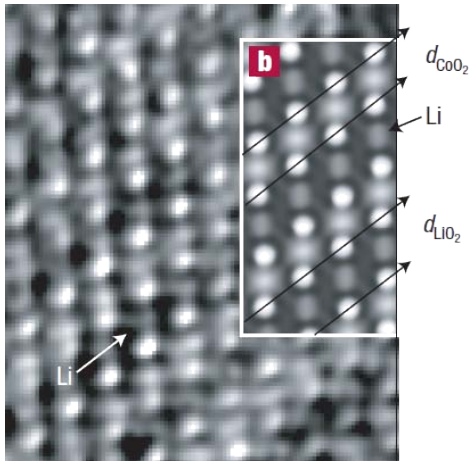
Battery functionality is determined by ionic transport across several length scales



Courtesy of Edwin Garcia



Shao-Horn, Solid State Ionics 2001



Shao-Horn, Nat. Mat. 2008

Device **Interface** **Grain** **Atom**

To understand the fundamental processes which define a battery, we need to look at small length scales < 100nm → **SPM**

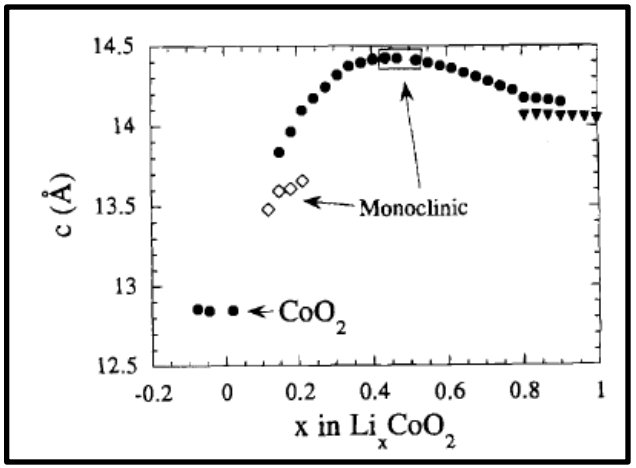
The Concept of ESM

Concept of **E**lectrochemical **S**train **M**icroscopy

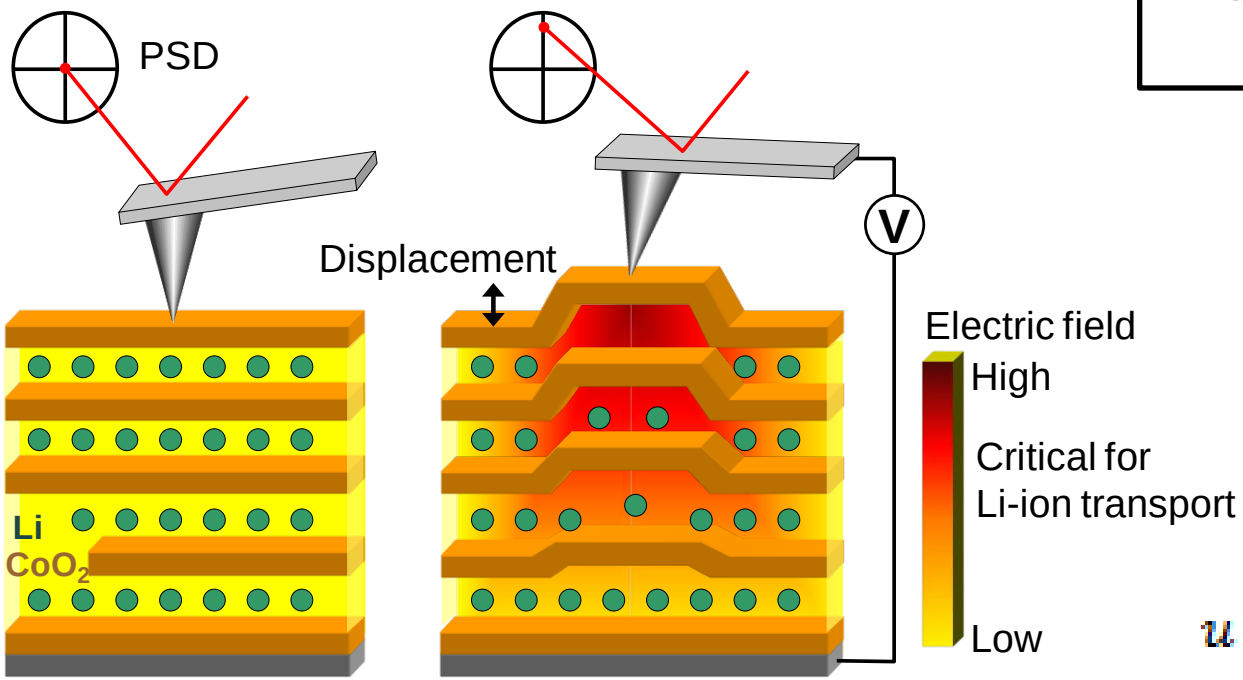
- Utilize the correlation between c(Li) and unit cell volume
- Induce local changes in c(Li) with biased SPM tip

Strain = f(bias)

Characteristic: volume change



Amatucci 1996



ESM signal:

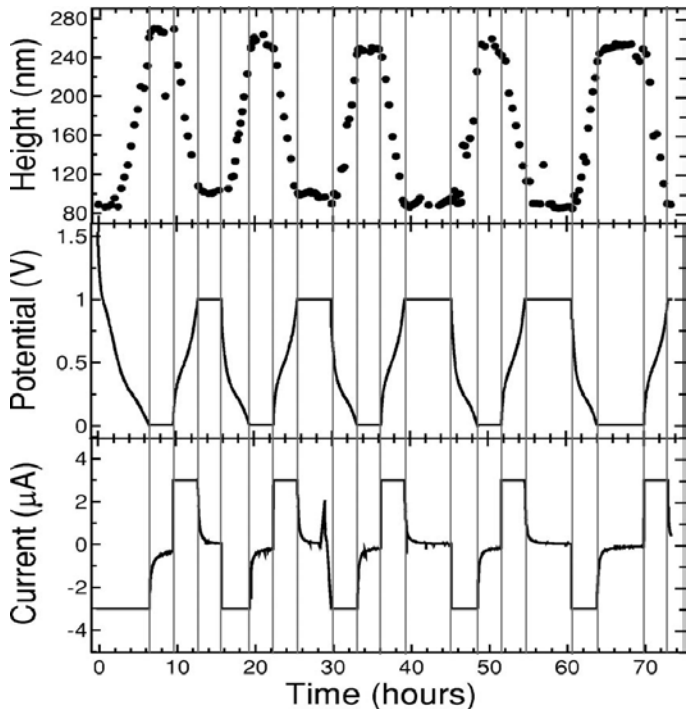
Surface displacement = measure for bias-induced Δc(local)

$$u = 2(1+\nu)\cdot\beta\cdot\frac{V_{ac}}{\sqrt{\omega}}\cdot\frac{\sqrt{D}}{\eta}$$

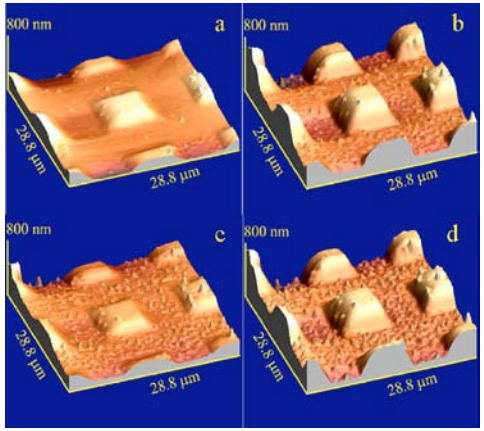
Anna Morozovska

The Concept of ESM

What is new with ESM (SPM + strain detection + local bias)?



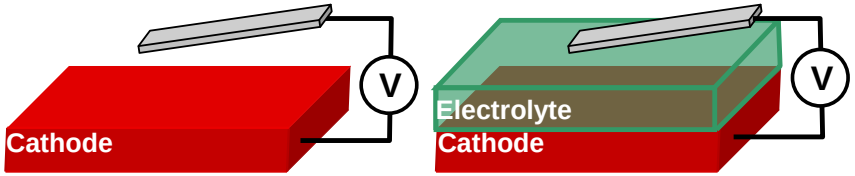
Lewis 2007



Sn-Co-C

ESM allows for mapping without changing charging state of the battery (probing ionic transport).

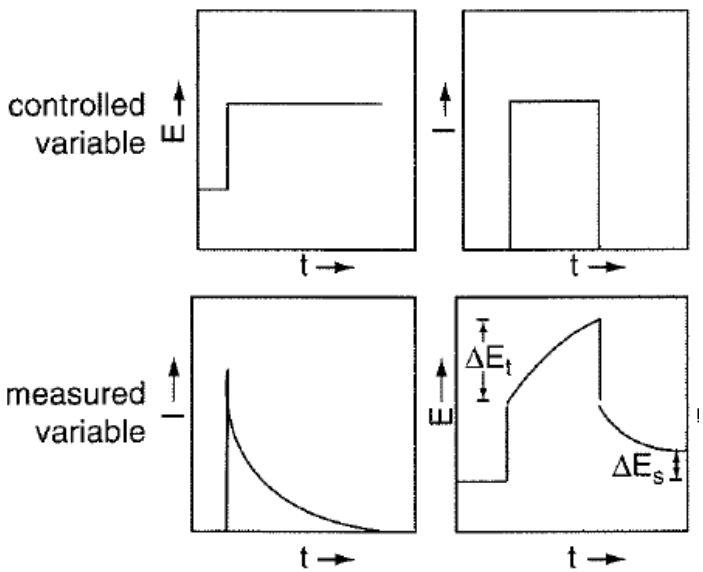
	Ion flow…	Length scale	Time scale
Macroscopic	through battery	1-10 μm	hours
SPM	localized	10-100 nm	seconds


V
Cathode
V
Electrolyte
Cathode

"Electrical" environment: Probing ionic transport

Macro

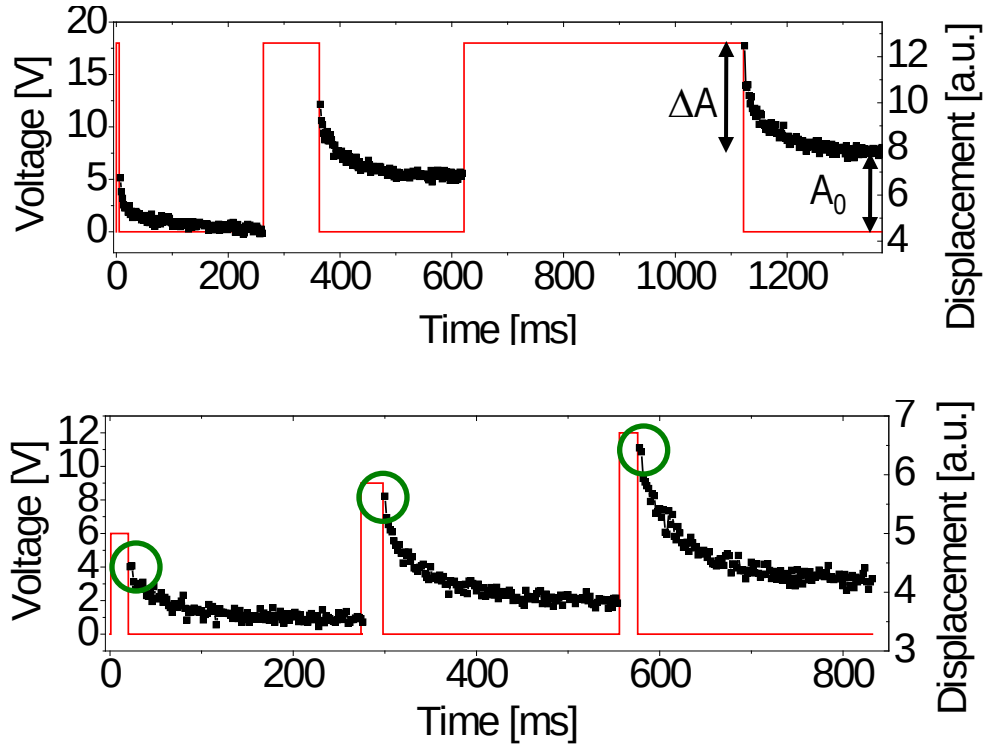
PITT and GITT
(potentiostatic and galvanostatic intermittent titration technique)



Huggins, *Advanced Batteries*, (2009)

Nano

Time and voltage spectroscopy



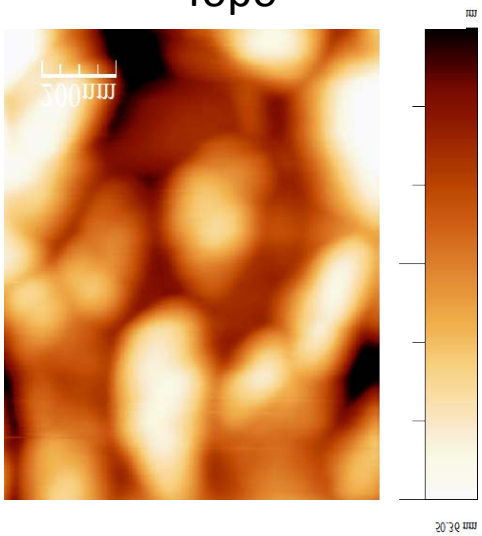
Goal: Develop strain analogs to traditional characterization techniques

Time spectroscopy on $LiCoO_2$

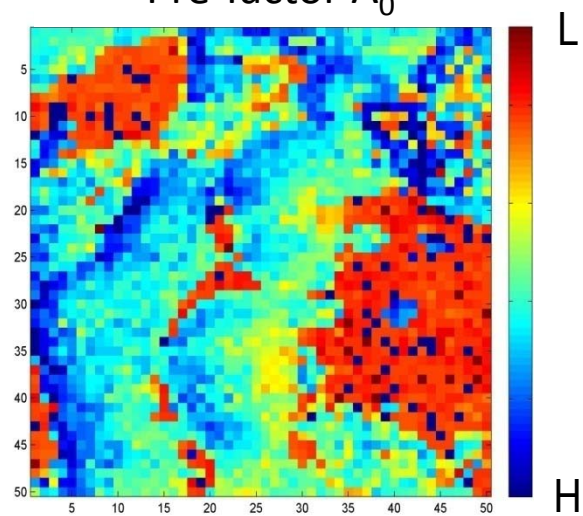
Ionic transport of Li described by diffusivity D [m^2/s] with $D \approx \exp(-E_a/RT)$

Relaxation after -10V/30ms voltage pulse measured with ESM
ESM as f(t) can be fitted by simple exponential decay $y = A_0 * \exp(-A_1/\tau) + A_2$

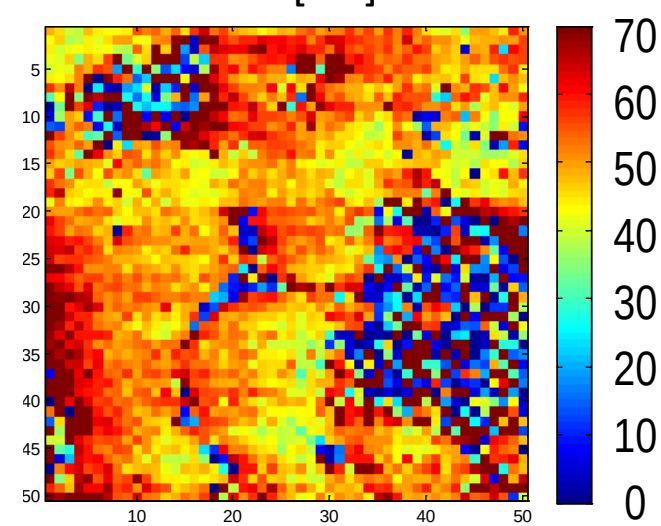
Topo



Pre-factor A_0



τ [ms]



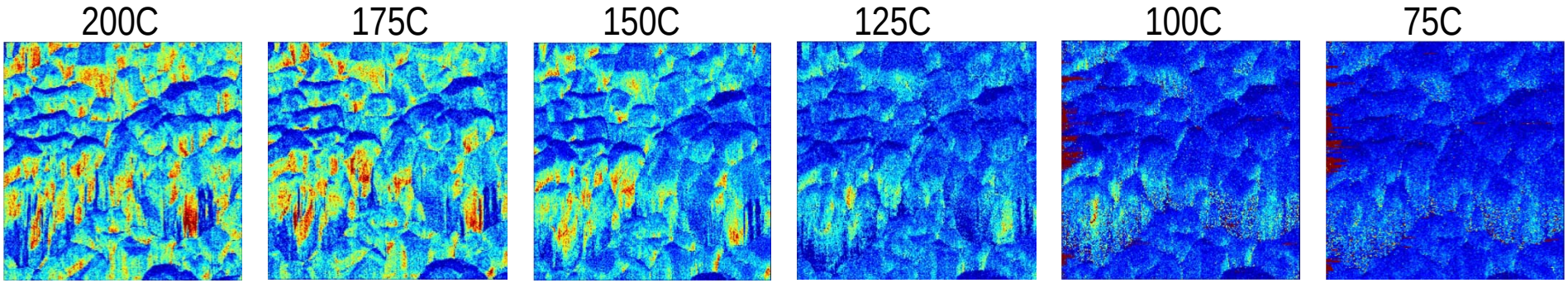
$$D = \frac{L^2}{\tau}$$

L^2 → tip radius 50 nm

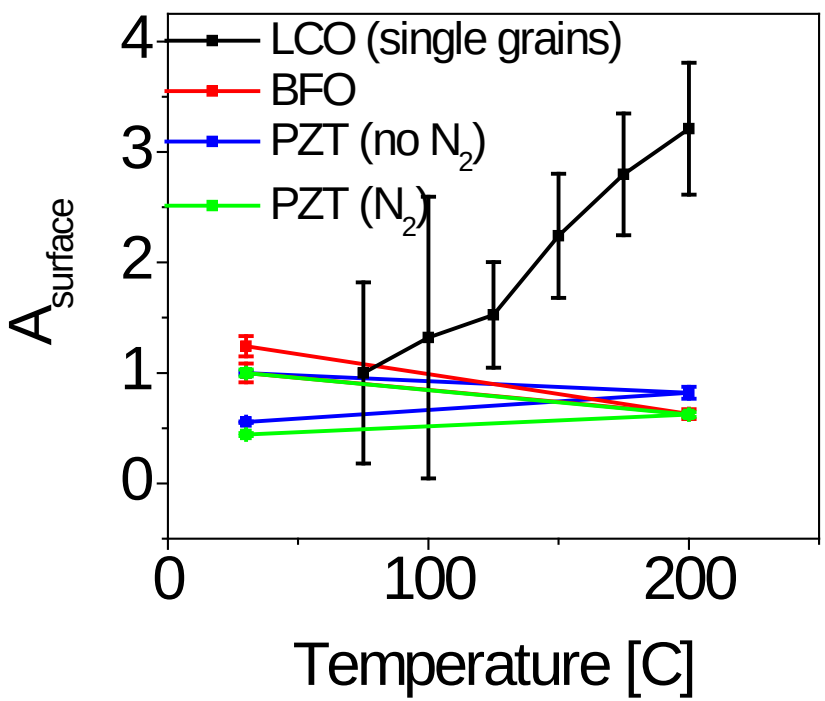
τ → from measurement 50 ms

Diffusivity of $5 \cdot 10^{-14}$ vs. $10^{-14} - 10^{-12} m^2/s$ in literature.

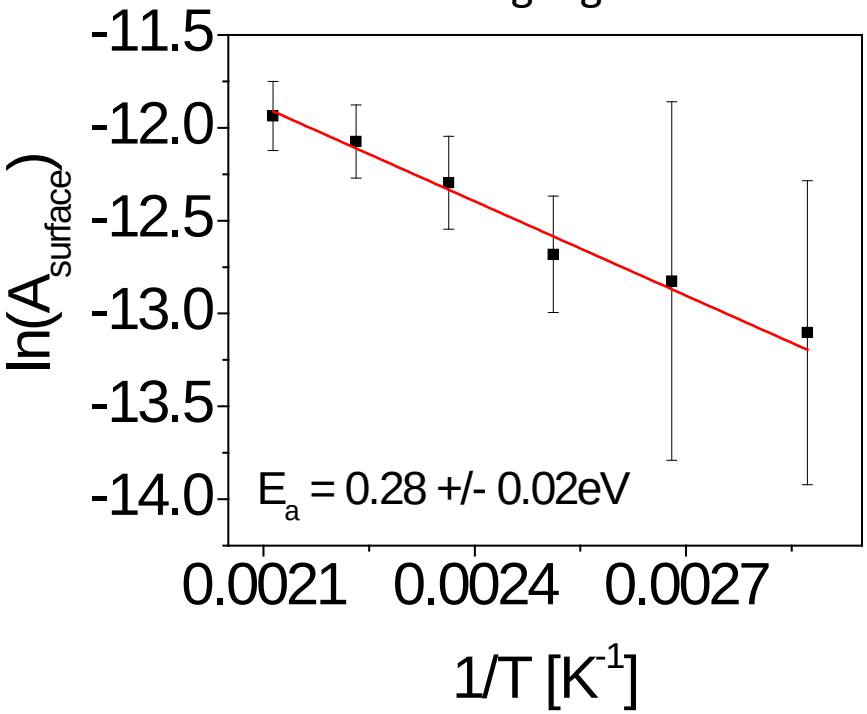
ESM as function of T on $LiCoO_2$



Compare to ferroelectrics



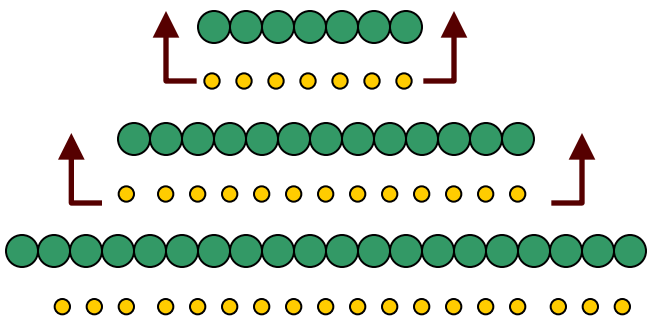
For single grains



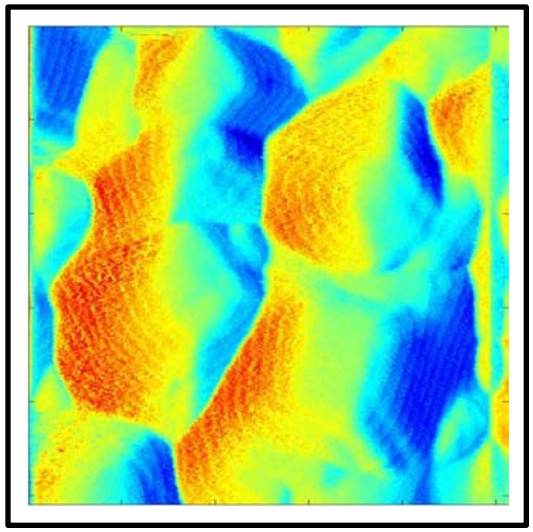
Activation energy for ionic transport 0.28 eV vs. 0.3 eV in literature.

Electrochemical activity of step edges on $LiCoO_2$

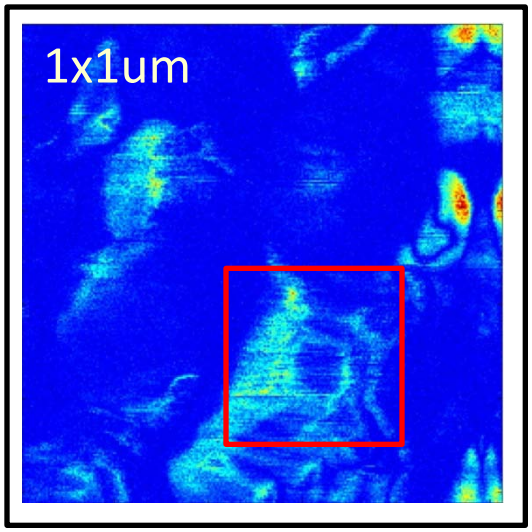
Coupling of ionic transport and grain morphology



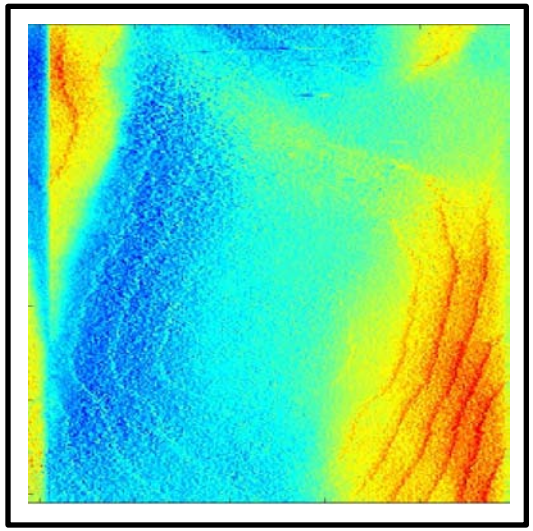
Deflection



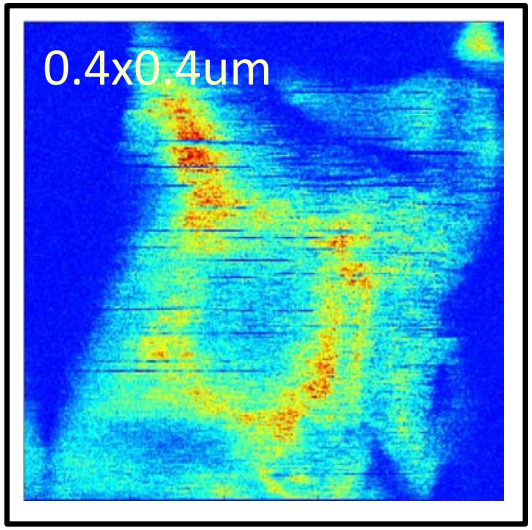
Li-ion activity



Deflection



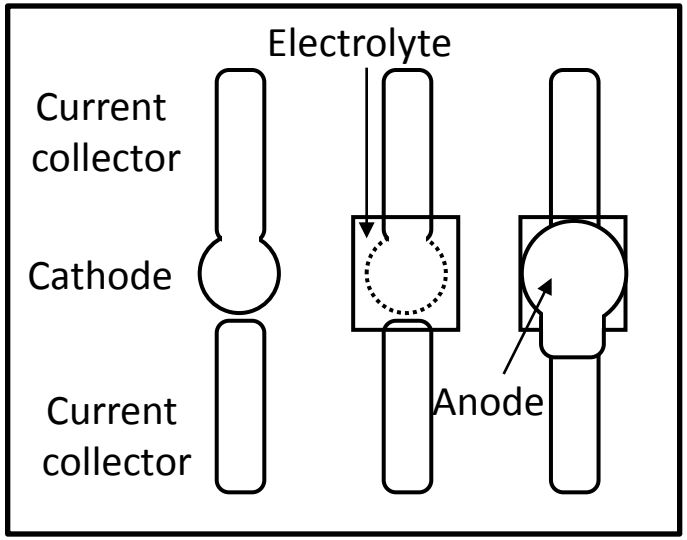
Li-ion activity



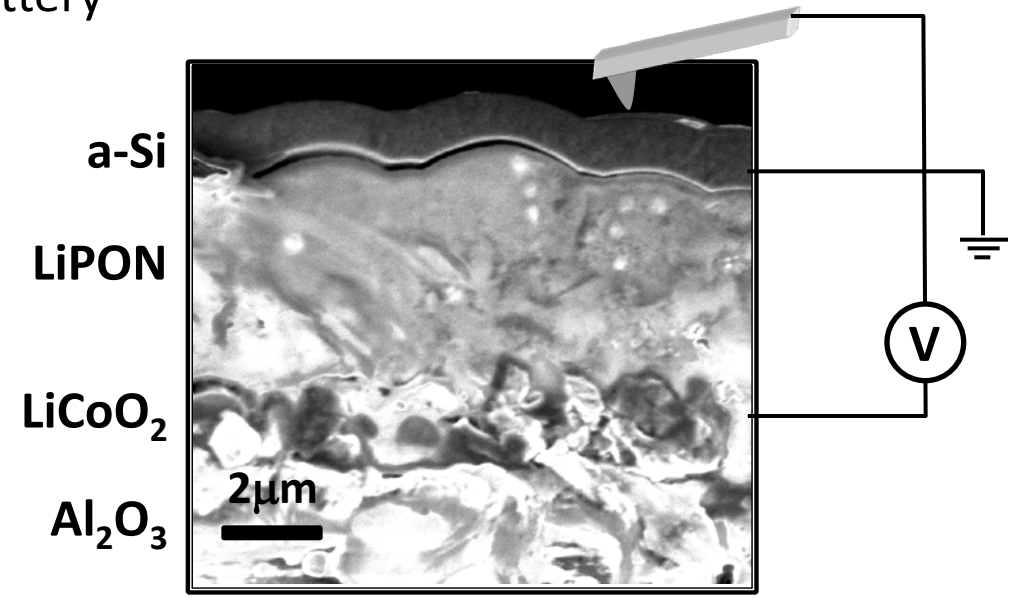
High resolution images allow to investigate processes at single step edges!

Ionic transport through a-Si/LiPON/$LiCoO_2$

Radio frequency sputtered thin film battery

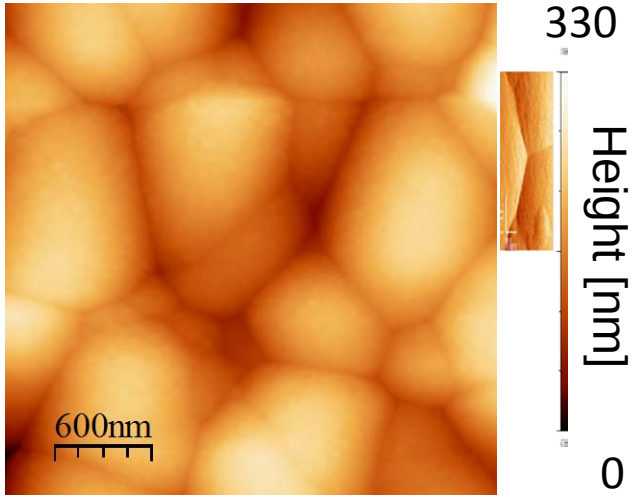


Dudney, J. Mater. Sci. Eng. B 116, 245 (2005)



- a-Si/LiPON/$LiCoO_2$
- LiPON: glassy lithium phosphorus oxynitride
- Thin film layers 500nm - 1µm

a-Si shows a substrate induced surface struture.

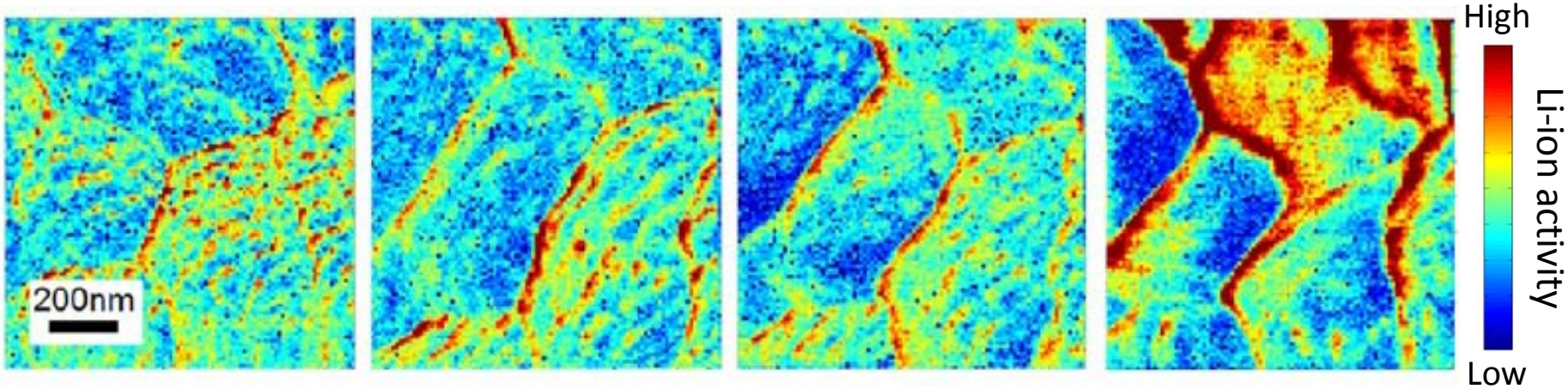


Balke et al., Nano Lett. 10, 3420 (2010)

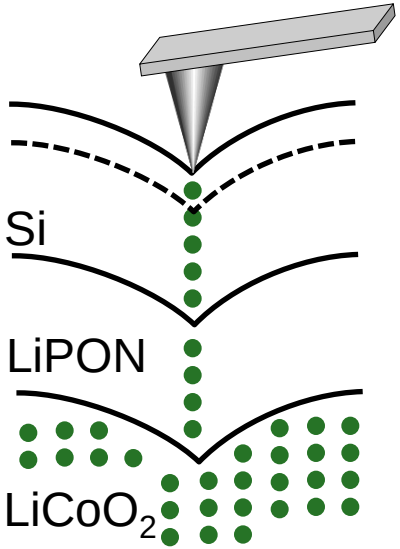
Tracking the charge transport through a-Si/LiPON/$LiCoO_2$

Evolution of Li activity with increasing state of charge:

Spatially resolved maps of Li activity:



Increasing charging state



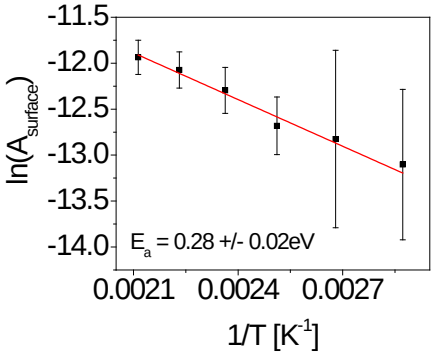
- Increased ionic transport along the boundary like features
- Good/bad for battery performance?

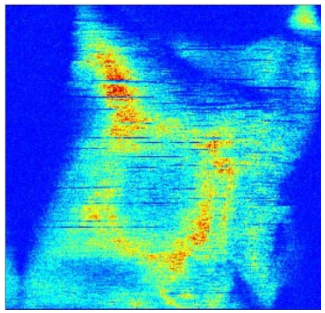
Balke et al., Nano Lett. 10, 3420 (2010)

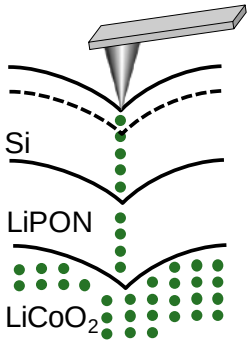
The Big Picture: ESM and ECA

Summary

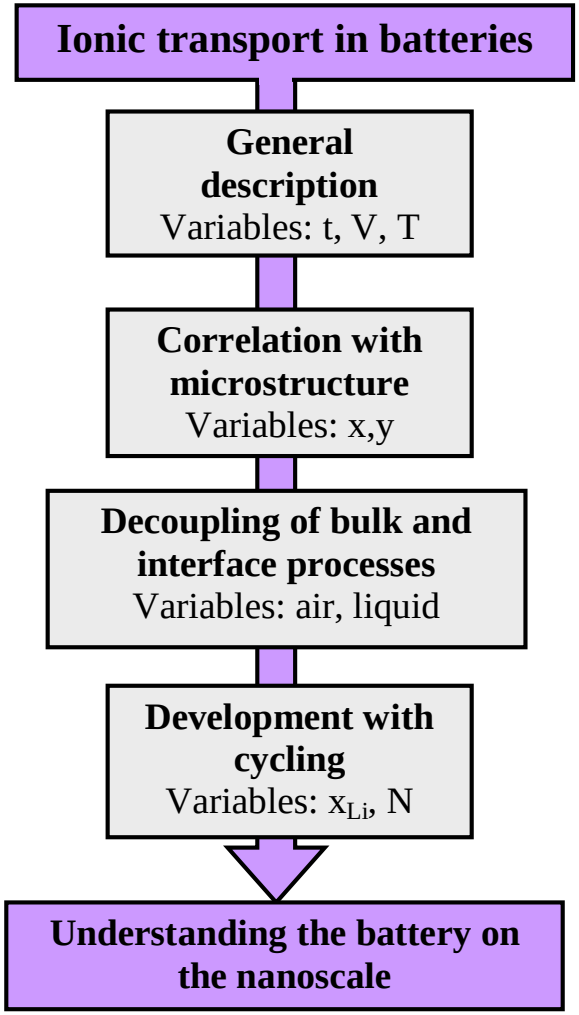
- ESM can be used to describe the ionic transport in time, voltage, and temperature domain
- The ionic transport can be correlated with the electrode microstructure
- The ionic flow through a battery can be observed







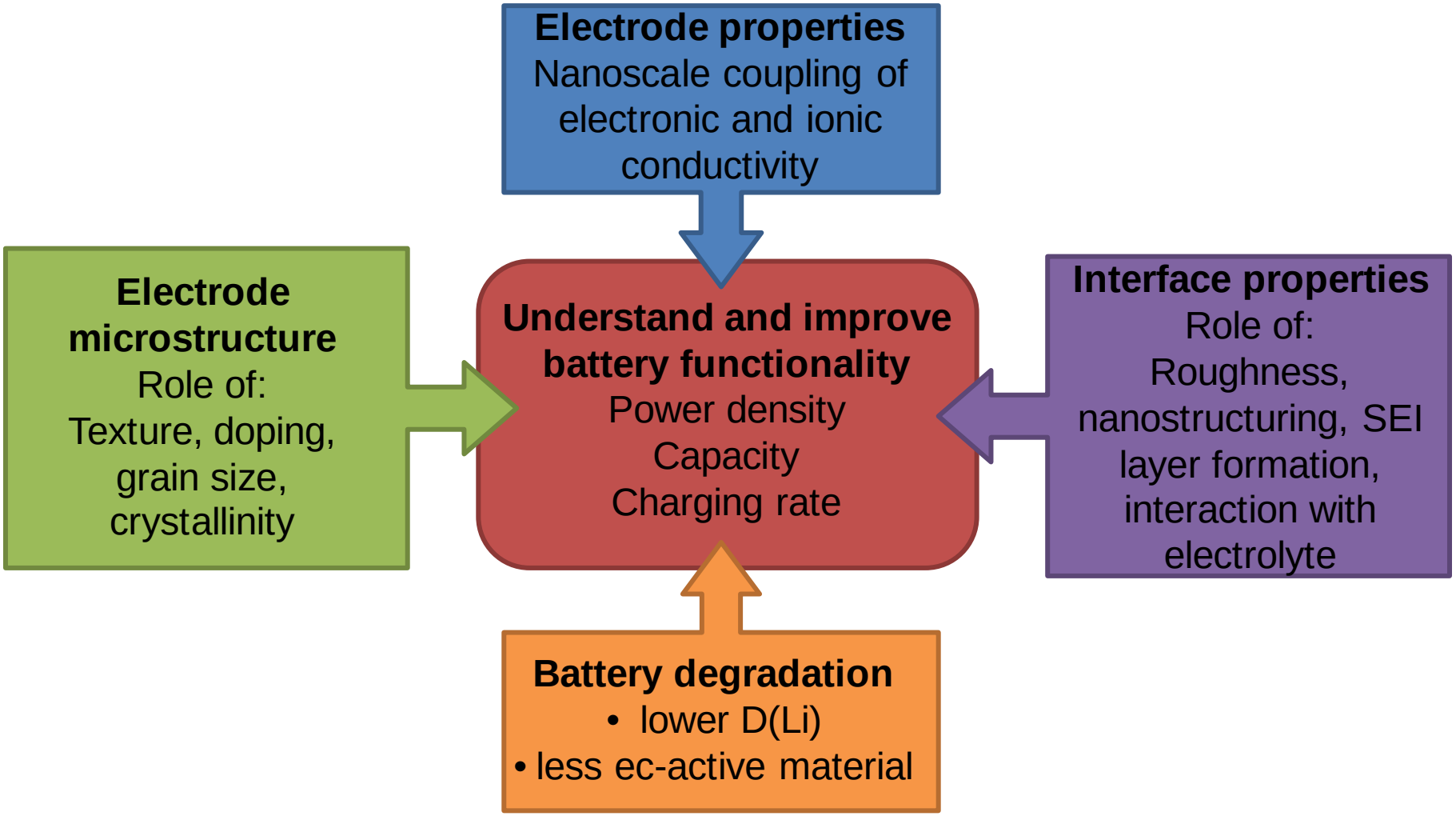
ECA work flow



The Big Picture: Experimental Milestones

Material/battery engineering through knowledge:

Nanoscale characterization can provide critically needed answers:



Collaborator Acknowledgement

OAK RIDGE National Laboratory

CNMS:
S. Jesse, S. Guo, T. Arruda, P. Maksymovych, I. Ivanov, A. Tselev, S. Kalinin
MSTD:
Y. Kim, L. Adamczyk, N. Dudney, S. Kalnaus, C. Daniel

PURDUE UNIVERSITY

D.-W. Chung, E. Garcia

НАН УКРАЇНИ ІФН ISP NAS UKRAINE
National Academy of Sciences of Ukraine
V. E. LASHKARYOV
INSTITUTE OF SEMICONDUCTOR PHYSICS
41, pr. Nauki, Kyiv, 03028, Ukraine,
tel.:38(044)525-40-20; fax; 38(044)525-83-42

A. Morozovska, E. Eliseev

Funding Acknowledgement

Part of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

Part of this material is based upon work supported as part of the Fluid Interface Reactions, Structures and Transport (FIRST), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences.

Partially support through the Feodor-Lynen program sponsored by the Alexander von Humboldt foundation.

Thank you for your attention!