Center for Nanophase Materials Sciences

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U.S. DOE Nanoscale Science Research Center

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

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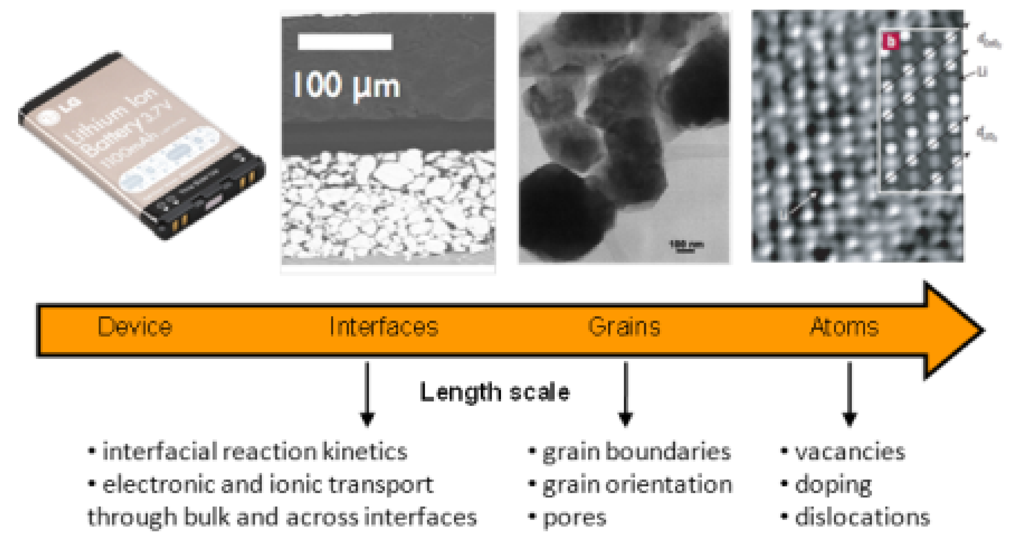
I. Introduction

Processes on different length scales determine battery performance.



In order to optimize battery functions, the role of interfaces, microstructure, and defects in the electrochemical process need to be investigated.

Scanning Probe Microscopy is a established tool to measure local strains and currents on the nanoscale and can be used to characterize battery materials.

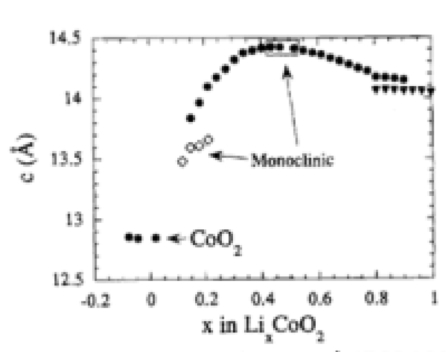
Images:
Edwin Garcia, Purdue University; Shao-Horn, Solid State Ionics 2001; Shao-Horn, Nat. Mat. 2008

II. Concept

A majority of battery materials exhibit a volume change upon lithium intercalation or extraction. Measurement of local strains can help to distinguish between ionic and electronic transport which is difficult with current measurements.

Flow of ...	I?	ΔV?
Electrons	yes	no
Li ions	yes	yes

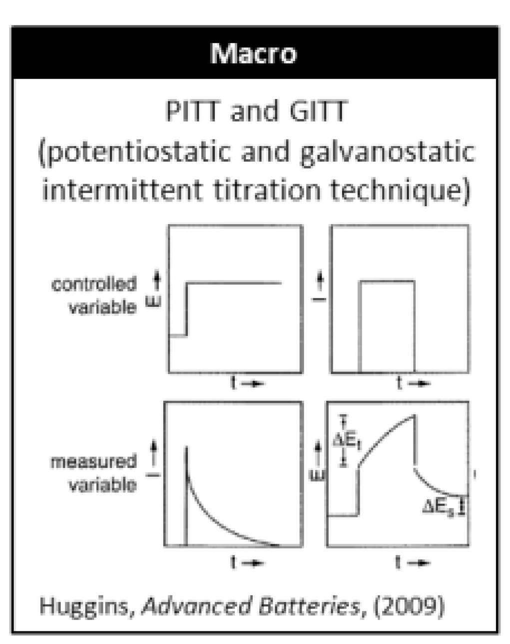
Electrochemical Strain Microscopy (ESM)
Detection of bias-induced volume changes mediated by ionic diffusion, migration, and electrochemical processes.



Amatucci, JECS 1996

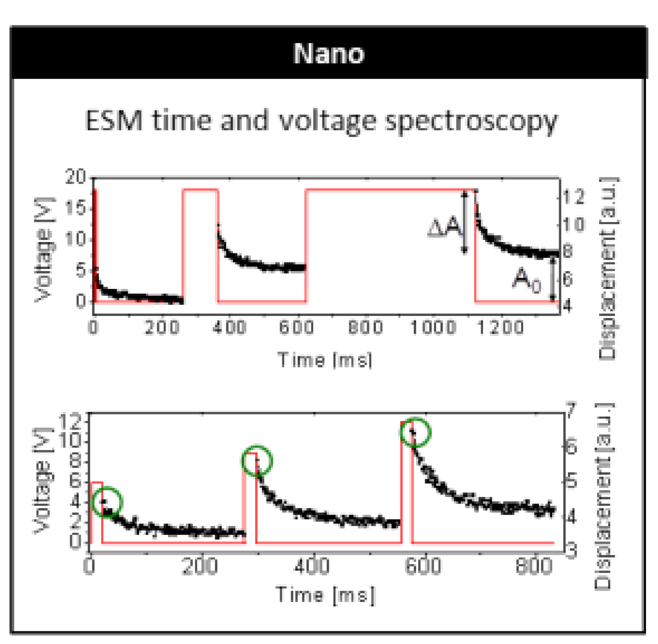
ESM can be used to perform time and voltage spectroscopy to get information about ionic transport on different time scales and under different driving forces.

Macro



Huggins, *Advanced Batteries*, (2009)

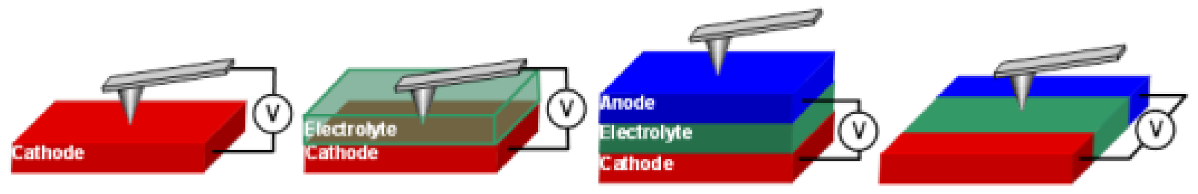
Nano



Goal: Develop strain analogs to traditional characterization techniques

III. Operational regimes

Based on the operational regime, ESM can be used to investigate the bias-induced Li-ion transport in electrode materials, the transport across the electrode/electrolyte interface, or the transport through the full battery.



Tip	active	active/passive	passive	passive
E	local	local/global	global	global
Δc(Li)	local	local/global	global	global
Li flow	in bulk	across interface	through battery	through electrolyte

Balke et al., Adv. Mater. 22, E193 (2010)

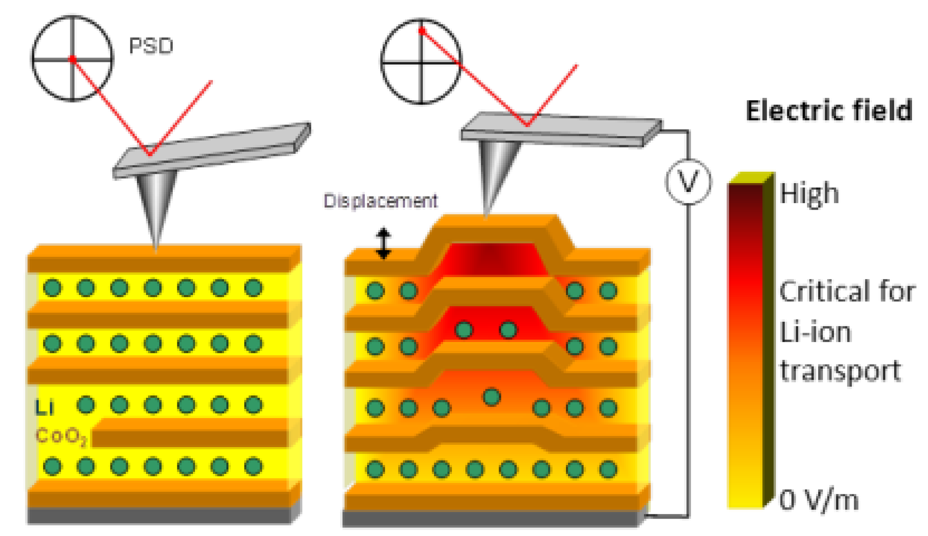
IV. Understanding the ESM signal for $LiCoO_2$

ESM signal

The local Li-ion concentration can be changed by the application of a local bias.

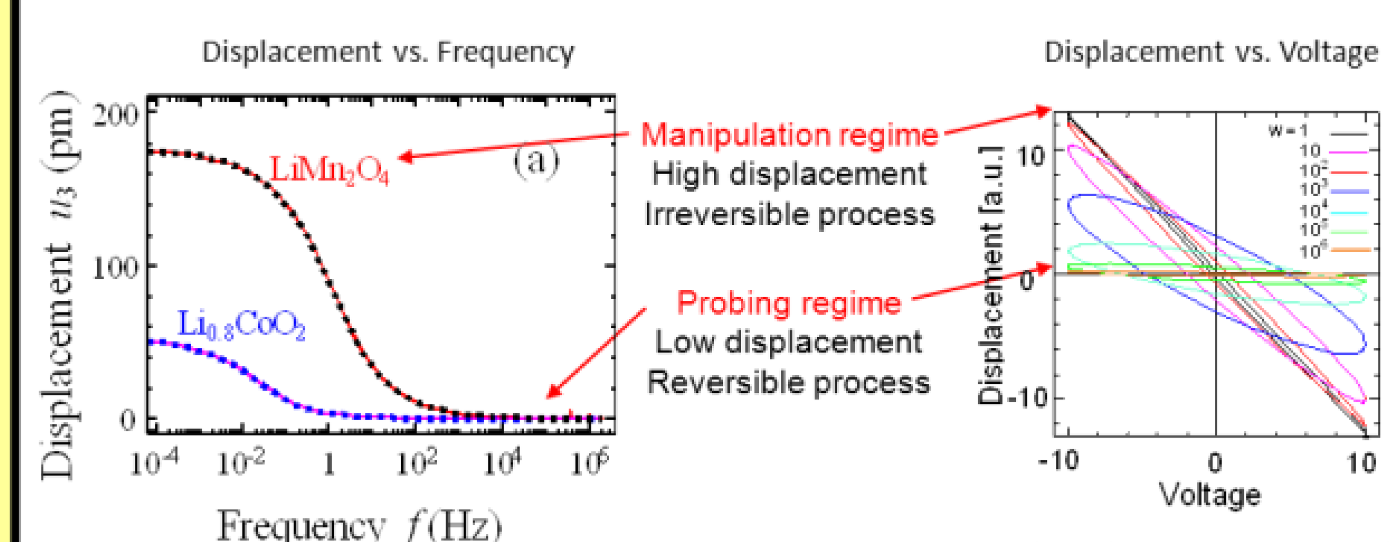
Information about Li-ion dynamics through dynamic concentration changes (V_{ac}).

The higher the Li-ion mobility, the higher the induced surface displacement.



Balke et al., Adv. Mater. 22, E193 (2010)

From analytical description (Anna Morozovska): Purely diffusional case



Morozovska et al., JAP 108, 053712 (2010)

V. The role of grain orientation and surface morphology

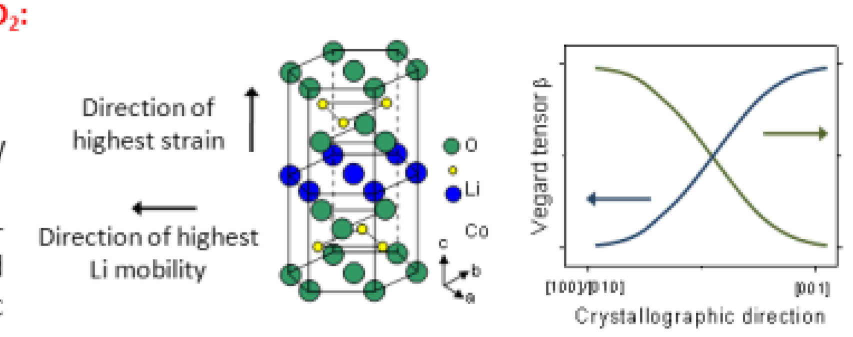
From analytical modeling shown above for high frequency regime:

$$u_3 = 2(1+\nu)\beta\frac{V_{ac}}{\eta}\cdot\frac{\sqrt{D}}{\sqrt{\omega}}$$

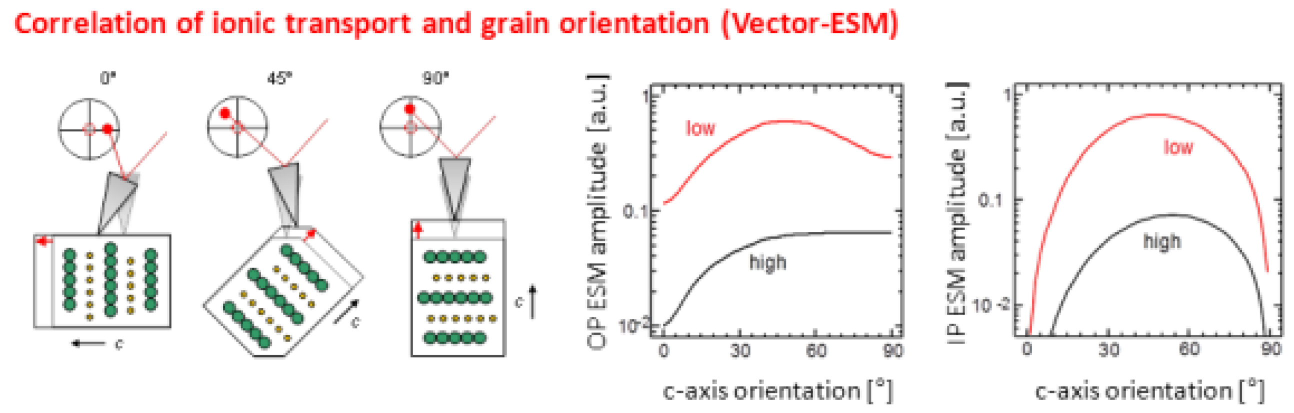
ν: Poisson coefficient
β: Vegard coefficient
V_{ac}: Probing voltage
η: Correlation between V and electrochem. potential
D: Diffusivity
ω: Probing frequency

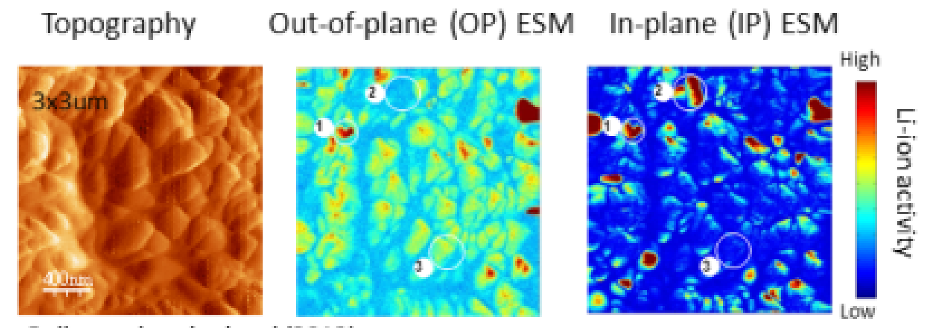
Anisotropic ionic transport in $LiCoO_2$:

- position-dependent ν, β and D determined by crystallographic orientation and surface morphology
- anisotropic volume expansion
- effective driving force acting on Li-ions depend on angle between field direction and direction of easy ionic transport



Correlation of ionic transport and grain orientation (Vector-ESM)



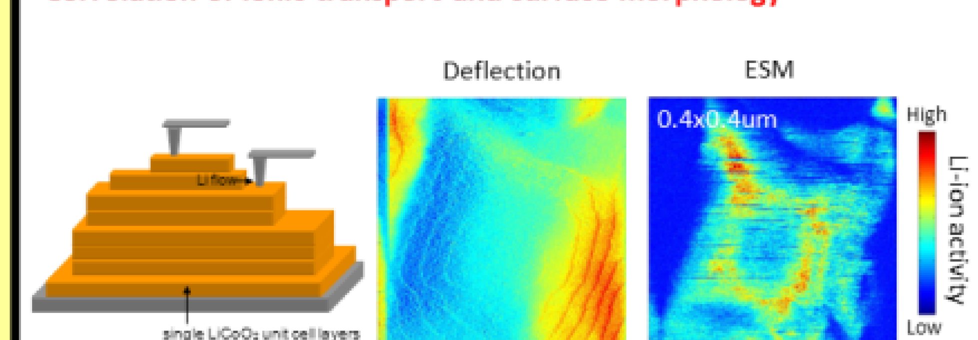


Balke et al., submitted (2012)

Vector-ESM shows independent OP and IP ESM.

Vector-ESM can be used to conclude on texture and identify optimum texture for ionic transport.

Correlation of ionic transport and surface morphology



Layered structure of $LiCoO_2$ results in step edges.

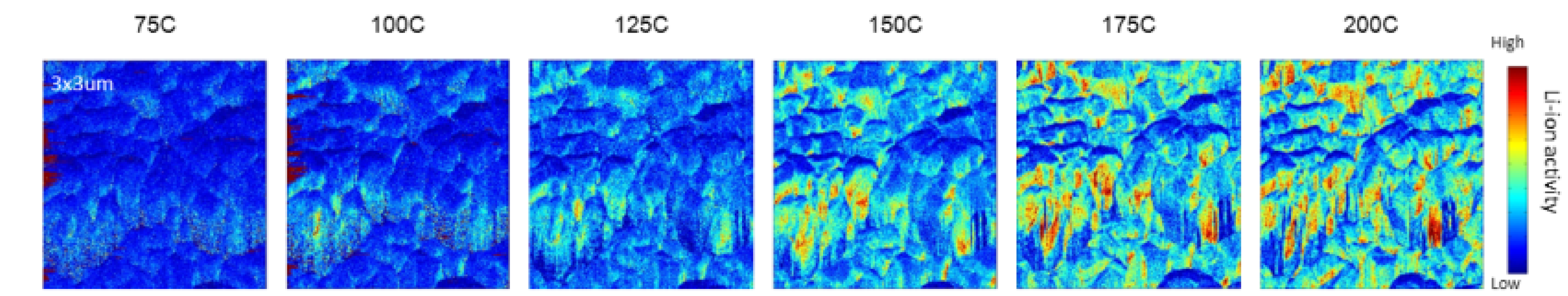
Higher ionic transport at step edges measured by ESM.

High resolution ESM imaging allows to identify transport enhancing surface morphologies.

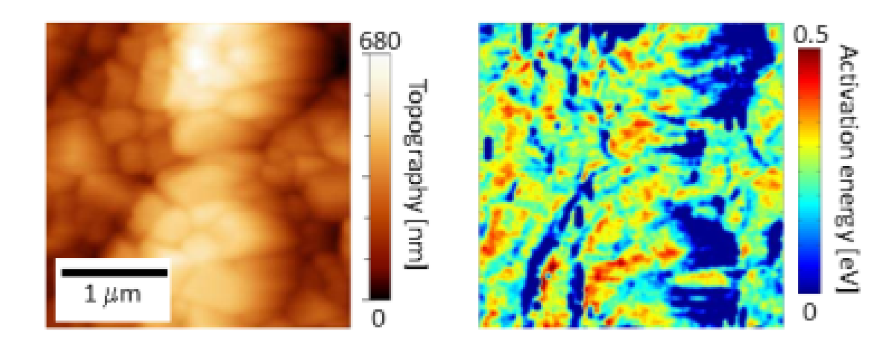
VI. Describing ionic transport in $LiCoO_2$ thin film cathodes

Ionic transport of Li-ions described by diffusivity D and activation energy E_a D ≈ exp($-E_a$/RT)

Local activation energy mapping: temperature-dependent ESM



The temperature-dependent ESM signal for each individual pixel show linear curves in Arrhenius-type plot. From the slope, we can extract spatially resolved maps of the activation energy (after image alignment and Gaussian filter application to reduce pixel-to-pixel noise).



Balke et al., submitted (2012)

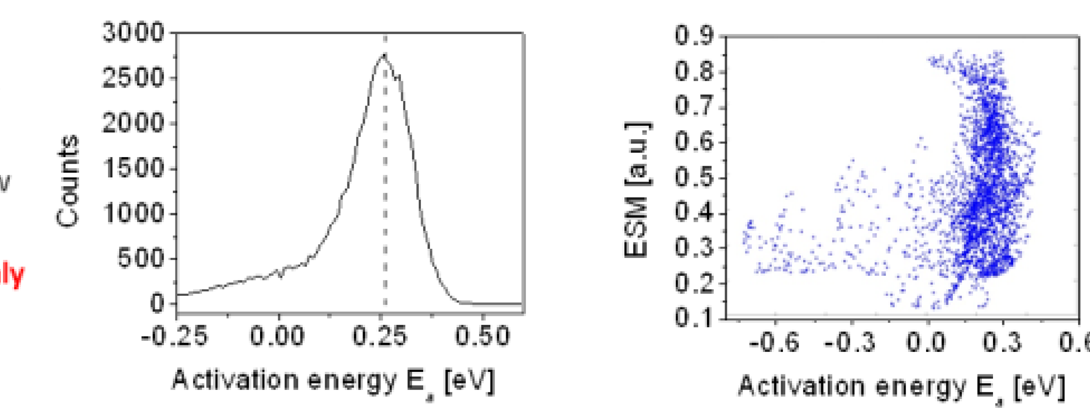
The activation energy map shows regions of zero where the sample surface is very steep (poor tip-sample contact).

The activation energy within grains is relative homogeneous with lower values at some grain boundaries.

An average activation energy of about 0.26 eV can be extracted (vs. 0.3 eV in the literature).

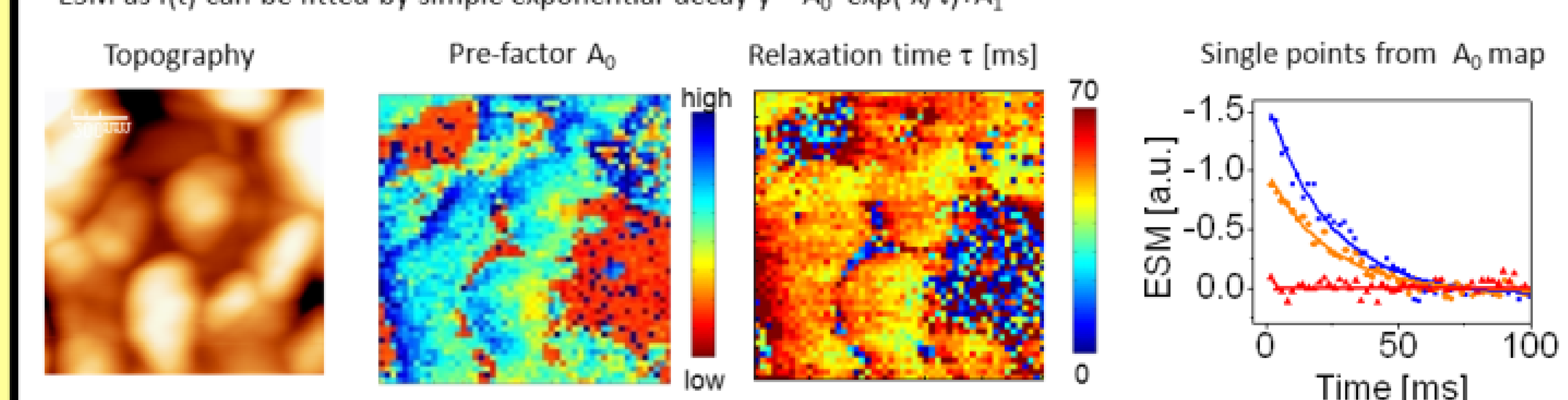
Areas with different absolute ESM signal strength show the same activation energy.

With the biased SPM tip, we induce ionic transport only along one direction!



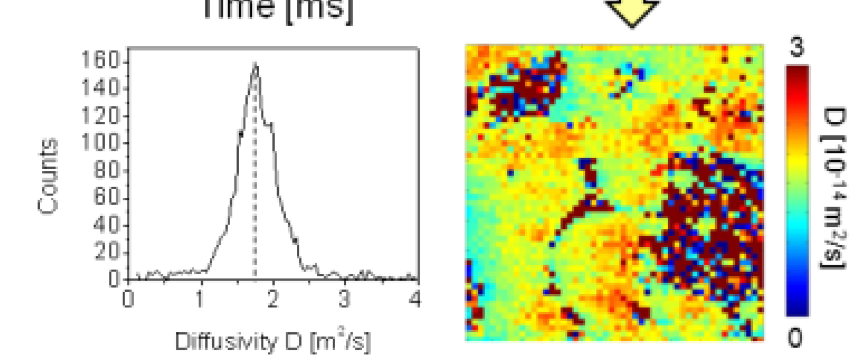
Local diffusivity mapping: time spectroscopy ESM

- ESM relaxation is recorded for 260ms after a -10V/30ms voltage pulse. The voltage pulse induces large concentration changes and ESM is used to track the ion diffusion back into the original configuration
- ESM as f(t) can be fitted by simple exponential decay y = A_0*exp(-x/τ)+A_1



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

L: tip radius 30 nm
τ: Relaxation time



The diffusivity map shows areas of different ionic transport.

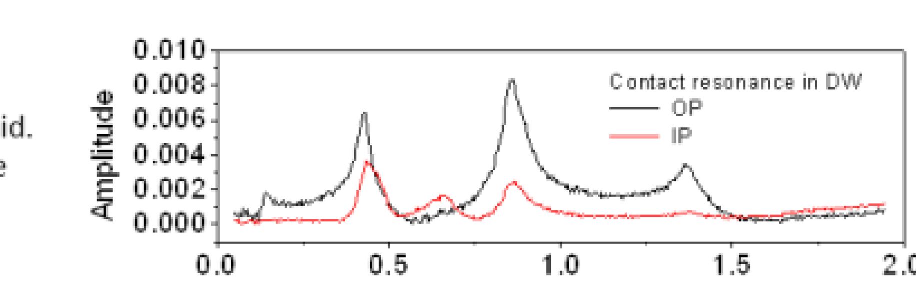
An average diffusivity of between 10^{-14} m²/s and 2.5 10^{-14} m²/s can be estimated (vs. 10^{-14} to 10^{-12} m²/s in the literature).

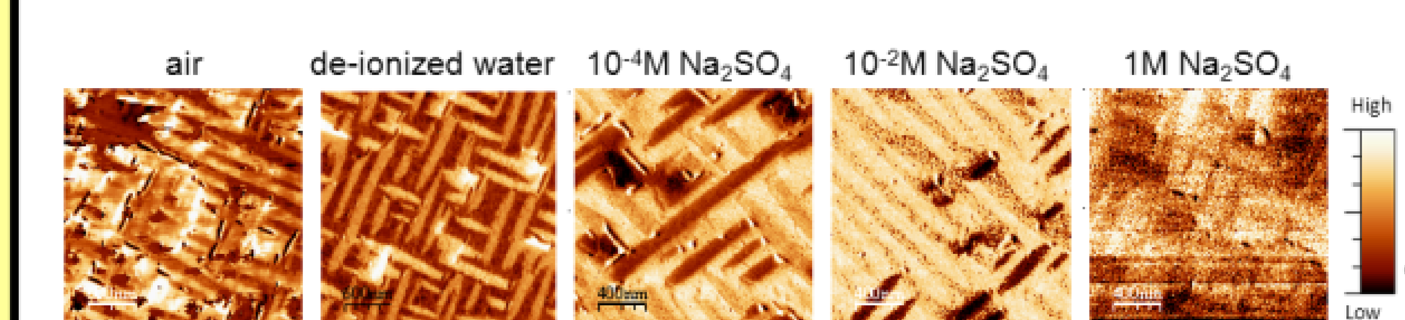
With ESM, it is possible to estimated the diffusivity for individual grains or grain boundaries!

VII. Future development: In-situ ESM in liquid

Technical challenge

- Application of electrical signals to tip surrounded by conductive medium.
- Using ferroelectrics as model system for electromechanical probing in liquid.
- $BiFeO_3$ shows stripy ferroelectric domain pattern in in-plane piezoresponse force microscopy (PFM) image.
- PFM has comparable excitation and detection principles to ESM.





High frequency excitation bias can be applied in electrolytes up to 1M ionic concentration.

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