Energy Storage: A Nanoscale View

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Theory

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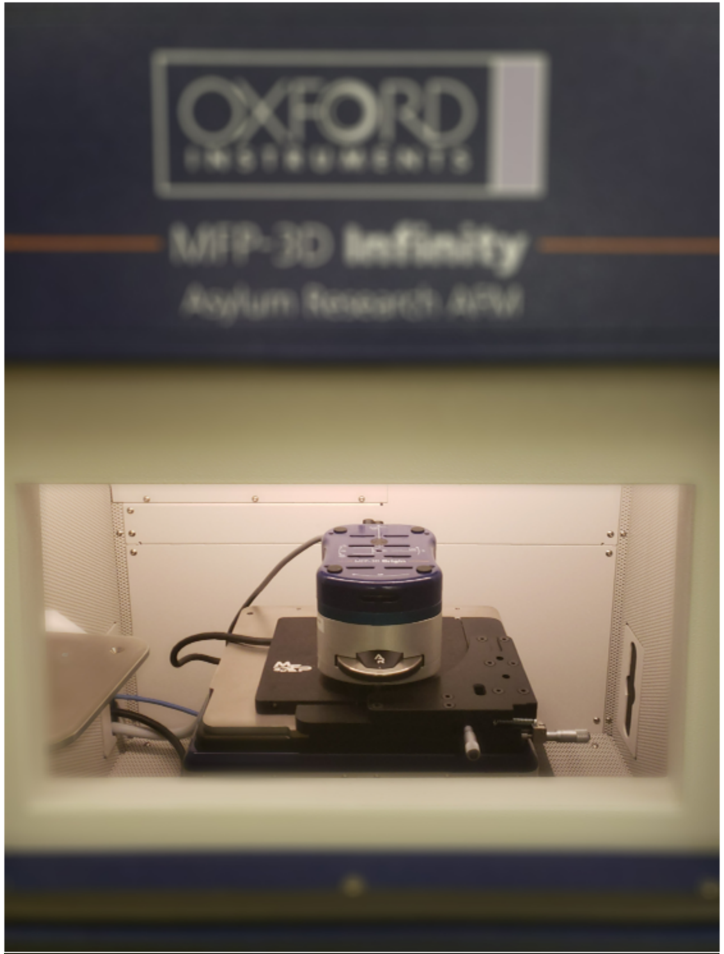
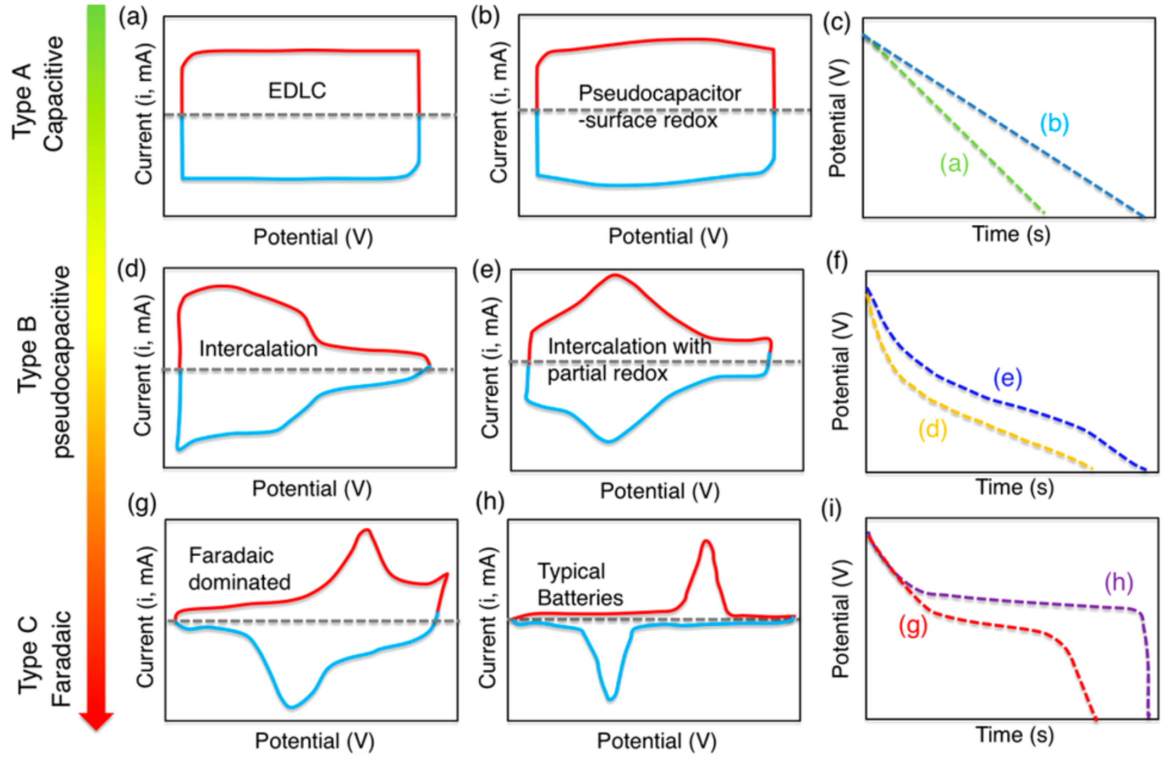
Outlook

- **Motivation**
  - Energy storage concepts
  - The nanoscale challenge
  - The importance of strain
- **Atomic Force Microscopy**
  - Limitations and opportunities
- **Case studies**
  - Porous electrodes
  - Layered electrodes
  - Transition metal oxides
- **AFM Modalities in Energy Storage**
- **Summary**



Energy Storage

From adsorption to ion insertion



R.M Penner and Y. Gogotsi., ACS Nano, 12, 2081 (2018).

Energy storage devices

EDL capacitor
- Electrostatic charge storage (adsorption)
- No charge transfer

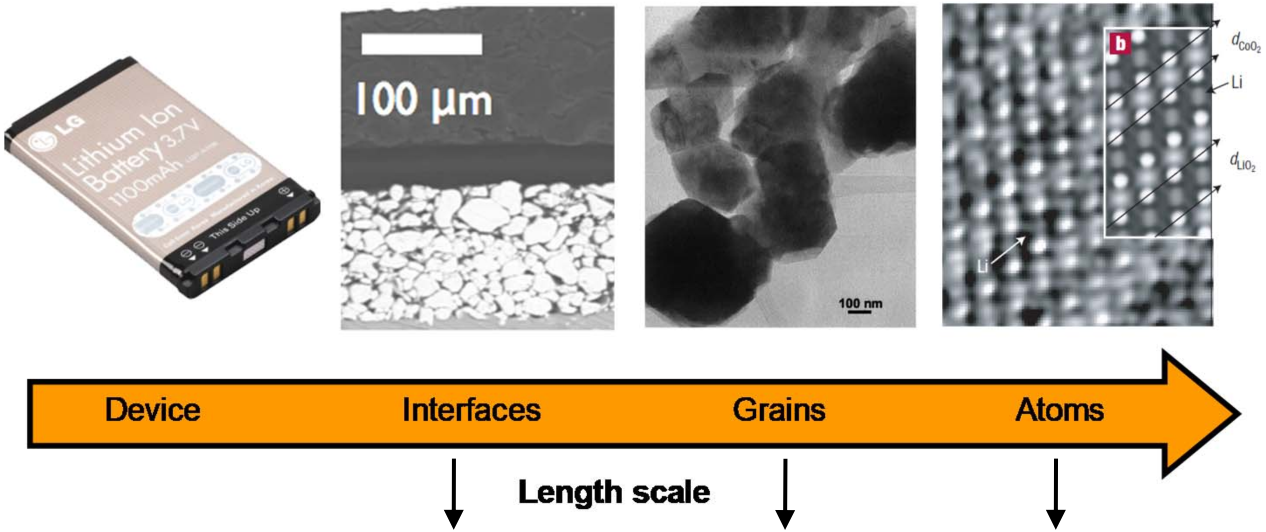
Pseudocapacitor
- Electrochemical charge storage (surface)
- Charge transfer

Battery
- Electrochemical charge storage (volume, intercalation)
- Charge transfer

The Nanoscale Challenge

Processes on different length scales determine energy storage performance.

Battery example



- interfacial reaction kinetics
- electronic and ionic transport through bulk and across interfaces

- grain boundaries
- grain orientation
- pores

- vacancies
- doping
- dislocations

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

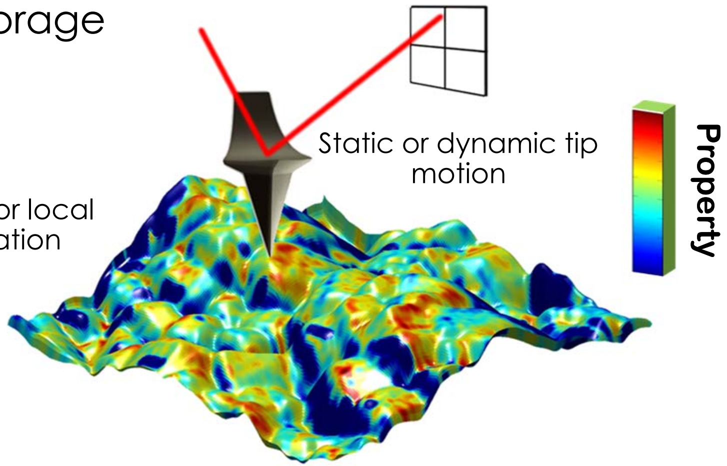
Images: Edwin Garcia, Purdue University; Shao-Horn, Solid State Ionics 2001; Shao-Horn, Nat. Mat. 2008

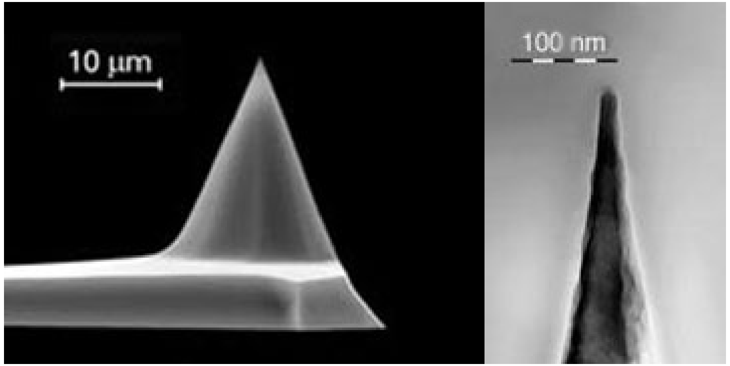
Atomic Force Microscopy

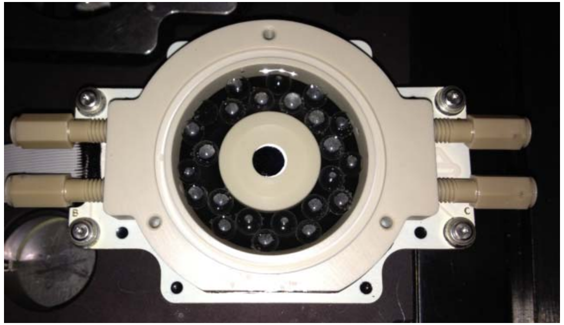
Use AFM to reveal nanoscale processes in energy storage

PRO:
- Nanoscale resolution (10's of nm)
- Volume changes
- Mechanical stiffness (Young's modulus)
- Local potential
- Electrical current

CON:
- Baseline drift (min)
- Liquid damping
- Electrochemical cell design*







In situ Electrochemical Cell
(Asylum Research)

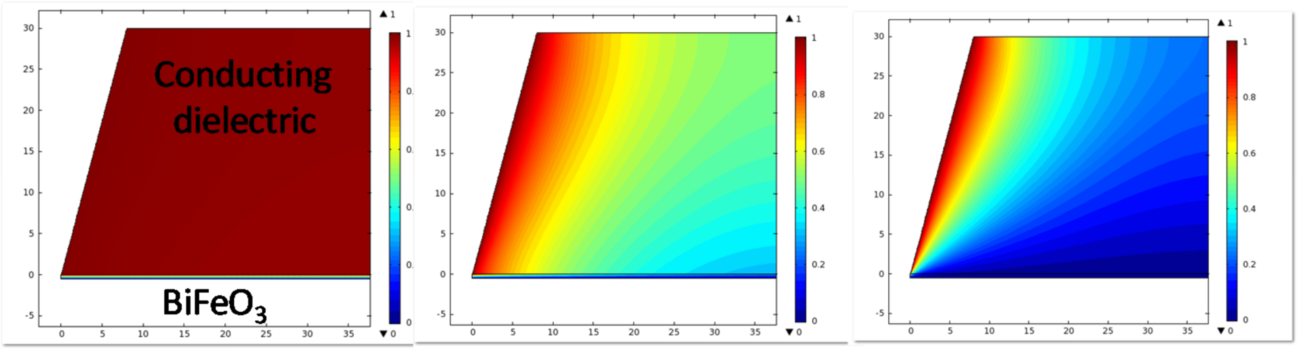
Atomic Force Microscopy

Challenges to transfer electrochemical methods to the nanoscale

- Very small contact area between AFM probe and sample → tiny currents
- Liquid environments prevent local probing

Electric potential

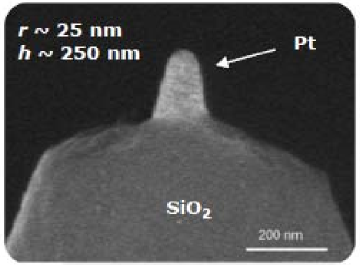
$$\tan\delta = \frac{\omega\epsilon'' + \sigma}{\omega\epsilon'}.$$



tan δ >>100 | tan δ ~100 | tan δ <1

Measurements with a biased tip in liquid challenging
→ restricted to measurements in air

Development of shielded probes

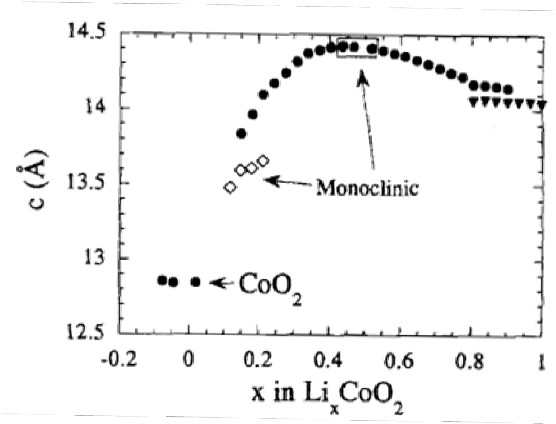


N. Balke et al., ACS Nano 6, 10139 (2012).

Chemical Expansivity

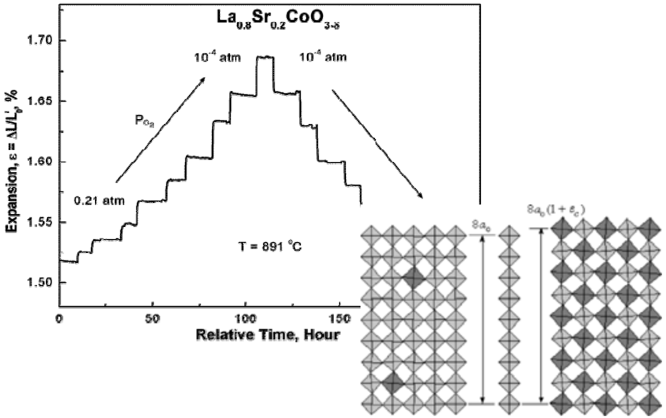
Challenge for nanoscale: Standard electrochemical measurements detect current; Faradaic and ionic currents are small (scale with volume)	**Solution:** • Use chemical expansivity in electrochemical reactions to study local phenomena (electromechanics) • Ion concentration is strongly coupled to a local change in strain (new measurement paradigm)

Lattice parameter in Li_xCoO_2



Amatucci et al., J. Electrochem. Soc. (1996)

Chemical expansion in oxides



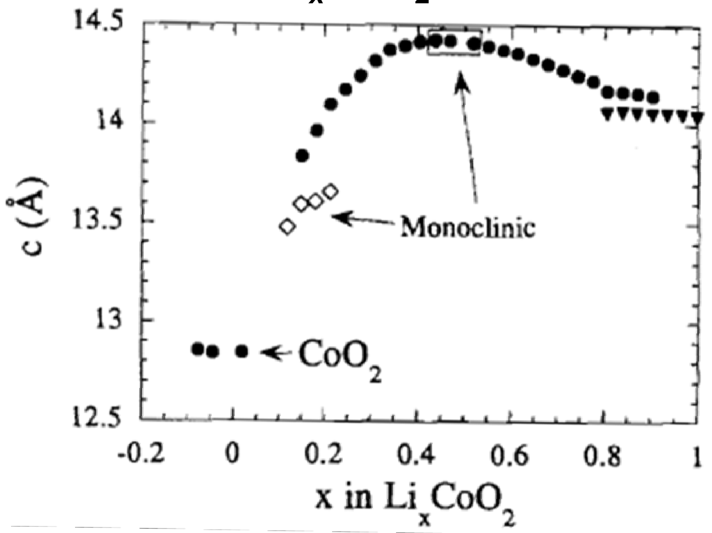
Chen et al., Chem. Mater. (2005)

Universal feature in many ionic processes.

The Importance of Strain

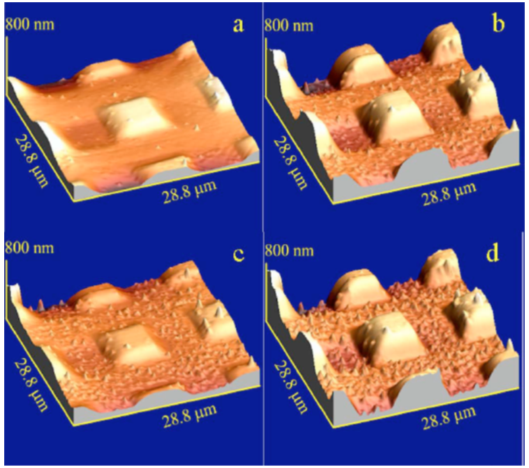
Strain is an integral part of energy storage

Li_xCoO_2 cathode



Amatucci et al., J. Electrochem. Soc. (1996)

Sn-Co-C anode



Lewis 2007

Typically discussed in the context of

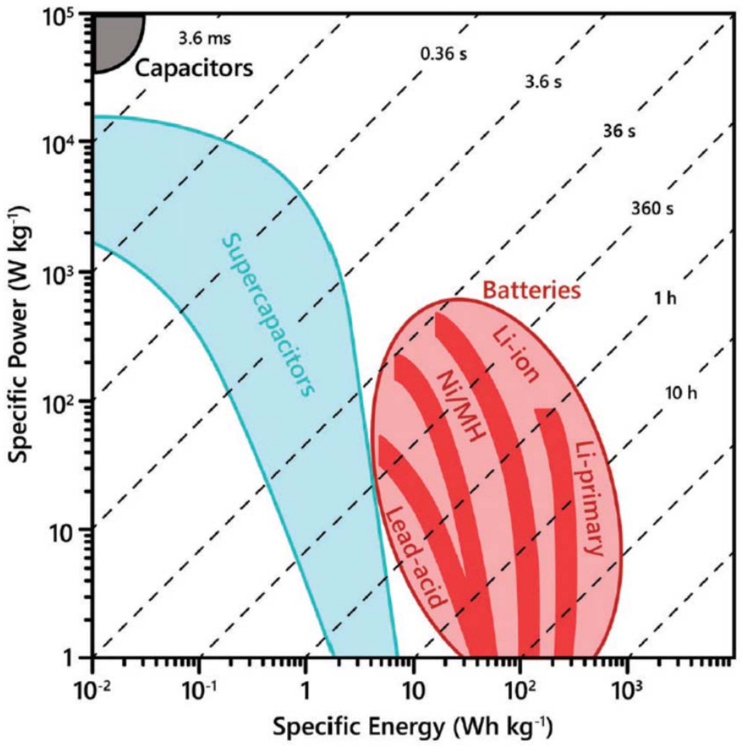
- Battery materials
- Mechanical degradation
- Monitoring state of charge

What we want

- Minimized volume changes
- Isotropic volume changes

The Importance of Strain

Strain as a design concept to achieve high power and high energy



Energy and power density are tightly coupled:

- A device that provides high energy density typically undergoes significant structural transformations
- Energy storage reaction with lower capacity show more gradual structural changes

} *more sluggish reaction*

Hypothesis: Coupling between electrochemical reaction and structural deformation is a pathway to enable simultaneous high power and high energy.

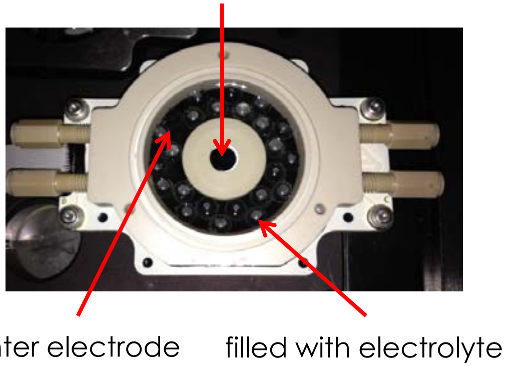
T. Mathis et. al. *Adv. Energy Mater.* **2019**, 9, 1902007

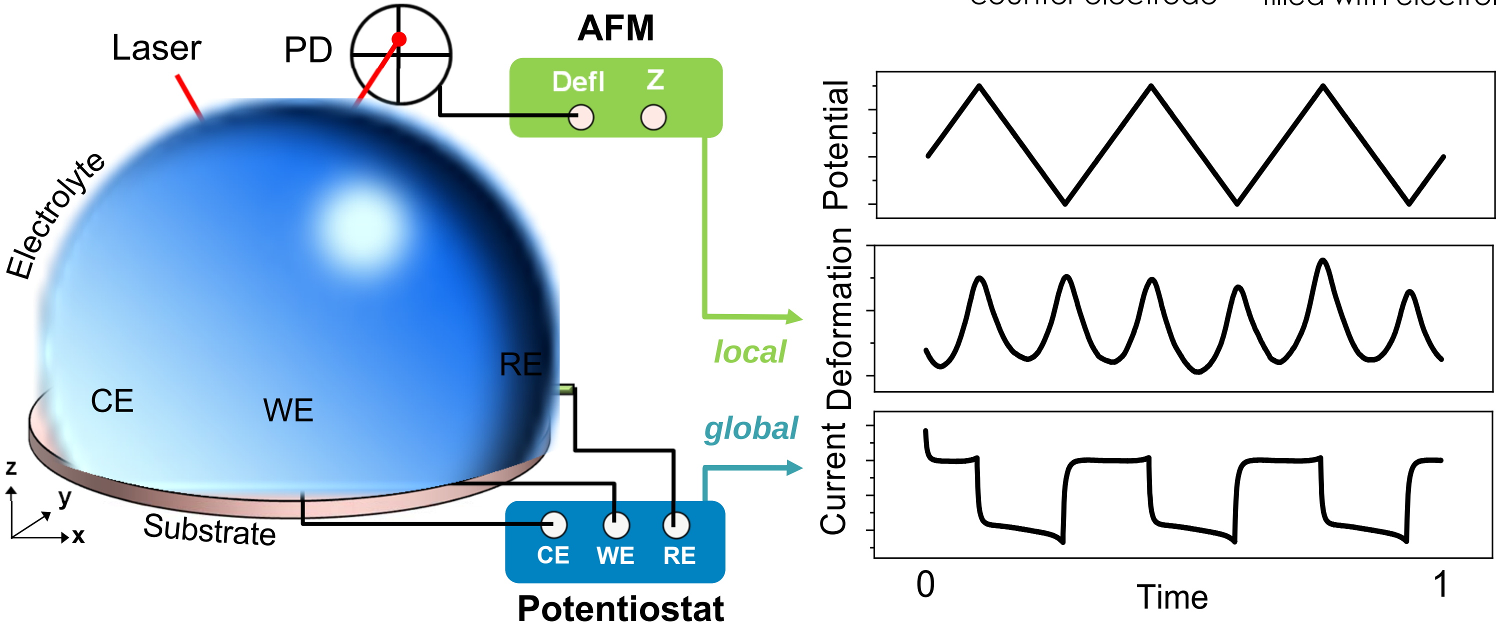
Nanoscale Strain Detection

Static Electrochemical Strain Microscopy (ESM)

- Operando technique (electrochemical cell)
- SPM tip as passive strain sensor
- "Nanoscale dilatometry"
- Mapping capabilities with **10's of nm resolution**

Electrochemical Cell (Asylum Research, MFP 3D)

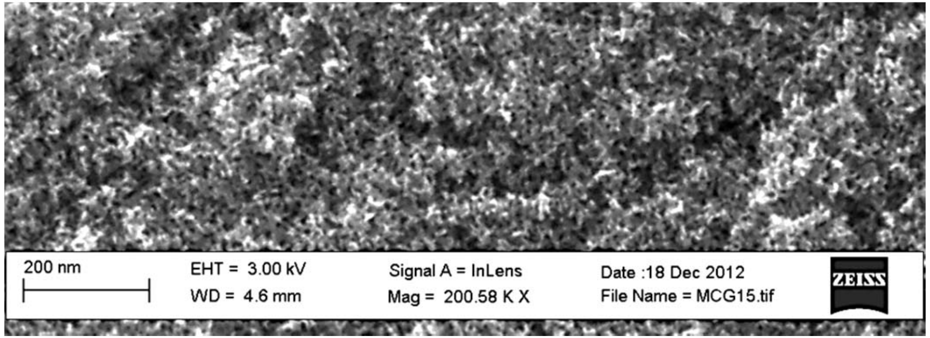


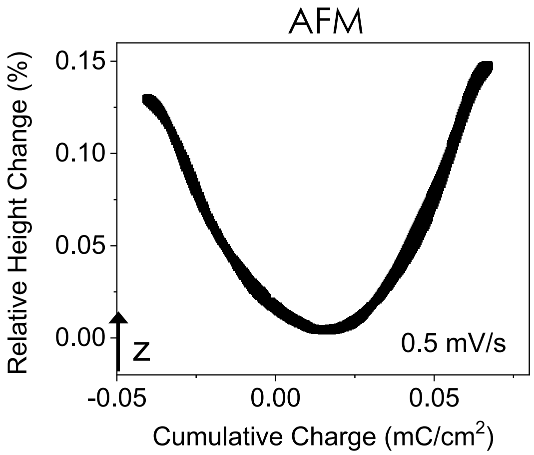


Electrode volume change along out of plane axis

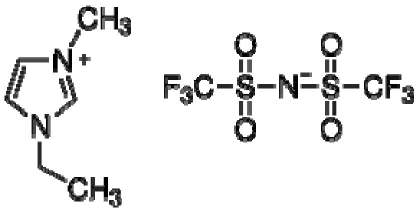
Porous EDL capacitor

Mesoporous carbon membranes (~20μm thick)





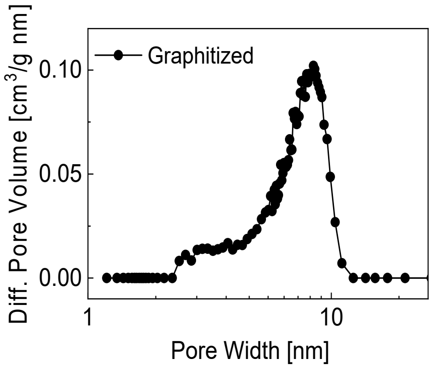
Emim-Tf_2N ionic liquid as electrolyte

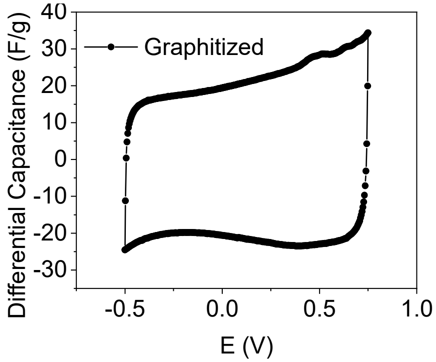


EMIM: 0.85×0.5×0.28 nm^3

Tf_2N: 1.09×0.51×0.47 nm^3

	BET Surface Area (m^2/g)	Young's Modulus (GPa)
Graphitized	282	9.66

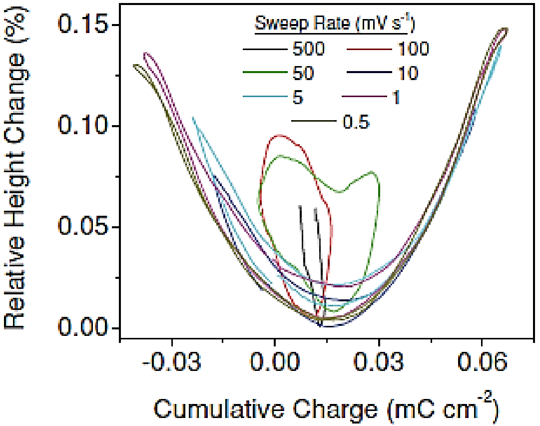




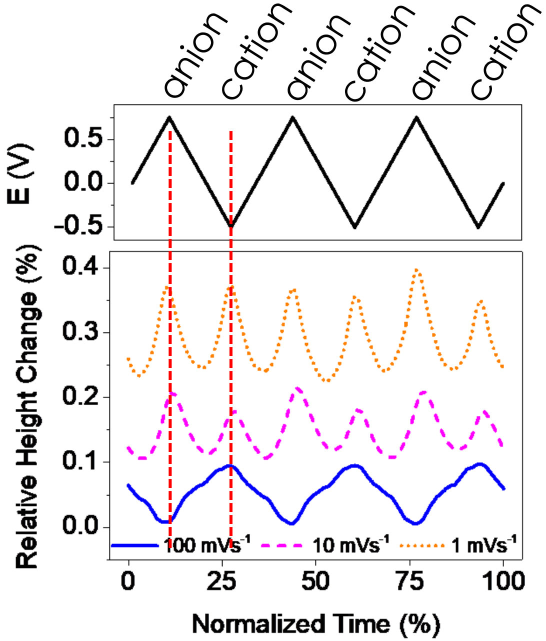
Black et al., Adv. Energy Mater. 4, 1300683 (2013).

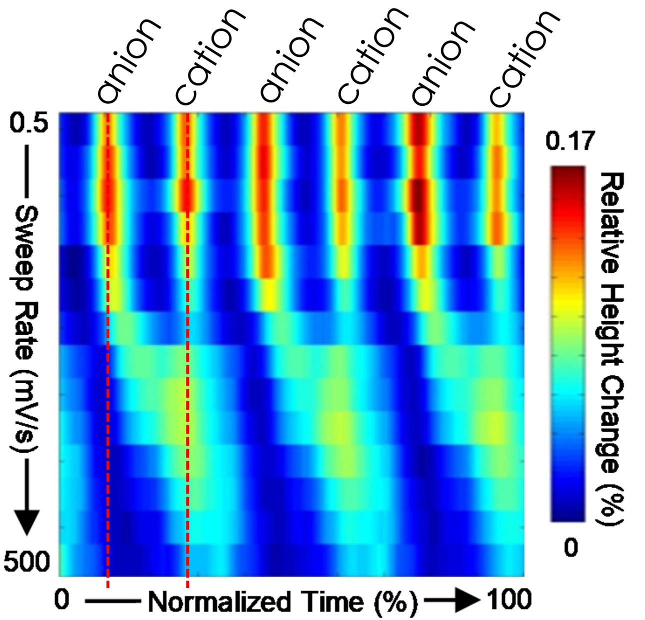
Porous EDL capacitor

Electrosorption and transport: scan rate dependence



Black et al., Adv. Energy Mater. 4, 1300683 (2013).

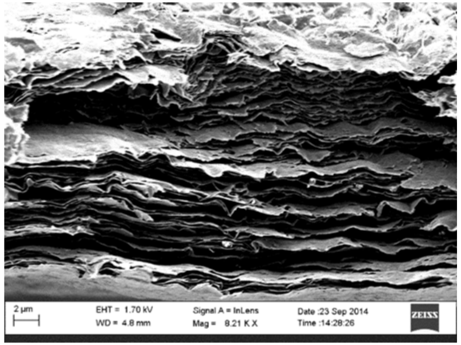




- Ions are not reaching the adsorption equilibrium because of transport limitations (Equilibrium condition: Phase shift between bias and strain = 0)
- Anions (bigger) are limiting kinetics

Layered Electrodes

MXene: $Ti_3C_2T_x$ (T_x = O, F)

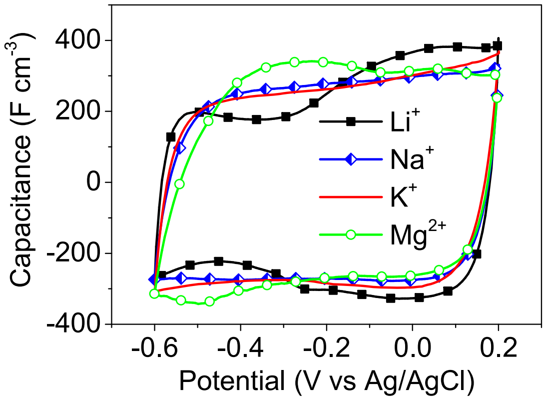


- Metallic conductivity
- Negative surface charge

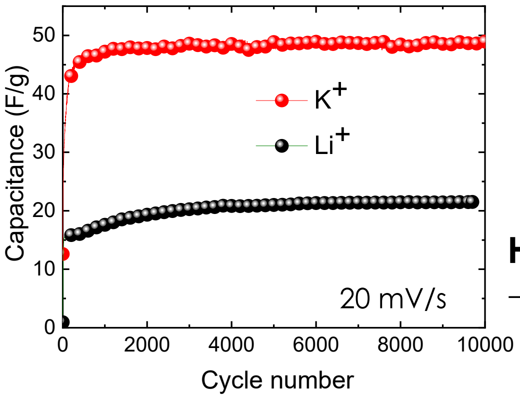
Aqueous sulfate electrolytes

	Ionic radius (Å)	Hydrated radius (Å)
Li^+	0.76	3.40
Na^+	1.02	2.76
K^+	1.38	**2.32**
Mg^{2+}	0.72	4.40

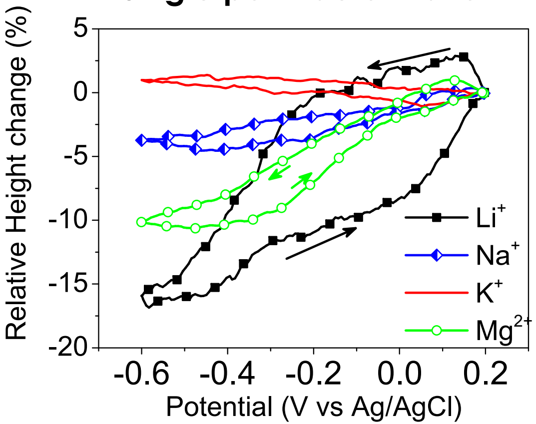
CVs @ 2mV/s



- Mostly EDL characteristics



Single point deformation



- Contraction instead of expansion
- No volume change for K^+
- Largest volume change for Li^+

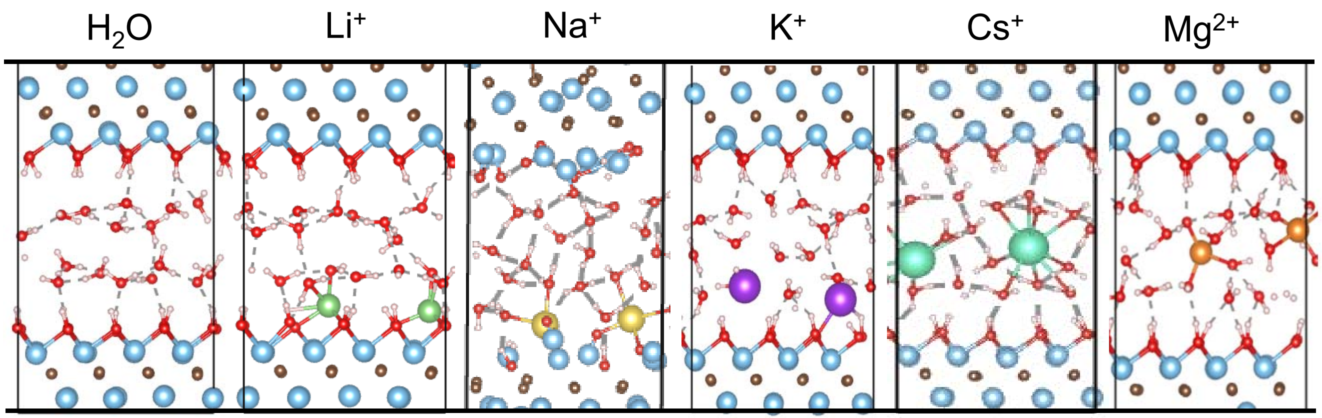
Higher Li^+ strain
→ slower intercalation kinetics

J. Come et al., Nano Energy **2015**, 17, 27

Layered Electrodes

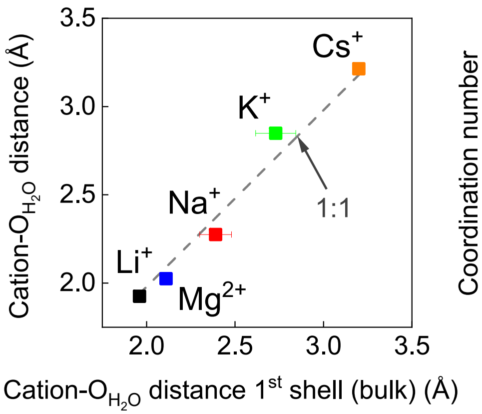
Theoretical insights

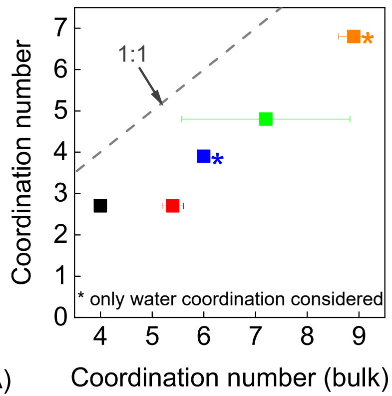
Where do the cations go and how do they interact with water and MXene?

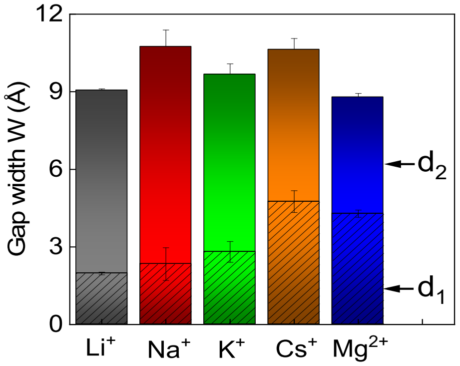


Most relevant properties

- Hydration shell radius
- Coordination number
- Distance to MXene



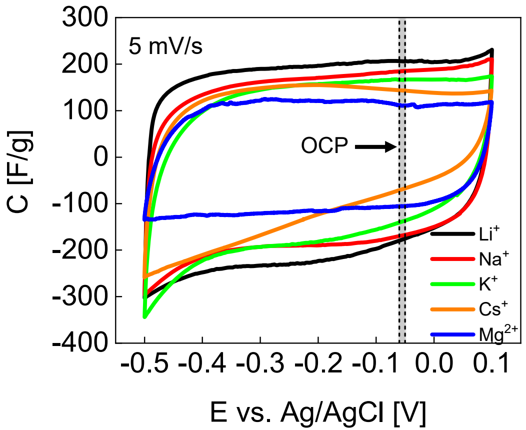


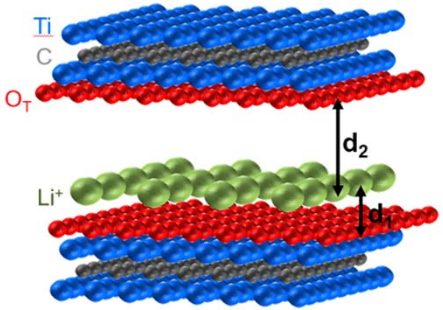


Gao et al., Energy Environ. Sci. 13, 25449, 2020

Layered Electrodes

Theory and experiment can explain charge storage properties



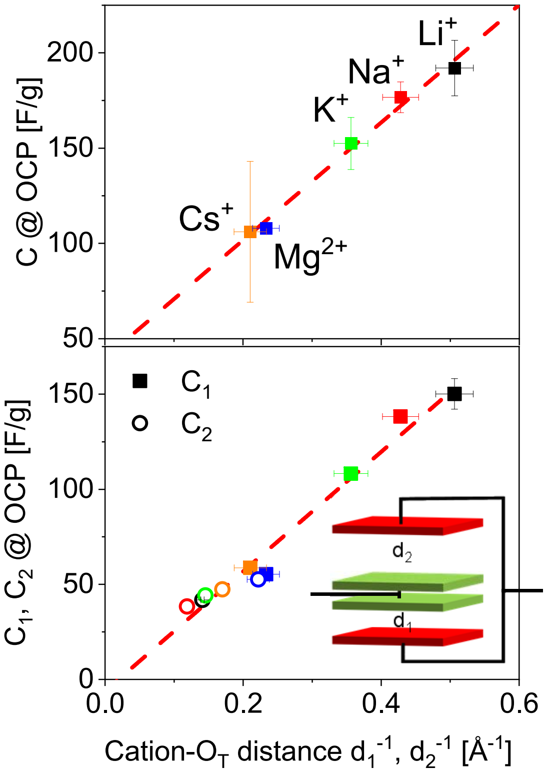


Simple EDL model

$$C = \frac{\varepsilon_0 \varepsilon \cdot A}{d}$$

Two-sided EDL model

$$C = C_1 + C_2$$



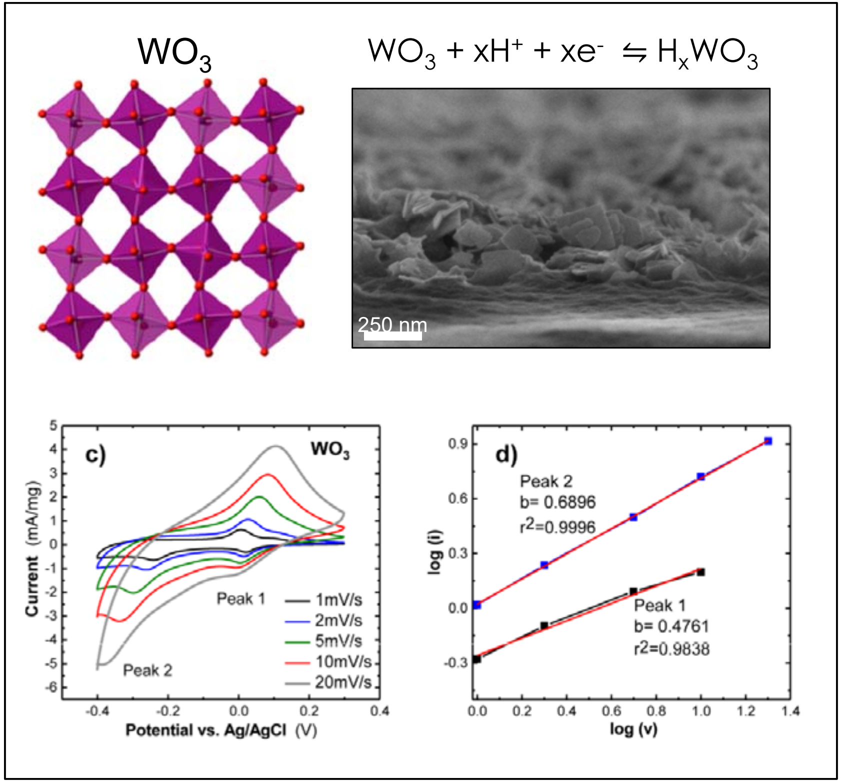
Correlation of atomic scale modeling and device performance (different time and length scales)

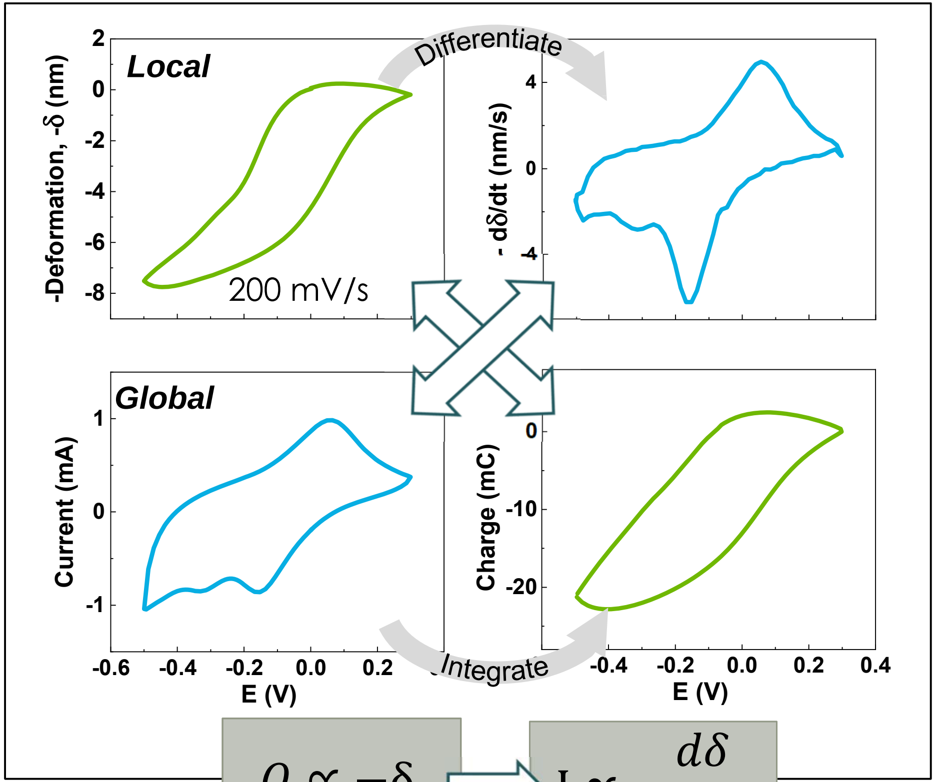
<u>Future steps:</u>
Correlating ion and strain response

Gao et al., Energy Environ. Sci. 13, 25449, 2020

Redox Reactions

WO_3 in H_2SO_4



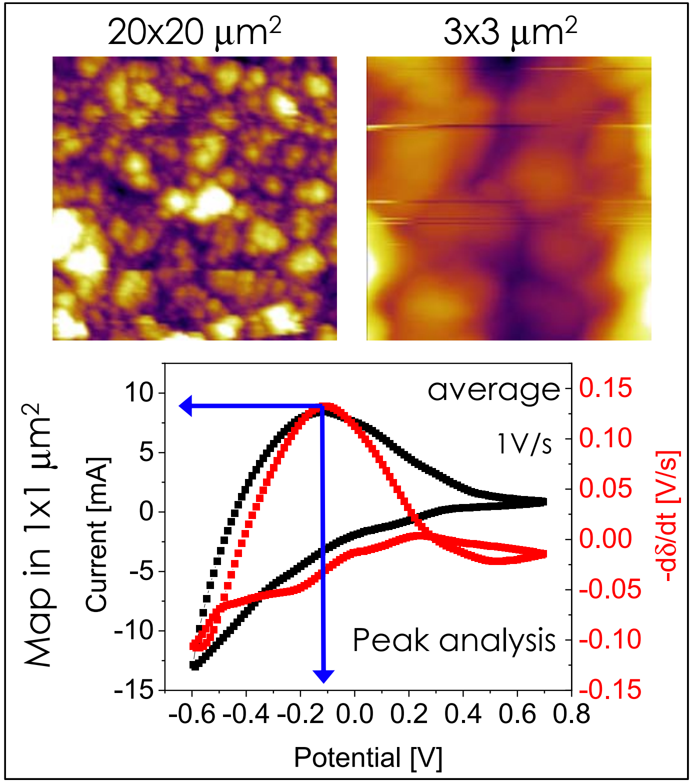


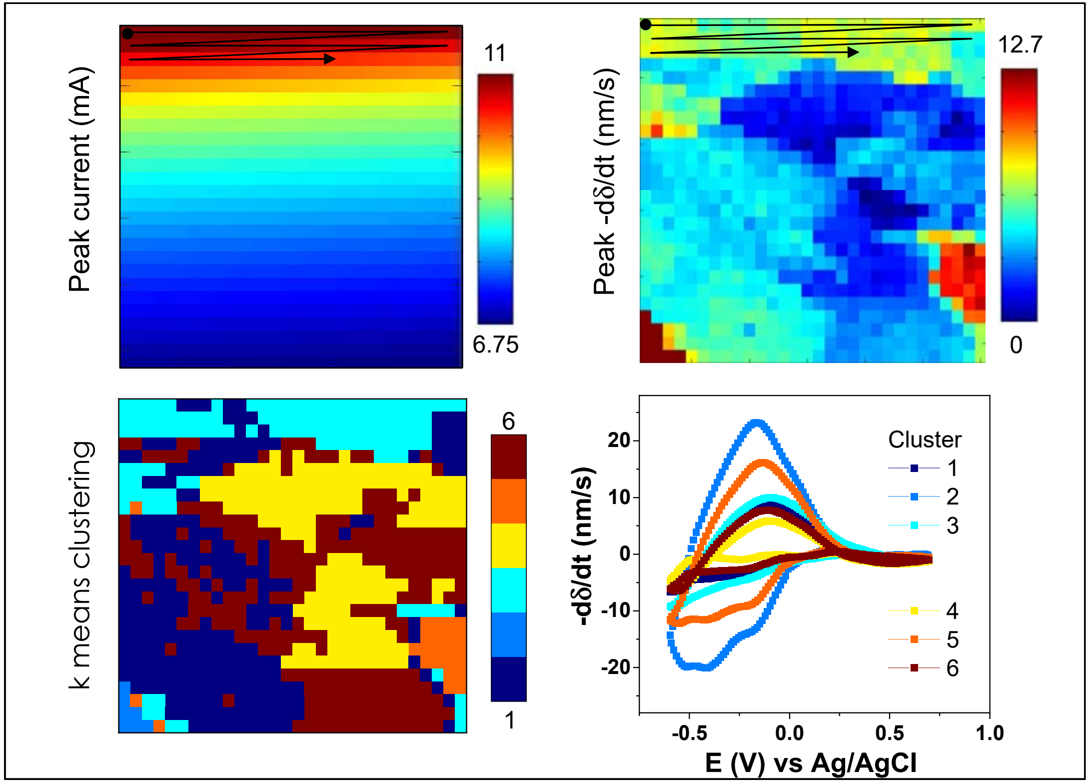
$$Q \propto -\delta \quad \Rightarrow \quad I \propto -\frac{d\delta}{dt}$$

Mitchell et al., Chem. Mater. 29, 3928, 2017.

Redox Reactions

Mechanical cyclic voltammetry (mCV)

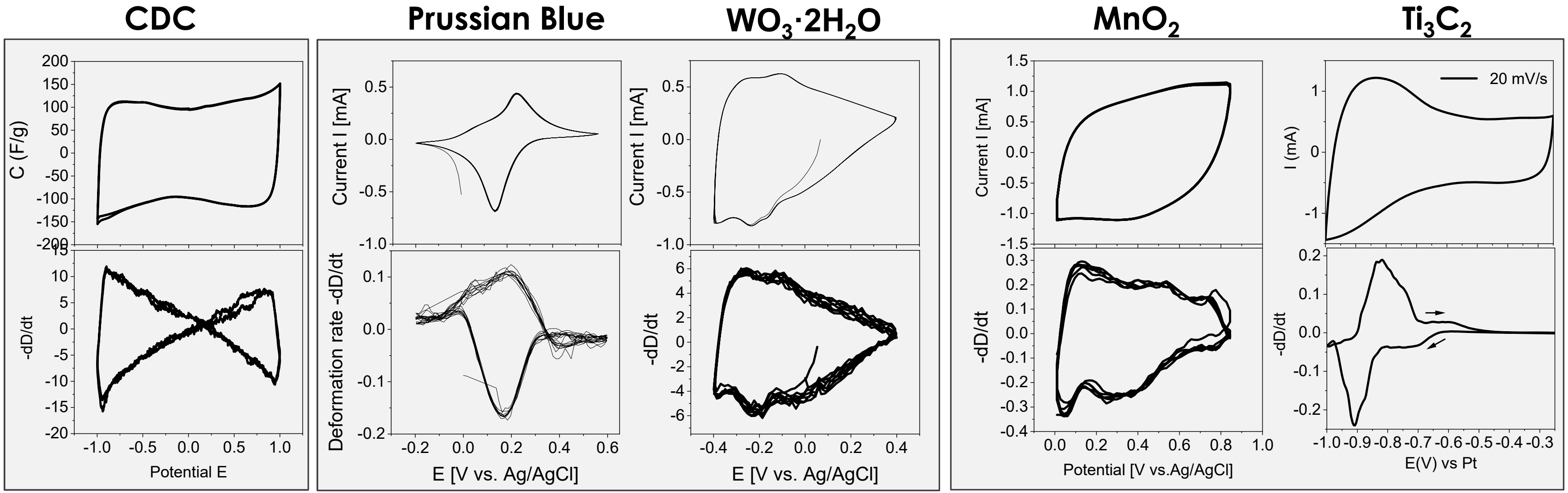




Tsai et al., Nano Energy 81, 105592 (2021).

General Application of mCV

Towards physical identification of redox peaks



No shape correlation

$\partial \propto Q^2$

~1:1

Information equivalent to current

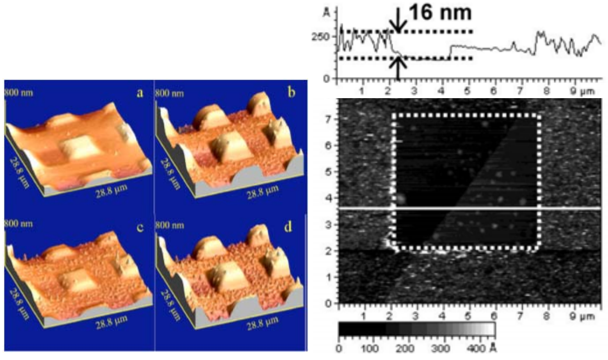
Beyond 1:1

More detailed information about ion intercalation process

AFM Modalities in Energy Storage

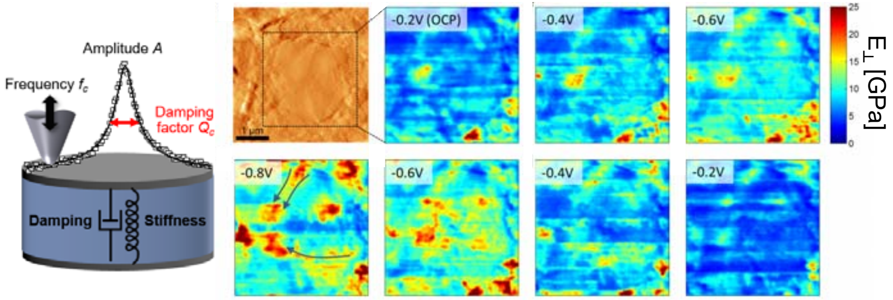
Topography

- SEI layer formation
- Crack formation
- Electrode swelling



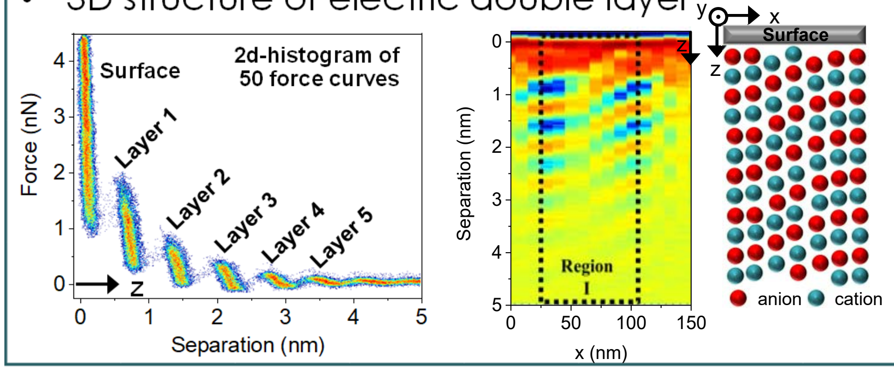
Contact resonance imaging

- Local stiffening



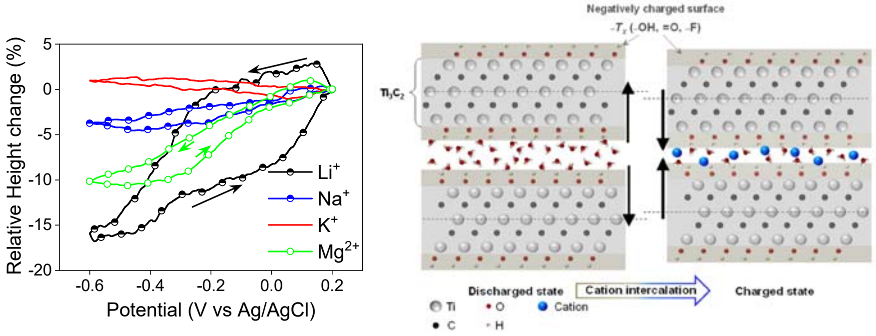
Force-distance curves

- Mechanical properties of SEI layer
- 3D structure of electric double layer



Volume changes (single point)

- Nanoscale dilatometry



Summary

- Electrode strain due to ion intercalation/insertion relevant for lifetime, electrochemical performance, and local ion detection
- AFM can detect electrochemical strains in a variety of energy storage materials (EDL to batteries)
- Mechanical CV curves can detect local deformation processes and are directly related to electrochemical current
- Universal in-situ approach working across many materials
- Potential applications towards single particle electrochemistry

$W_2O_6 \cdot H_2O$:
Single particle electrochemistry