Linking electrochemical performance with microstructural evolution in high performance cathode materials

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Project Id: ES 186

Overview

Timeline

- Start: March 1, 2012
- End: Sept. 30, 2014
- Percent complete: 20%

Barriers

- ***Voltage fade*** in *x* $Li_2MnO_3 \bullet (1\text{-}x) LiMO_2$-based cathode materials
- ***Performance degradation*** in high capacity cathode materials
- ***Correlating global behavior with local structure***

Budget

- FY12: \$ 88 K
- FY13: \$151 K

Partners

- Voltage Fade Team
- Yuxin Wang, Advanced Photon Source, Argonne

Objectives

- Develop an improved understanding of voltage fade in high capacity cathode material at the particle and single grain level
  - *complement full cell measurements that represent average behavior of large-scale ensembles*

- Establish the relationship between electrochemical performance and structure/microstructural evolution in high capacity cathode materials
  - *focus on critical link between structure and performance, especially through operando (in situ) characterization*

- Develop new approaches to characterize battery materials to provide new insight into materials behavior
  - *address the most significant challenges, not technique-based approach*

Milestones

- Develop approach for *operando* microstructural characterization of cathode particles during electrochemical cycling November 2012
- Establish experimental approach to measure electrochemical behavior of cathode oxide single particles March 2013
- Obtain electrochemical data from $x\ Li_2MnO_3 \bullet (1\text{-}x)\ LiMO_2$ single particles to correlate with full cell measurements October 2013
- Perfect *operando* approach to include TEM-scale characterization of single grains during electrochemical cycling May 2014
- Apply coordinated characterization to provide electrochemical data and comprehensive structural characterization on the same single particle and single grain of material September 2014

Relevance

Establishing the correlation between structure/microstructure and electrochemical performance can provide insight and guidance into materials design for improved performance

- High energy composite cathode materials (*x* $Li_2MnO_3 \bullet (1\text{-}x)\ LiMO_2$) offer great potential for safe, cost effective, and high-range batteries, but voltage fade limits performance

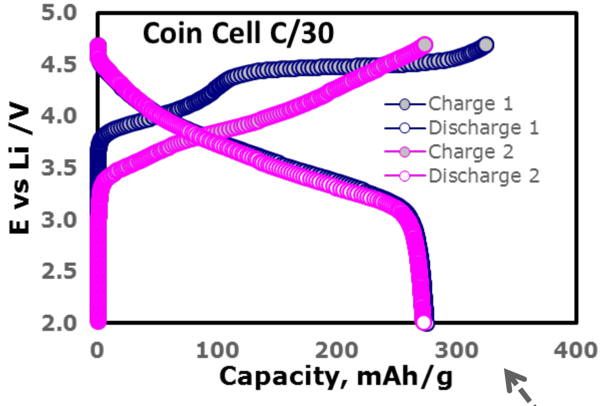
- *since voltage fade originates from structural changes of the cathode material (see Abraham, et al. poster ES 188), establishing the link between structure and performance can provide guidance on strategies to mitigate voltage fade*

- Structure and microstructure of the anode and cathode materials are prominent among the factors that influence long-term performance of Li-ion batteries

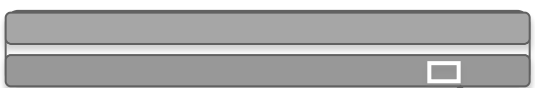
- *other microstructural phenomena besides voltage fade also impact performance; our approach provides insight into fundamental materials behavior that has broad applicability*

Relevance

- Need to ***correlate global behavior with local structure***
- Coexistence of multiple phases, evidence for non-uniform behavior of cathode particles within the same coin cell, (see results) further motivates this approach.

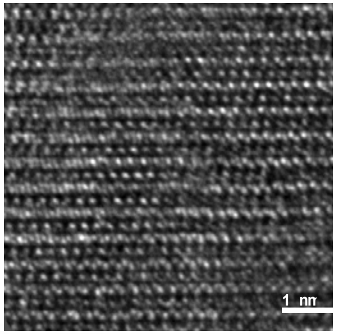


Electrochemistry
on **billions**
of particles



SEM cross-section of electrode

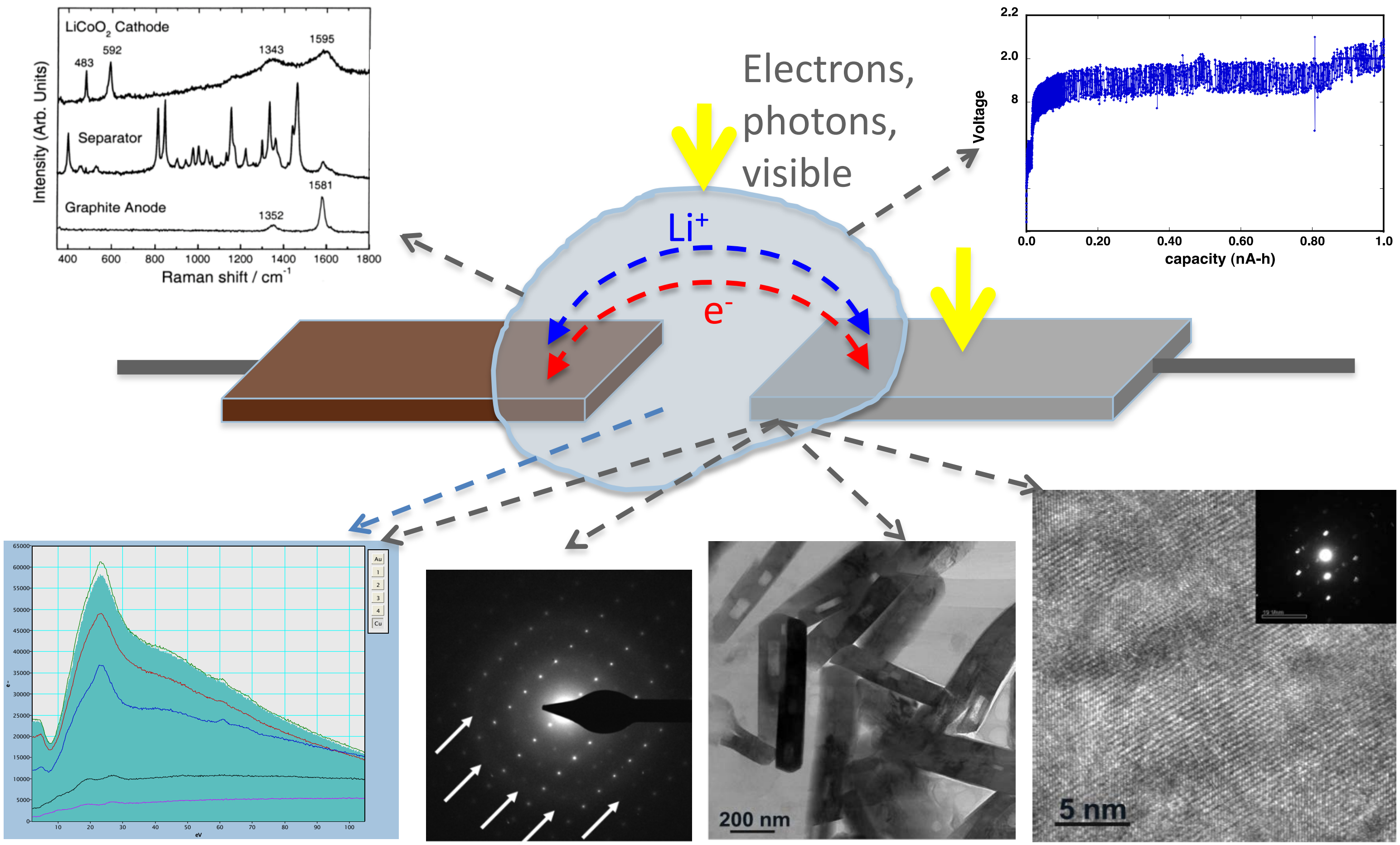
TEM on
one billionth
of a particle



Improving this correlation will provide better insight into performance

Approach

Develop and exploit ***coordinated characterization*** to correlate electrochemical behavior and structure ***at the micro- and nano-scale***

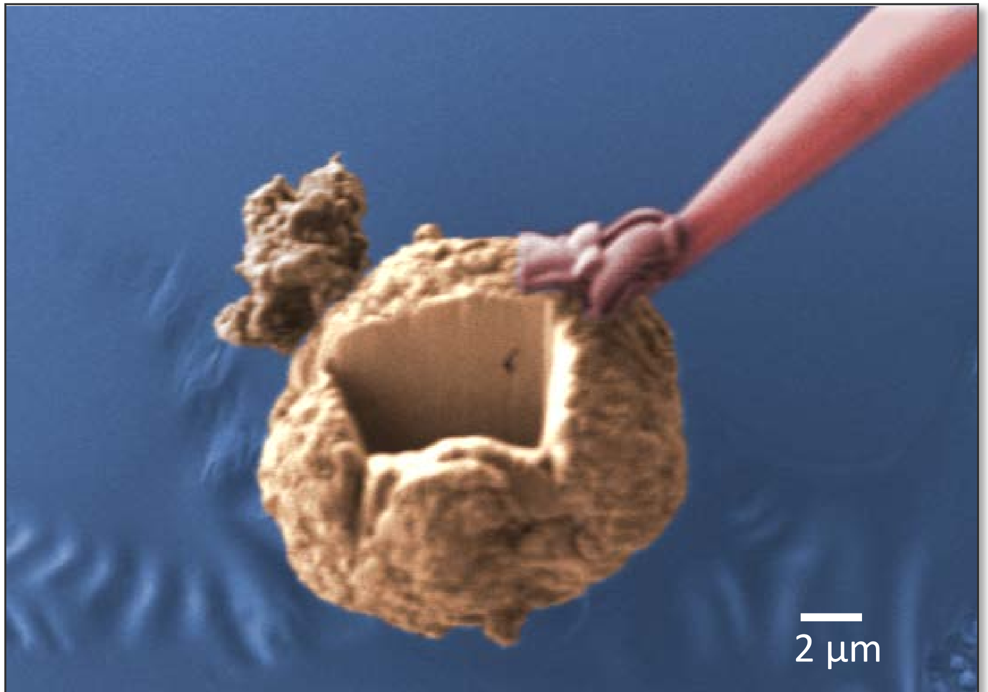


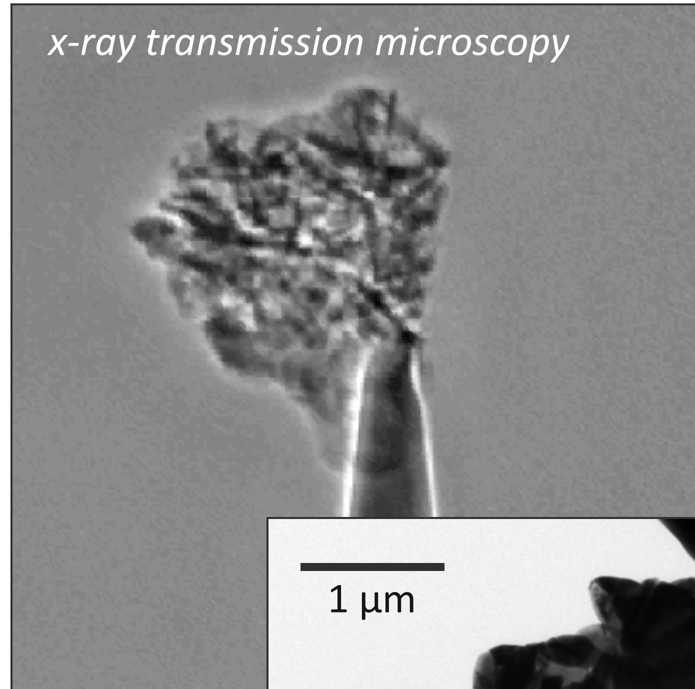
• *bring **all characterization to focus on a single piece of cathode material** many orders of magnitude smaller than that in coin cells*

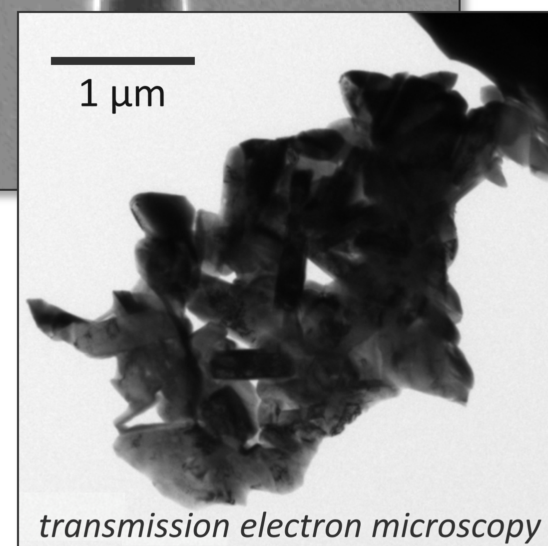
Approach

- single particle, single grain electrochemistry and characterization

- coordinated characterization (e.g. SEM, TEM, XAS, tomography) all on the same particle,







- coordinate ***electrochemical measurements and characterization on the same piece of material***

Technical Accomplishments and Progress

(1) Baseline microstructural characterization of *0.5* Li_2MnO_3 • *0.5* $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$ was completed

- *demonstrated non-uniform behavior among particles within a single electrode, motivating a more incisive approach to characterization*

(2) A new approach for *operando* SEM-based microscopy during electrochemical cycling of single particles was developed

- *developed a new approach for operando microscopy to study cathode oxides during electrochemical cycling*
- *demonstrated effect of particle fragmentation on performance in* $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$
- *showed that particles with different microstructure exhibit different behavior*

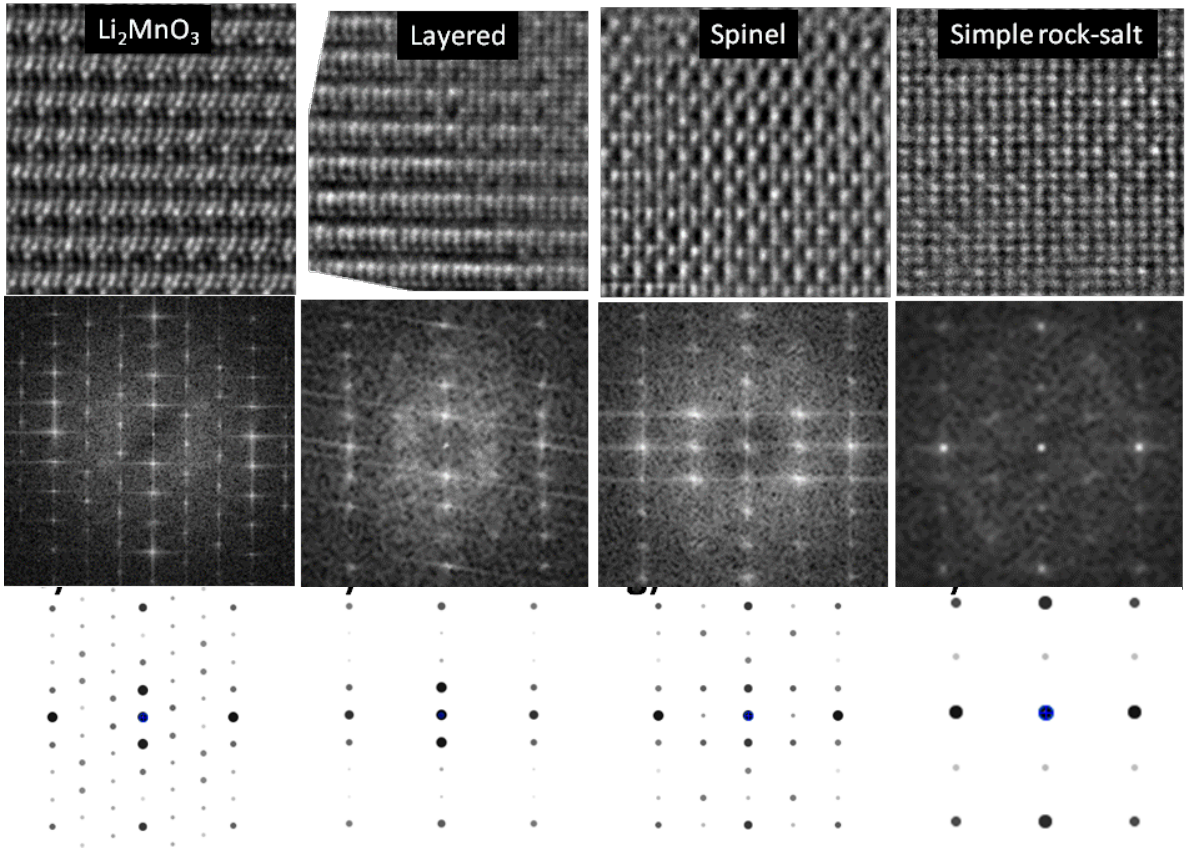
(3) Measurement of electrochemical behavior of single cathode particles comparable to that of practical cells was perfected

- *correlated single particle measurement with full-cell battery*
- *moved the challenge for characterization from billions of particles in a coin cell to the single particle level*

Baseline characterization of 0.5 Li_2MnO_3 • 0.5 $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$

- TEM was carried out on as-prepared and cycled material to identify key structural transformations that may be linked to voltage fade

TEM revealed four different phases co-existing within the same coin cell cycled 1500 times

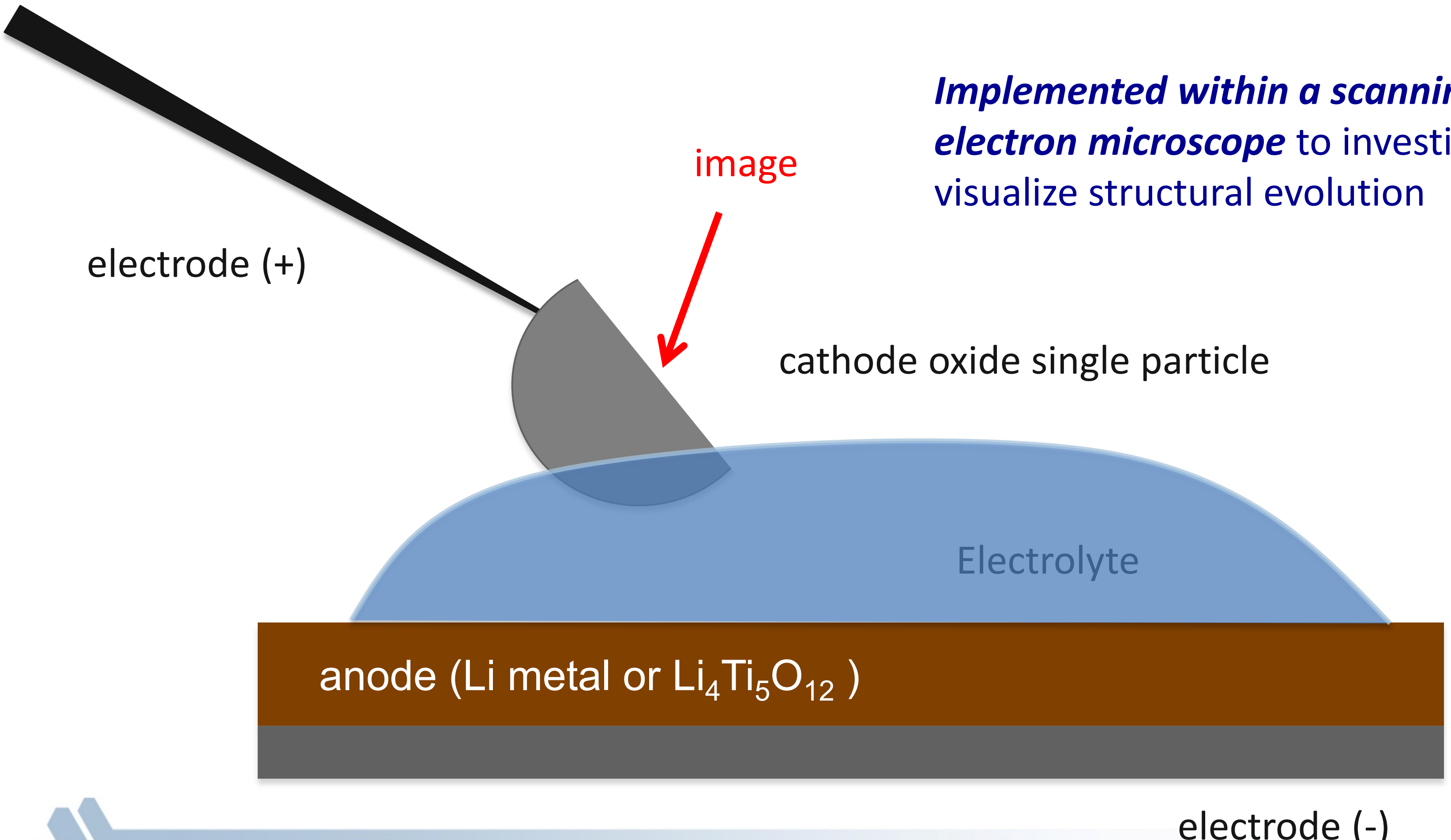


*This result suggests **non-uniform behavior among particles within an electrode** and **motivates a more incisive approach to characterization***

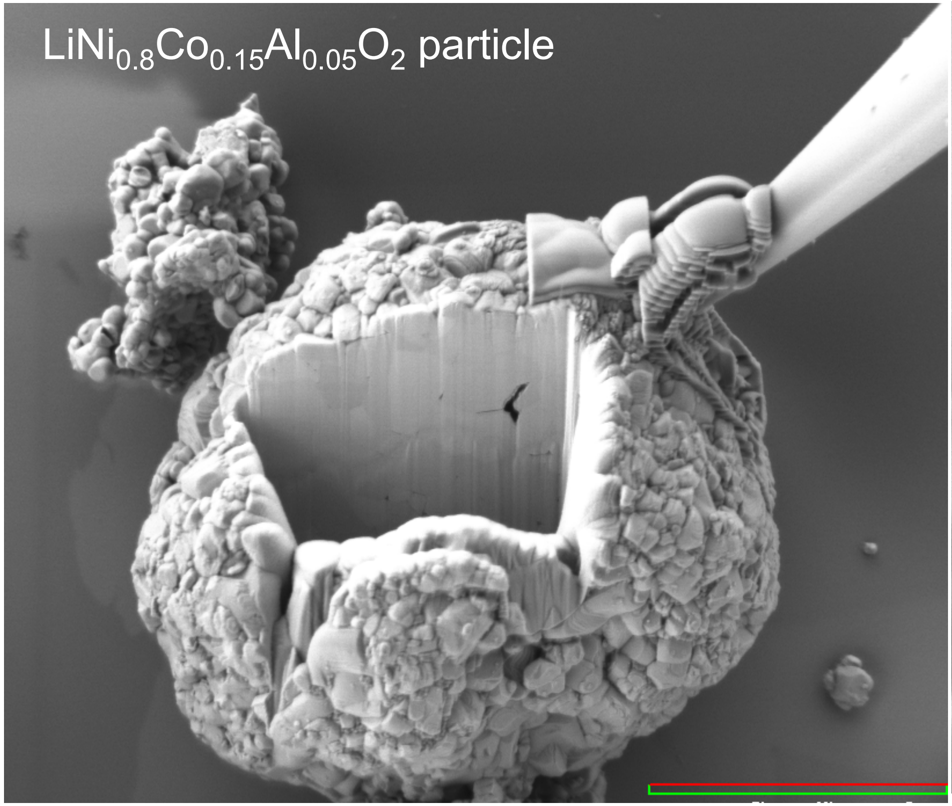
A new approach for *operando* microscopy during electrochemical cycling

- electrochemistry and microstructural changes on same particle
- dynamic observation of processes

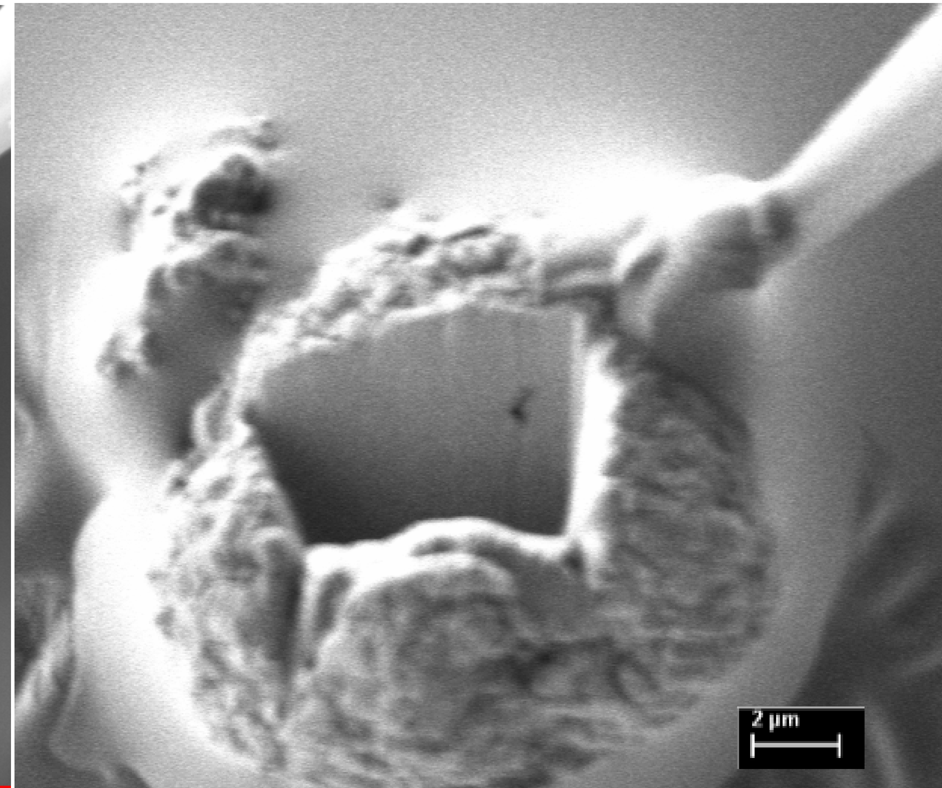
Implemented within a scanning electron microscope to investigate & visualize structural evolution



Single particle *operando* cell in a scanning electron microscope



Particle prepared for in situ experiment



Partial immersion for cycling and imaging

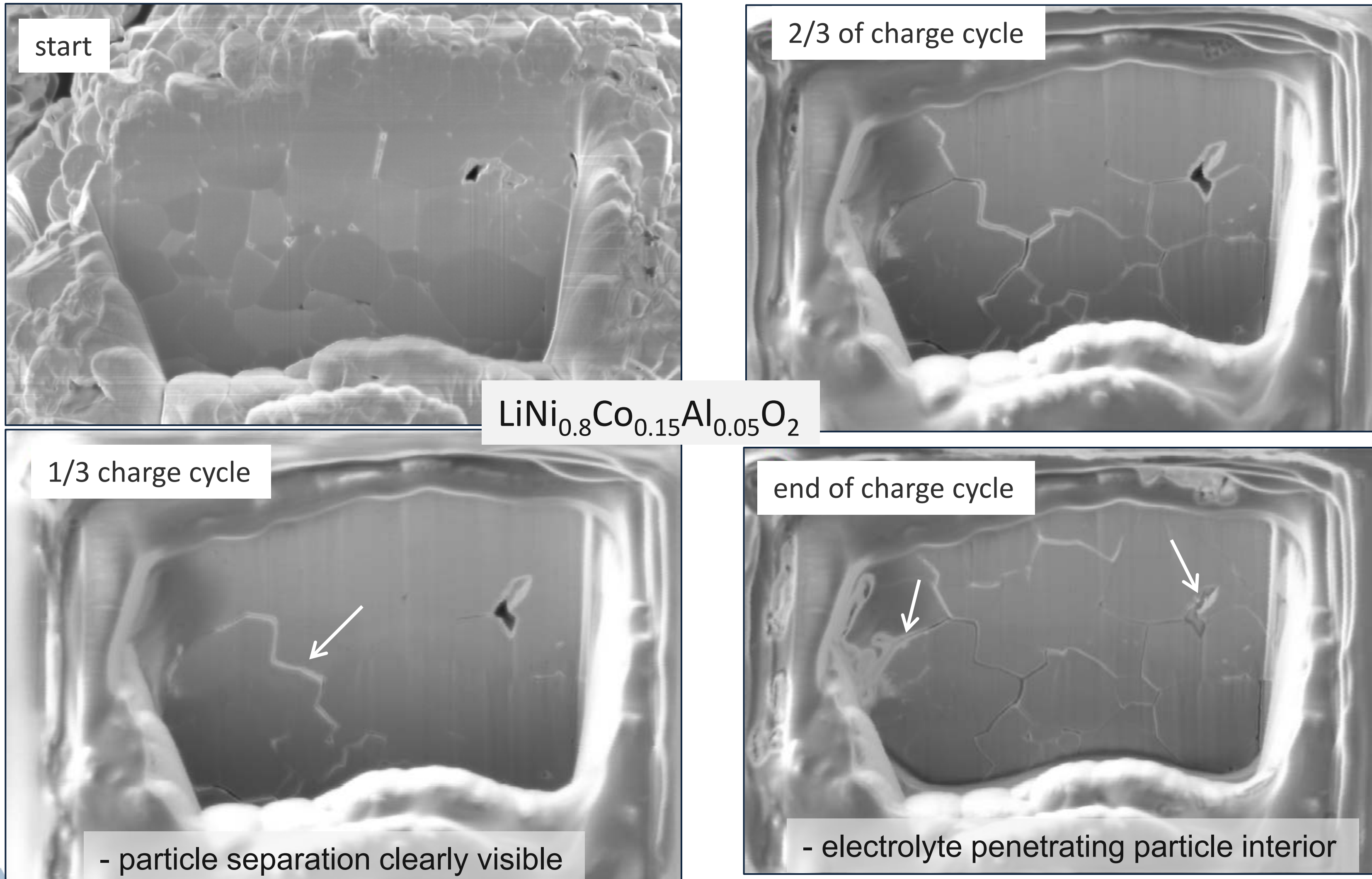
- *a particle attached to a manipulator probe (electrode) is partially immersed in electrolyte covering an anode (typically Li metal) to form a micro-scale battery*

Operando microscopy provides new insight

during initial charge cycle:

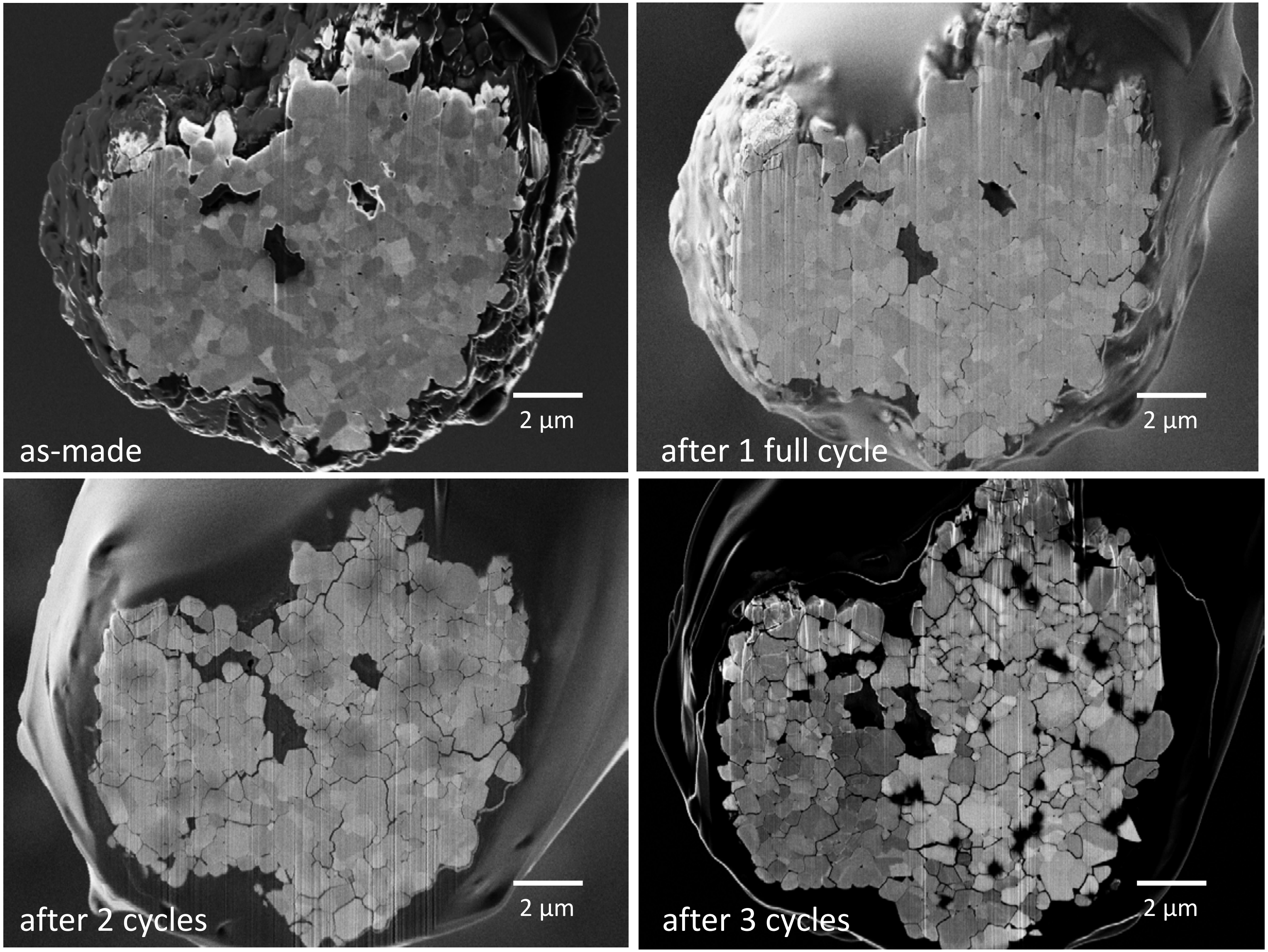
- ***primary particle (grain) separation***
- ***electrolyte penetration to interior of particle***

charge at 1 nA (≈ 1C)



Frame captures from video during cycling

“Snapshots” of microstructural evolution during cycling reveal progression of particle fragmentation upon cycling

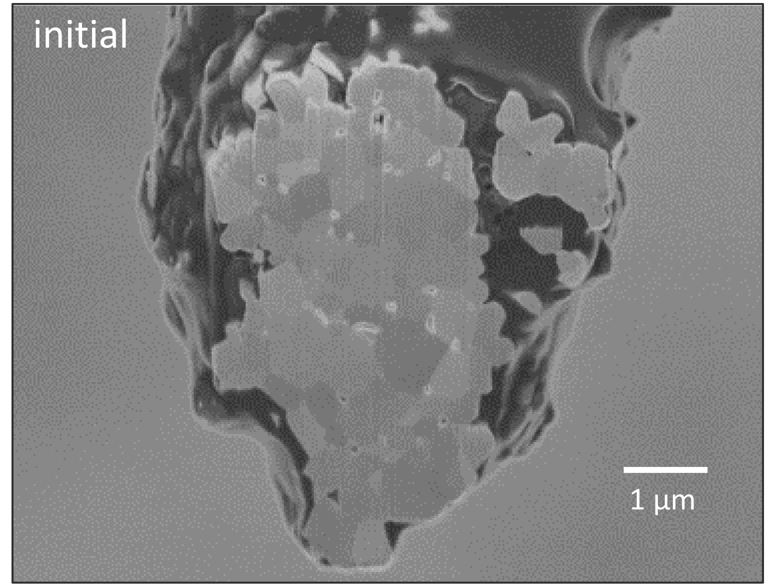


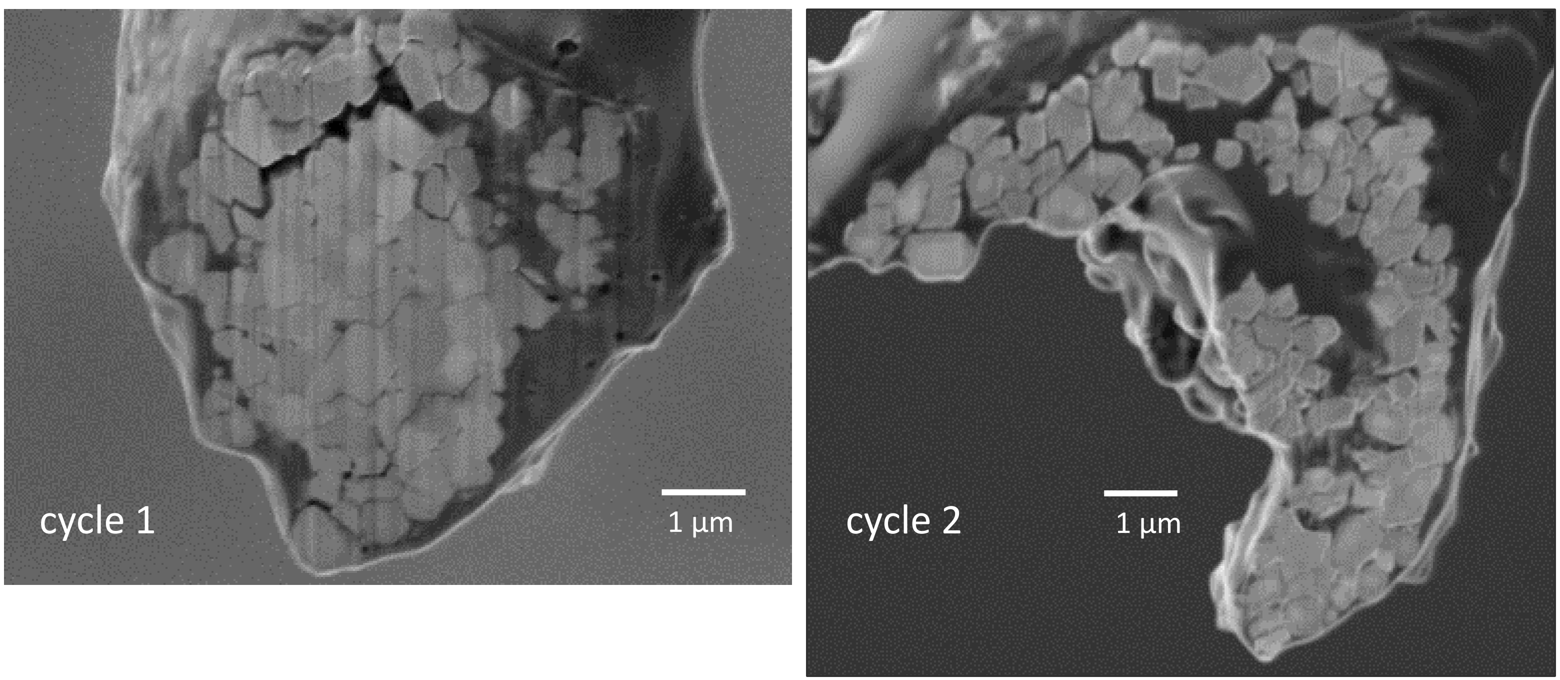
Cycle @ 1 nA (≈ 1C)

Imaging in between cycles

Particle fragmentation leads to loss of grain-to-grain connectivity

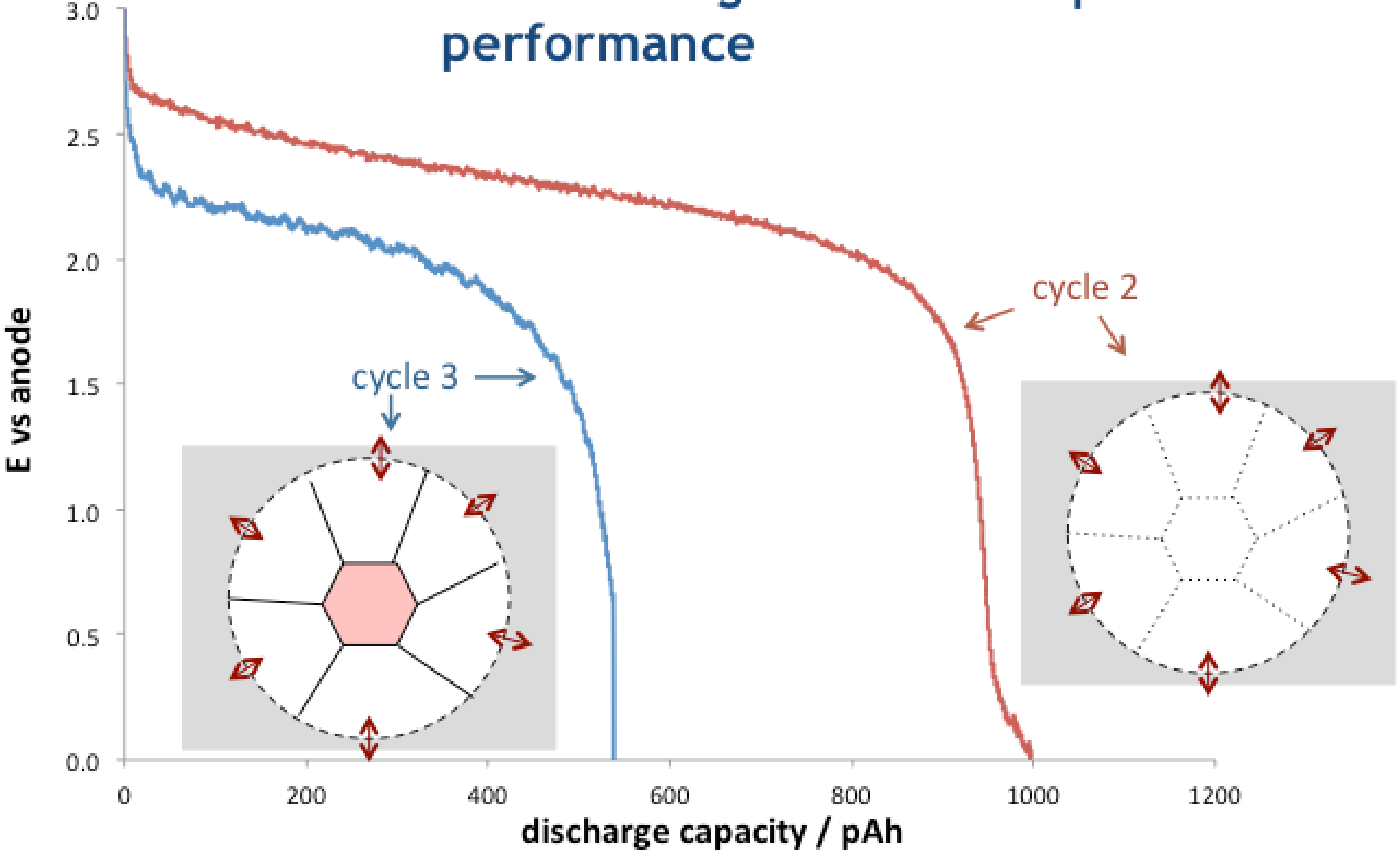
- *in extreme cases of fragmentation, particle fragments can be lost, reflecting* ***complete loss of connectivity***





Imaging in between cycles

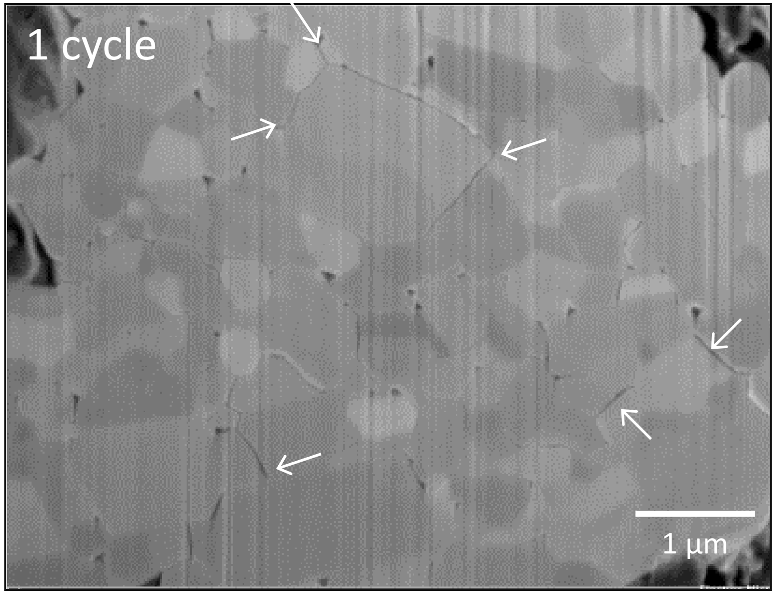
Particle fragmentation impacts performance

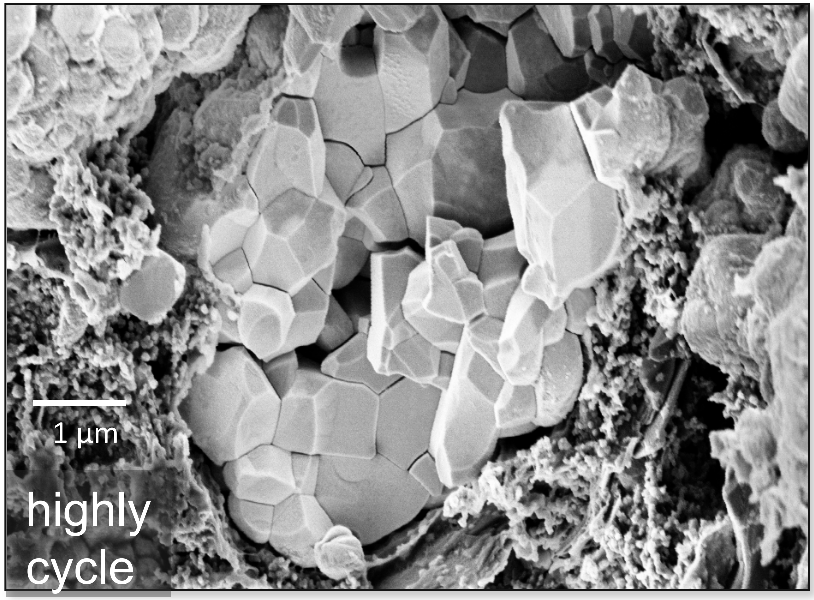


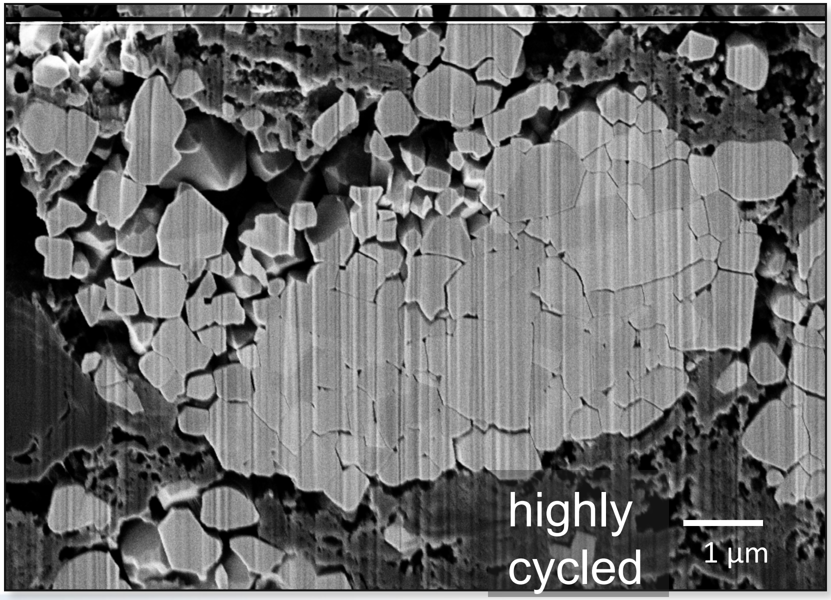
- *particle fragmentation leads to decrease in capacity*
- *mechanism is related to loss of connectivity between grains*

Good correlation with microstructural evolution in practical batteries

Microstructure of cathode particles embedded in laminate harvested from cycled coin cells

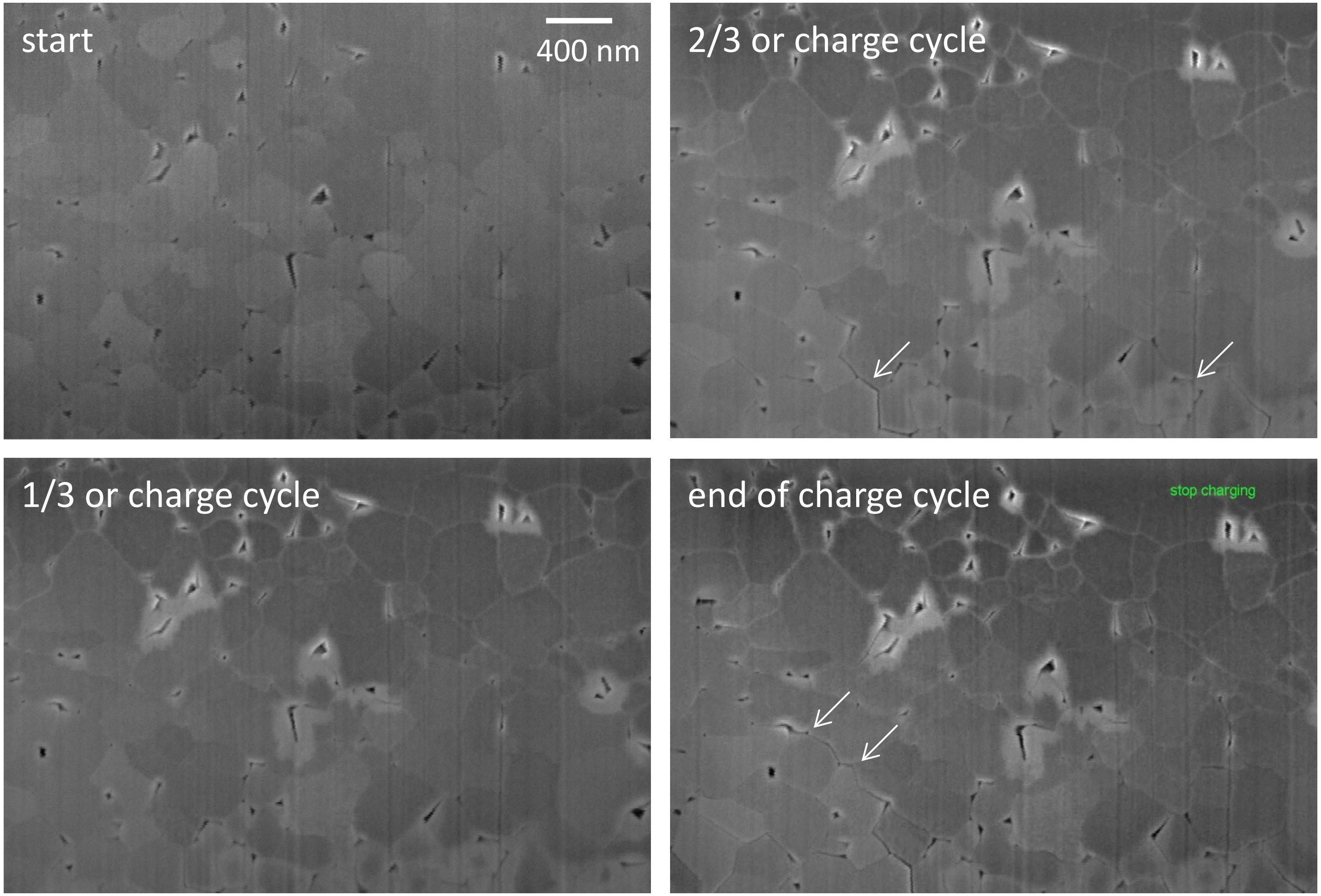






- *cathode particle fragmentation takes place in practical cells (even on the 1st cycle)*
- *particles embedded in laminate remain "intact" despite extreme fragmentation, but still can lose electrical conductivity*

Not all cathode particles behave the same

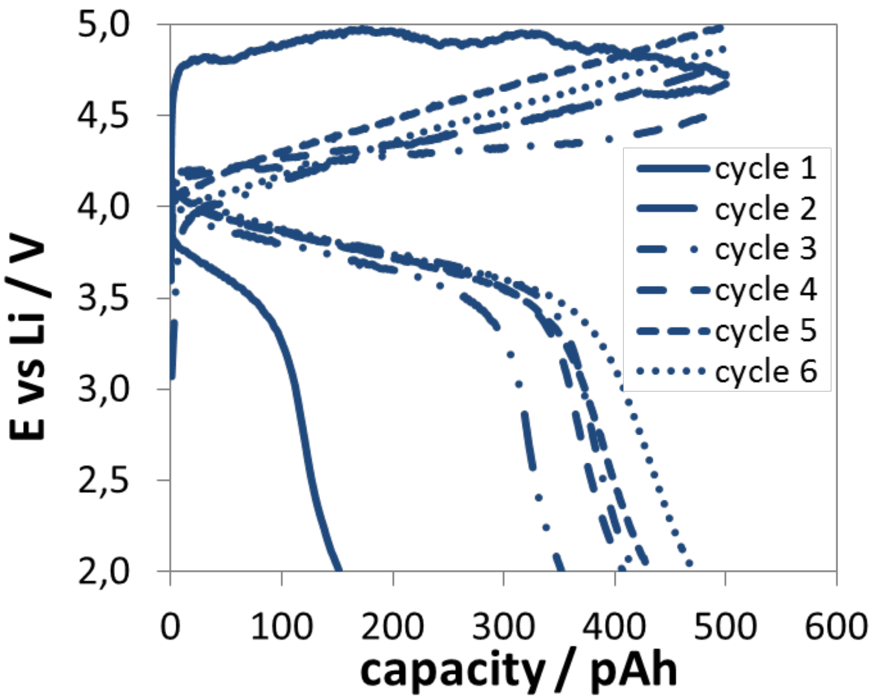


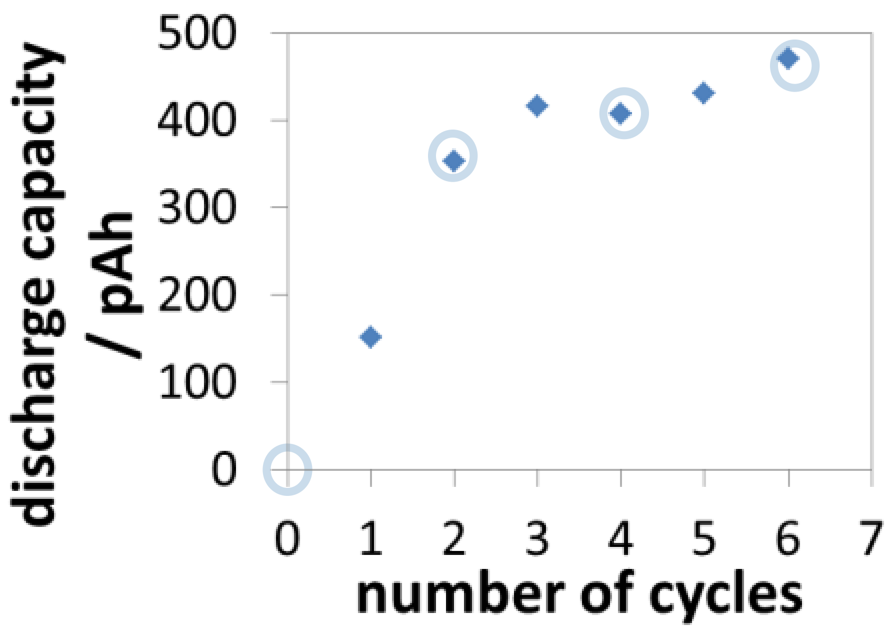
- ***particles with different microstructure exhibit different behavior****; in this example a refined grain morphology minimizes particle fragmentation*
- *the microstructure of individual particles and their location within the electrode can influence electrochemical behavior*

Frame captures from video during cycling

Measurement of electrochemical performance of single cathode particles

- electrochemical data can be distorted by the electron beam during operando experiment, so an additional focus has been on perfecting single particle electrochemical cycling



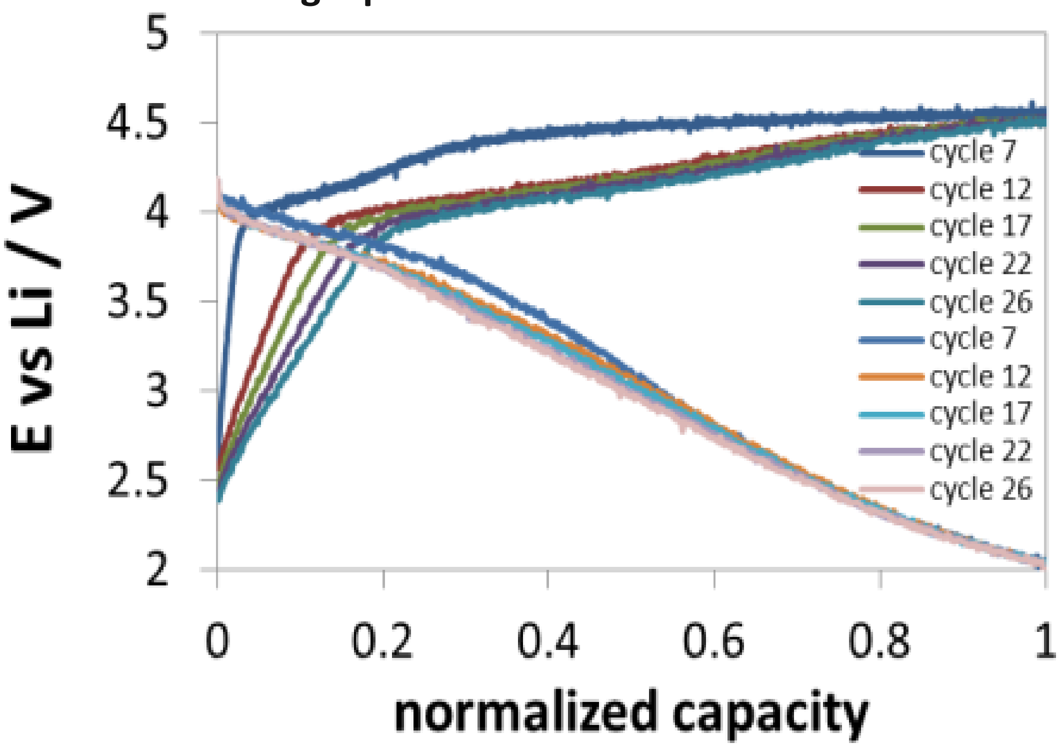


- *correlating single particle measurement with real-world battery behavior requires reliable electrochemical data*

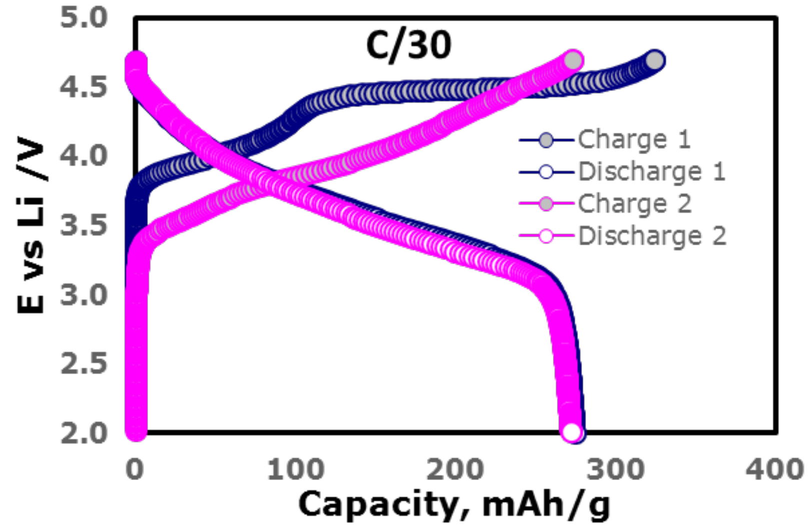
Single particle electrochemistry – relevance to voltage fade

$0.5Li_2MnO_3 \cdot 0.5LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$

Single particle measurement



Coin cell measurement



- *comparison with measurement of a "real world" sample shows our single particle measurement has good correlation with the essential signatures of voltage fade*

Future Work

Develop and exploit ***coordinated characterization*** **to correlate electrochemical behavior and structure at the micro- and nano-scale**

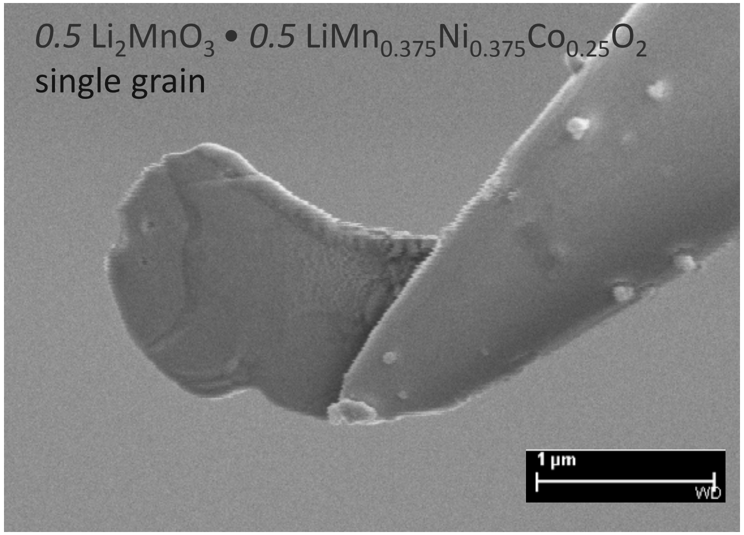
- obtain statistically reliable cycling data from single particles of

0.5 Li_2MnO_3 • *0.5* $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$

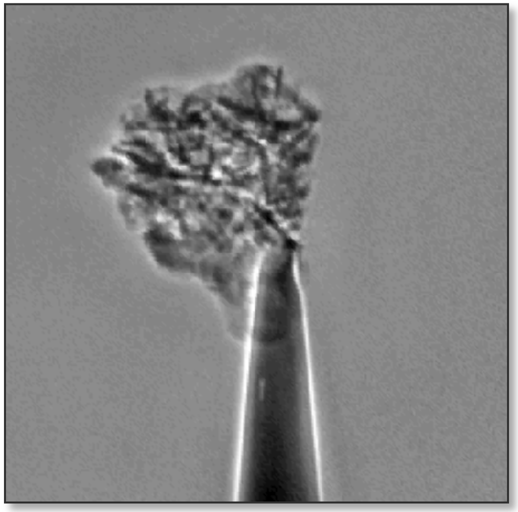
- assess voltage fade in single particles and particle-to-particle variations, use insight to help interpretation of full cell measurements

- implement *operando* approach for characterization of single grains during electrochemical cycling, especially at the TEM scale, to correlate with structural evolution

- move the challenge for characterization from billions of particles in a coin cell to the single particle & single grain level

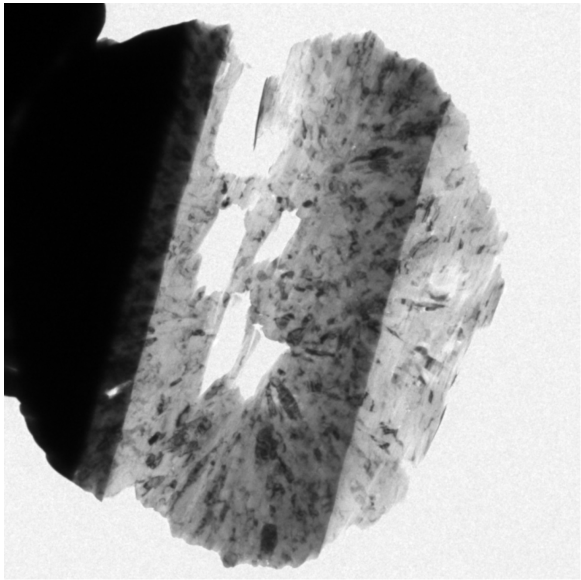


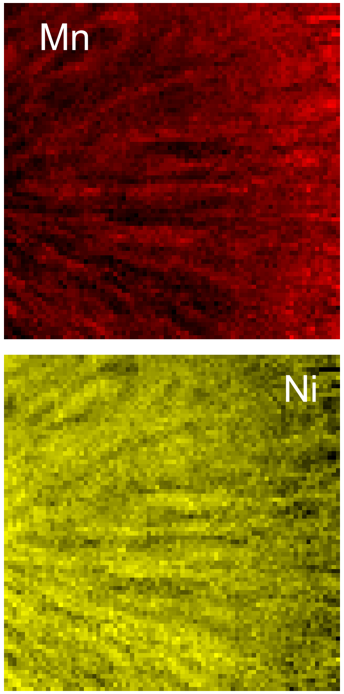
Future Work



- apply coordinated characterization to provide electrochemical data and comprehensive structural characterization on the same single particle and single grain of material

- *exploit complementary capabilities such as x-ray tomography, XAS & XES, SEM, TEM*





- expand application of our advanced characterization capabilities more broadly within the Vehicle Technologies program

- *utilize our expertise to address the most important challenges in vehicle technologies*

Collaborations and Coordination

Research involves extensive collaboration with the entire Voltage Fade team

- guidance and evaluation of electrochemical measurement

(esp. D. Abraham,, M. Bettge, J. Bareño, K. Gallagher, J. Croy)

- complementary characterization and approaches to coordinated characterization

(esp. M. Balasubramanian, L. Trahey, Y. Ren)

- high-capacity cathode materials development

(esp. C. Johnson, K. Amine, M. Thackeray)

New collaborations are sought to expand the impact of our approach to the most important challenges in vehicle technologies

Summary

- We developed a new approach for *operando* microstructural characterization and electrochemical cycling of single cathode particles
  - *baseline characterization of 0.5 Li_2MnO_3 • 0.5 $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$ showed non-uniform behavior among particles, motivating this approach*
- Operando microscopy of $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ revealed new insight into structural evolution
  - *primary particle (grain) separation and electrolyte penetration to interior of particle can take place during the very first charge cycle*
  - *particle fragmentation contributes to loss of capacity by decreasing grain-to-grain connectivity and this mechanism takes place in full cells*
  - *the degree of fragmentation can be influenced by particle microstructure*
- Measurement of electrochemical behavior of single cathode particles was perfected
  - *single particle measurements are well-correlated with full-cell performance*
  - *Small particle measurements offer a pathway to more direct correlation of performance with structure and microstructure*