Transport in Rechargeable Batteries V

Lecture 25

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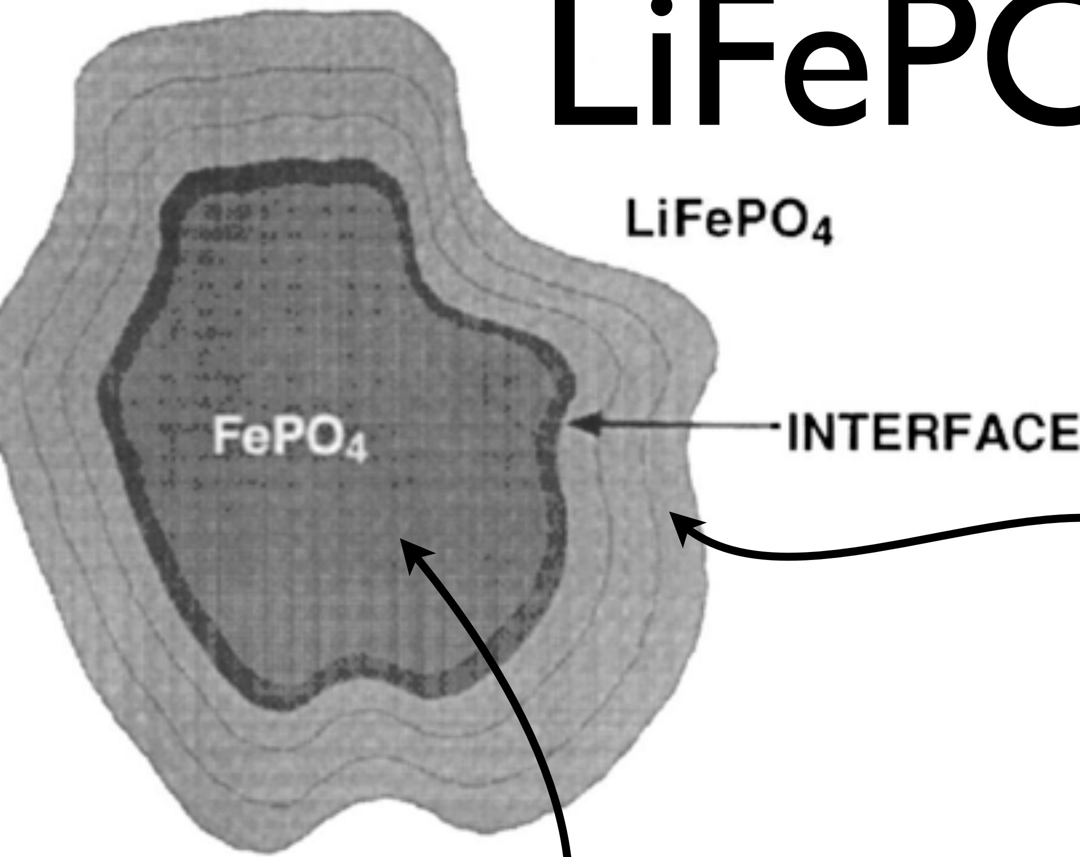
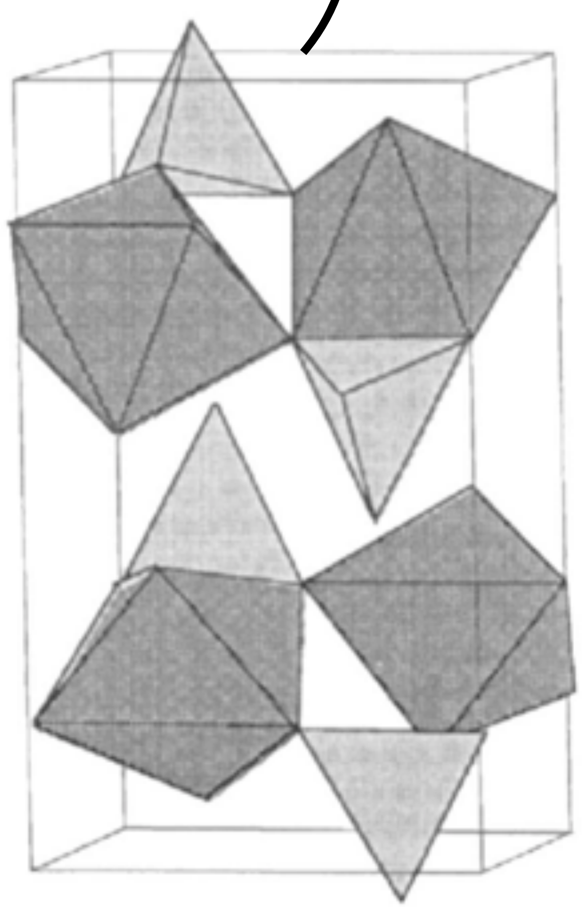
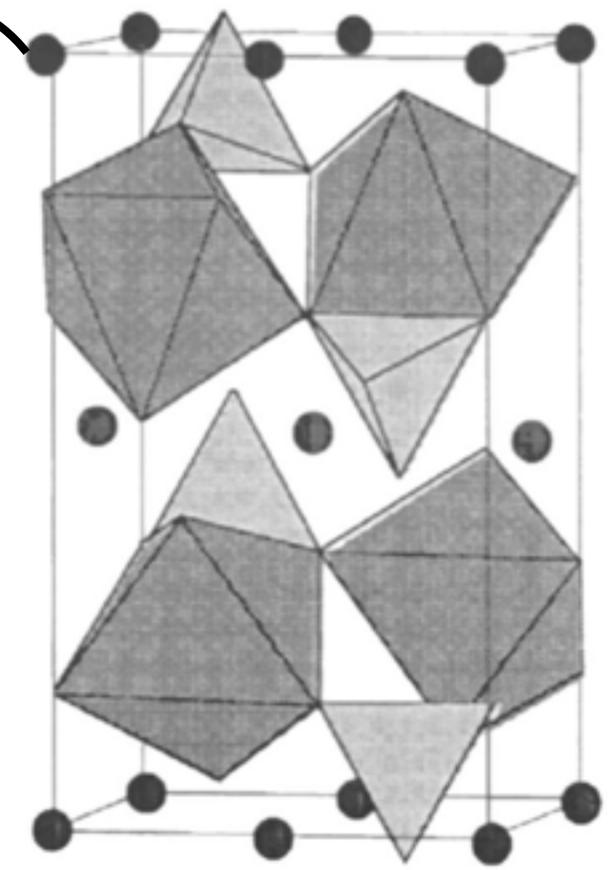
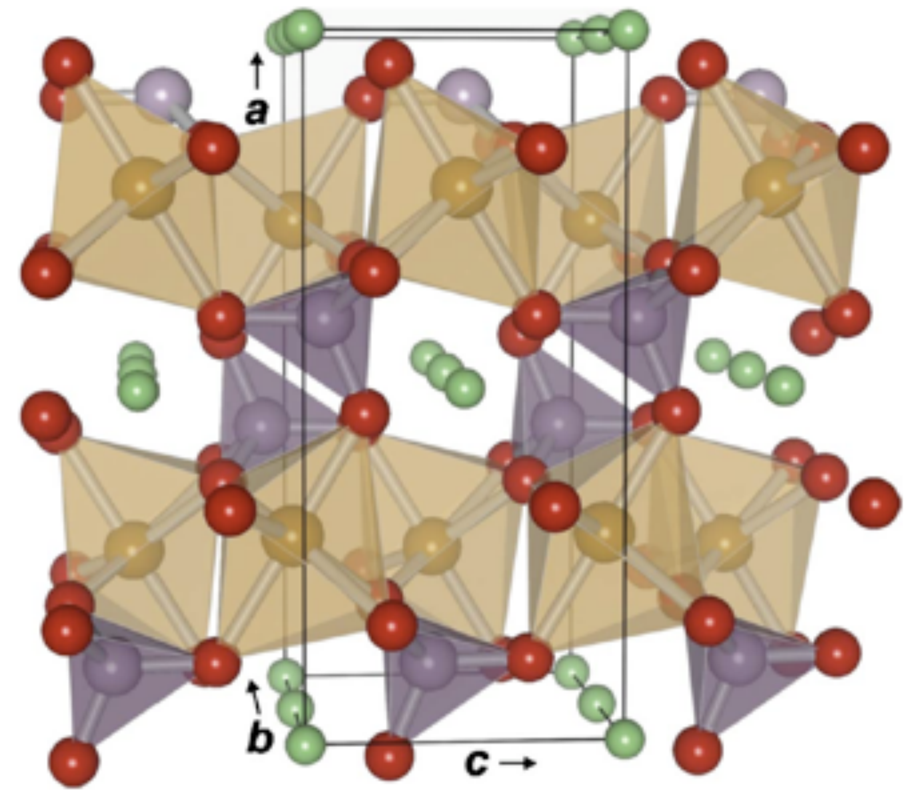
$LiFePO_4$ Crystal Structure



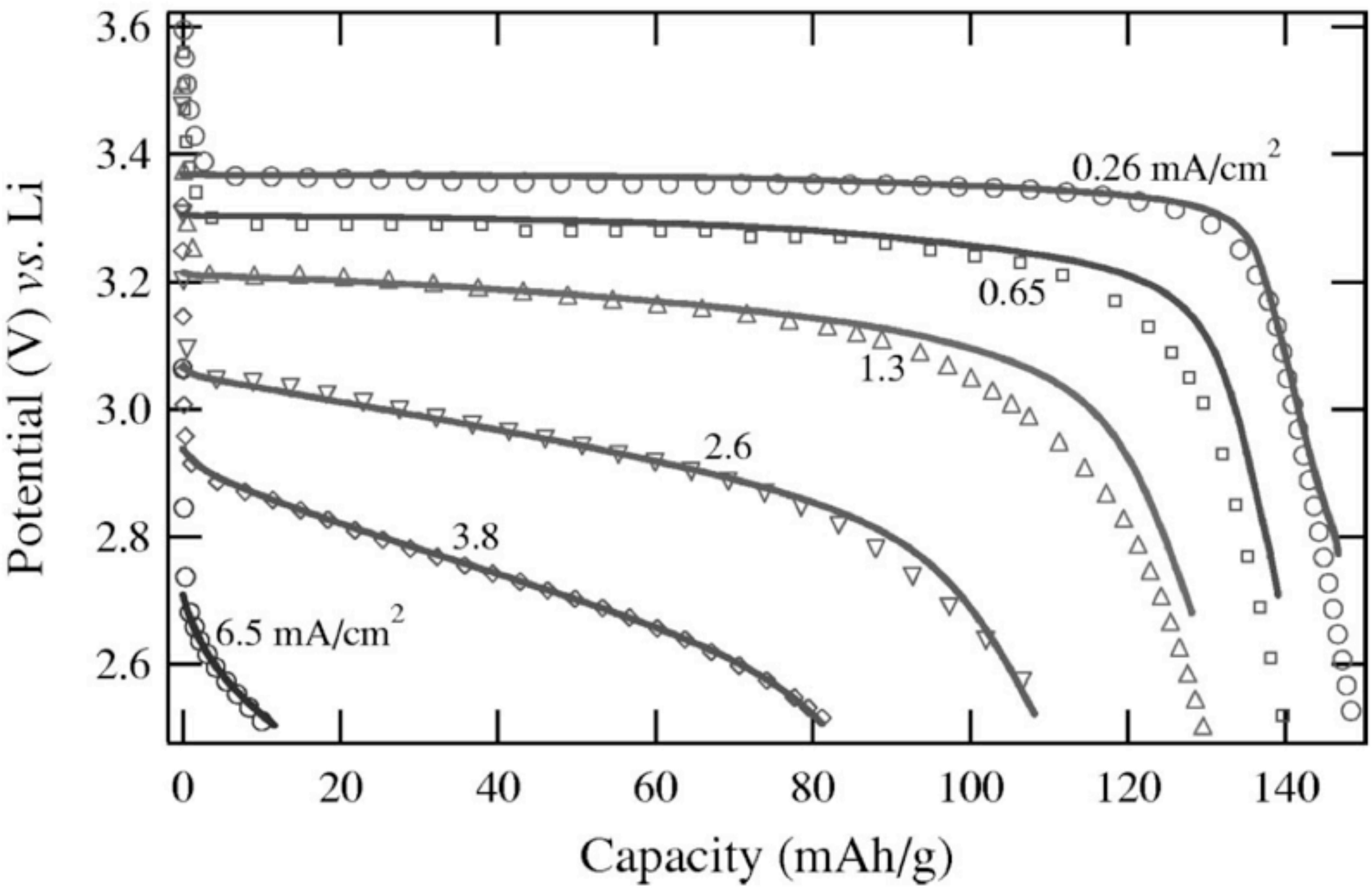


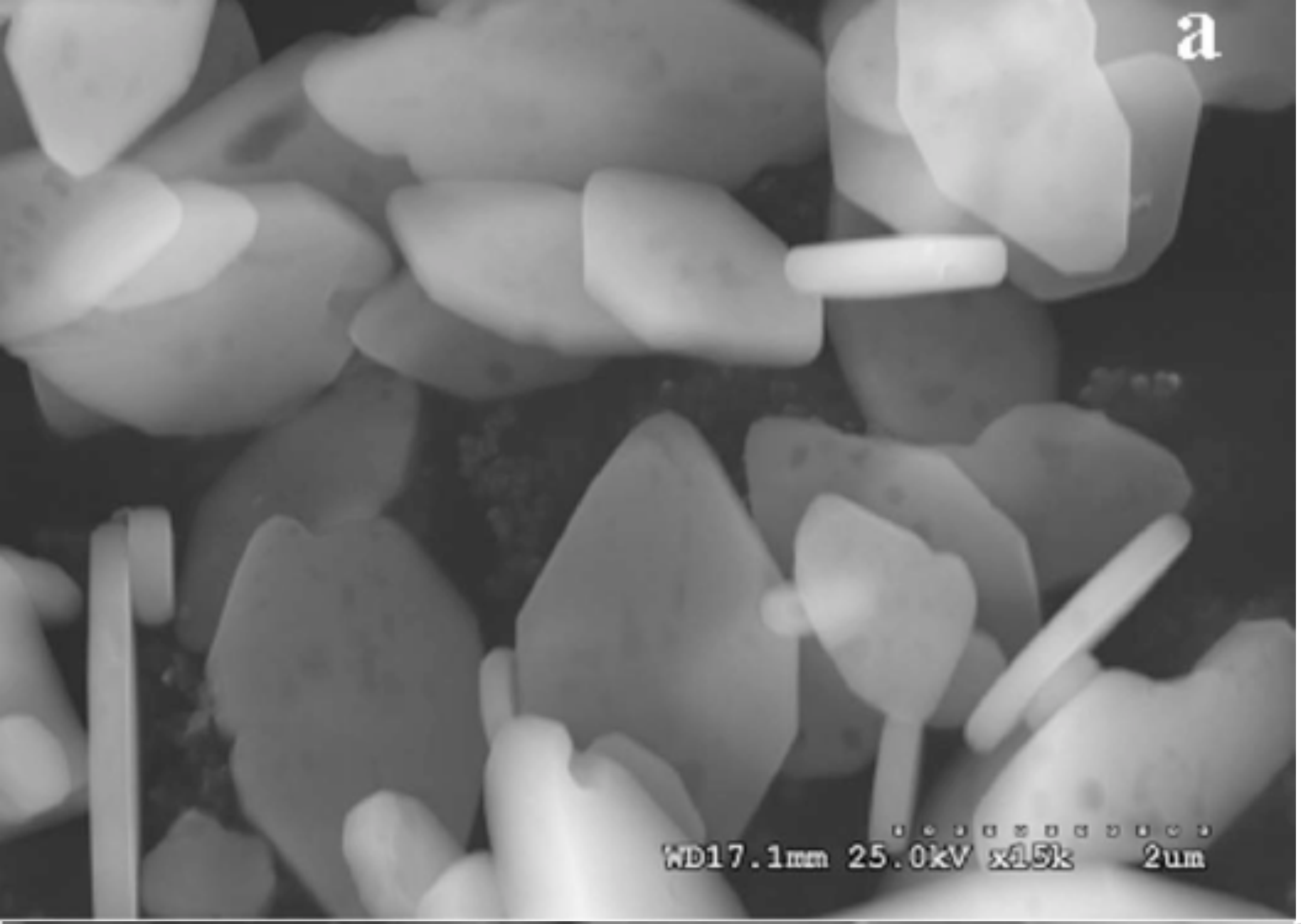




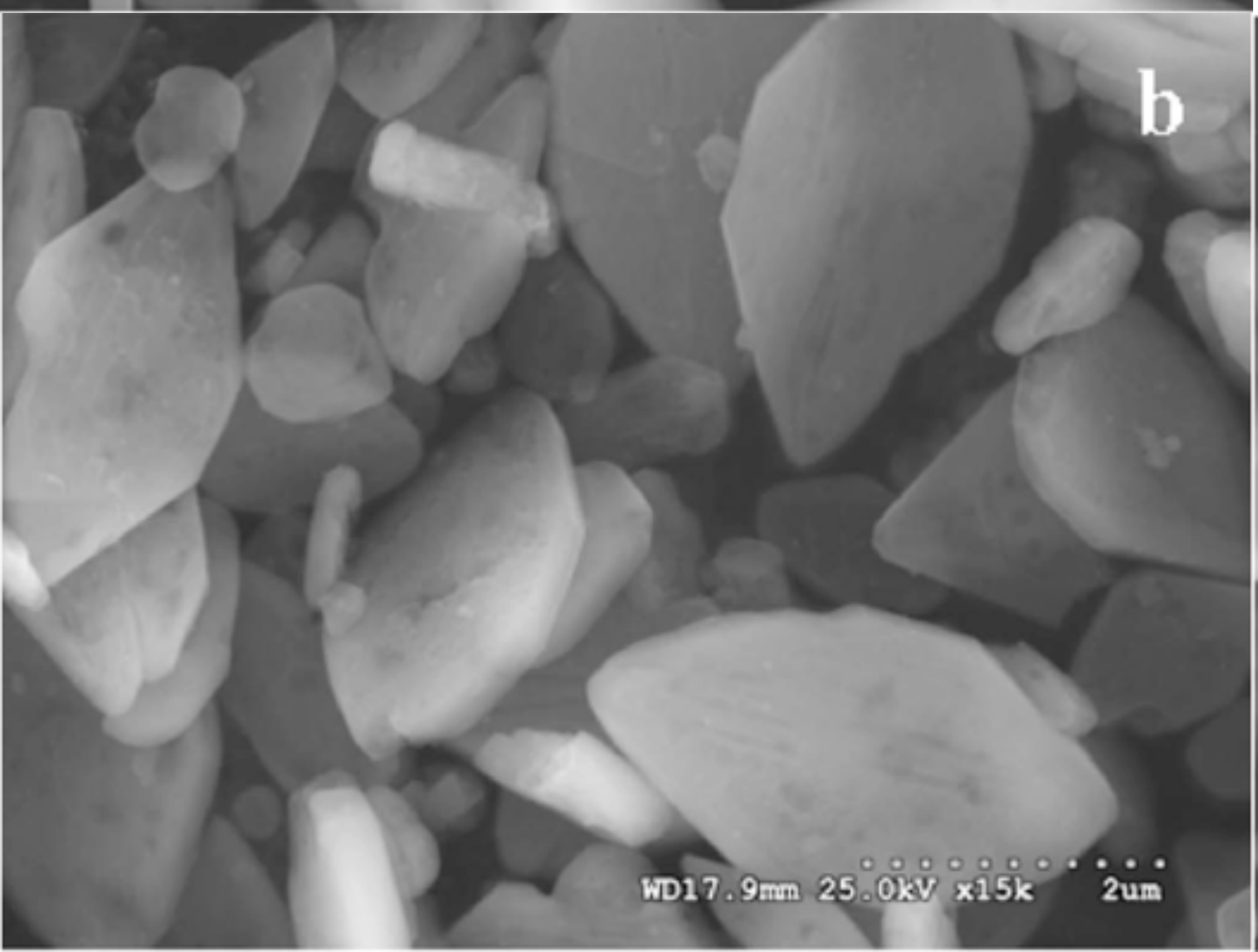
	$LiFePO_4$	$FePO_4$
Space Group	Pb nm	Pb nm
a (Å)	6.008 (3)	5.792 (1)
b (Å)	10.334 (4)	9.821 (1)
c (Å)	4.693 (1)	4.788 (1)
Volume (Å^3)	291.392 (3)	272.357 (1)

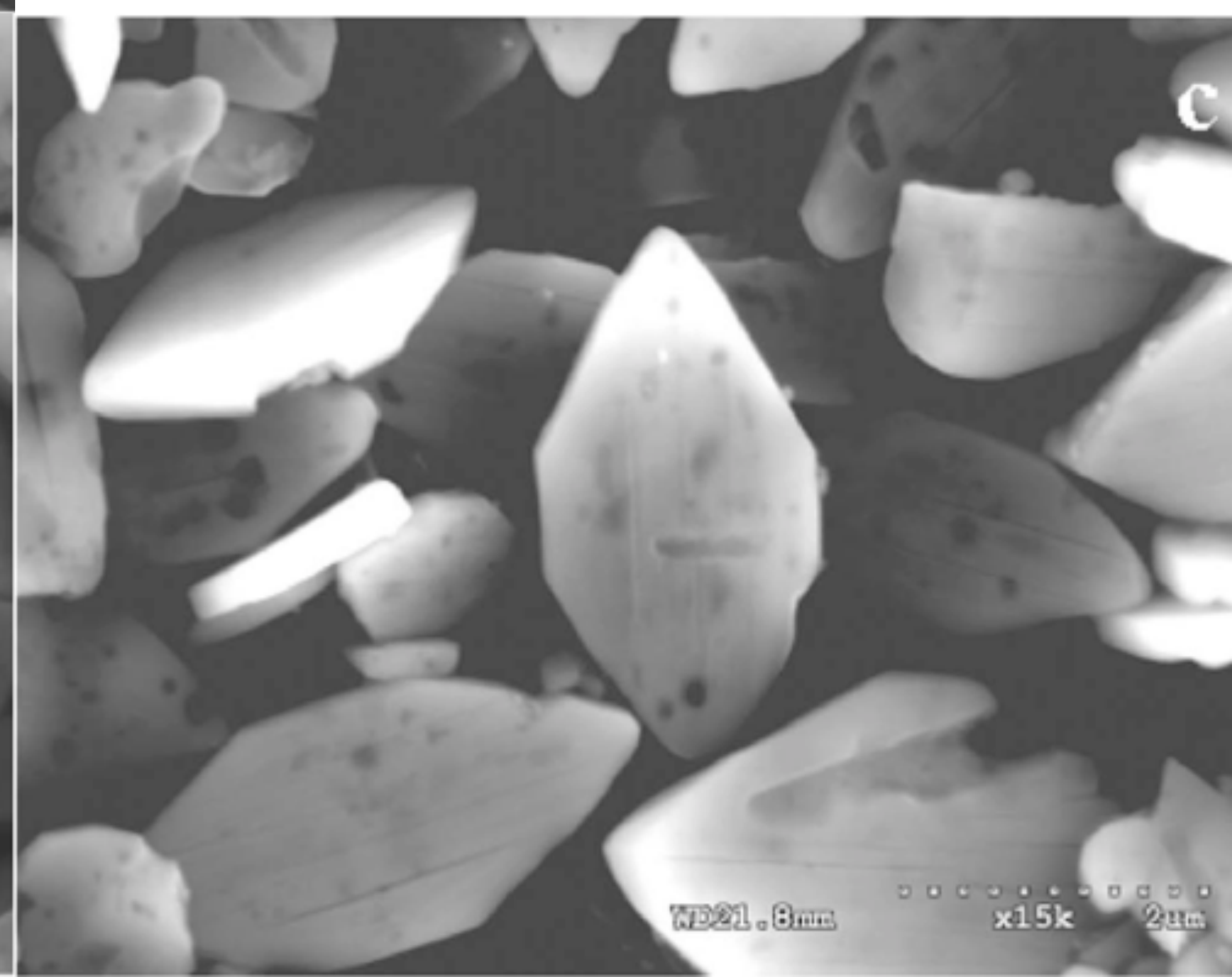
Voltage-Capacity Plot



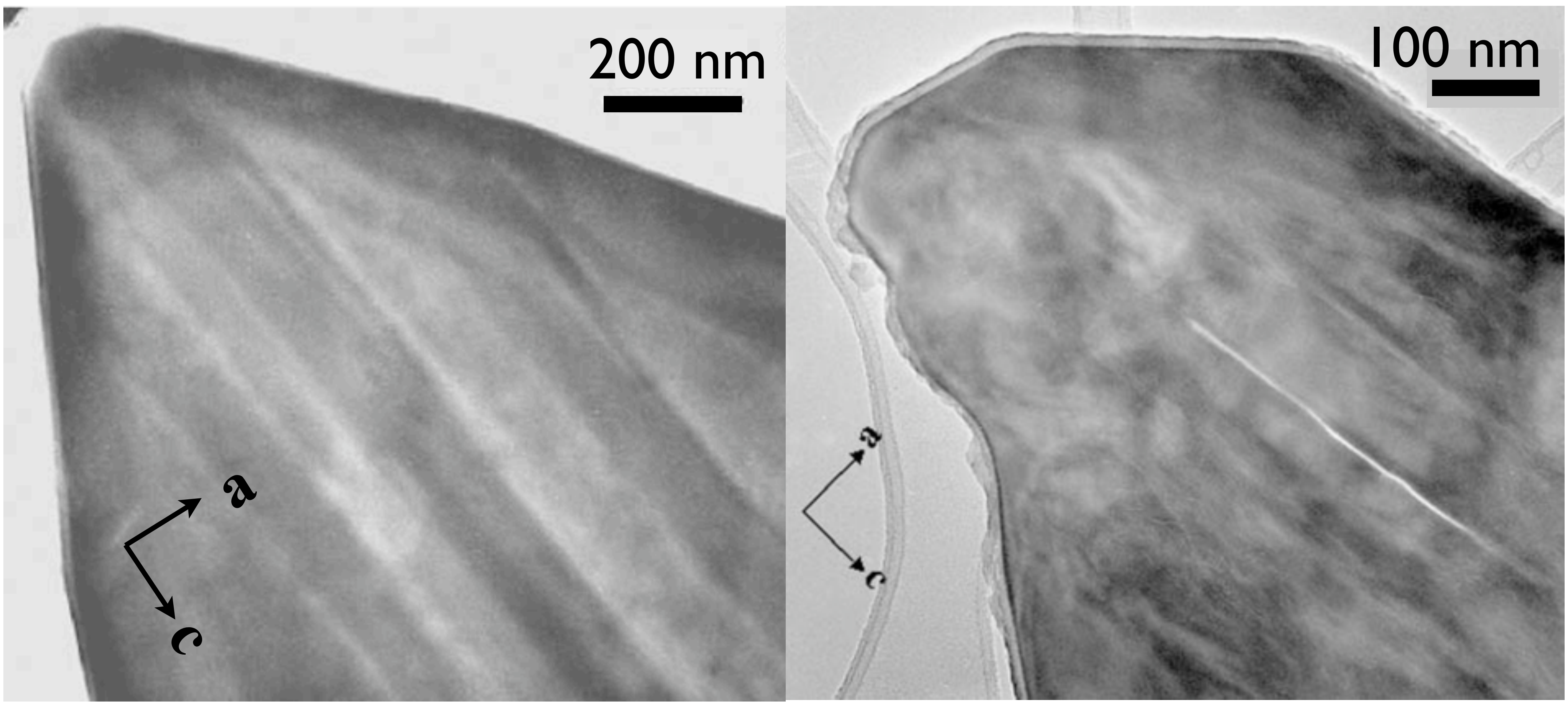


Real-Life $LiFePO_4$ Particles



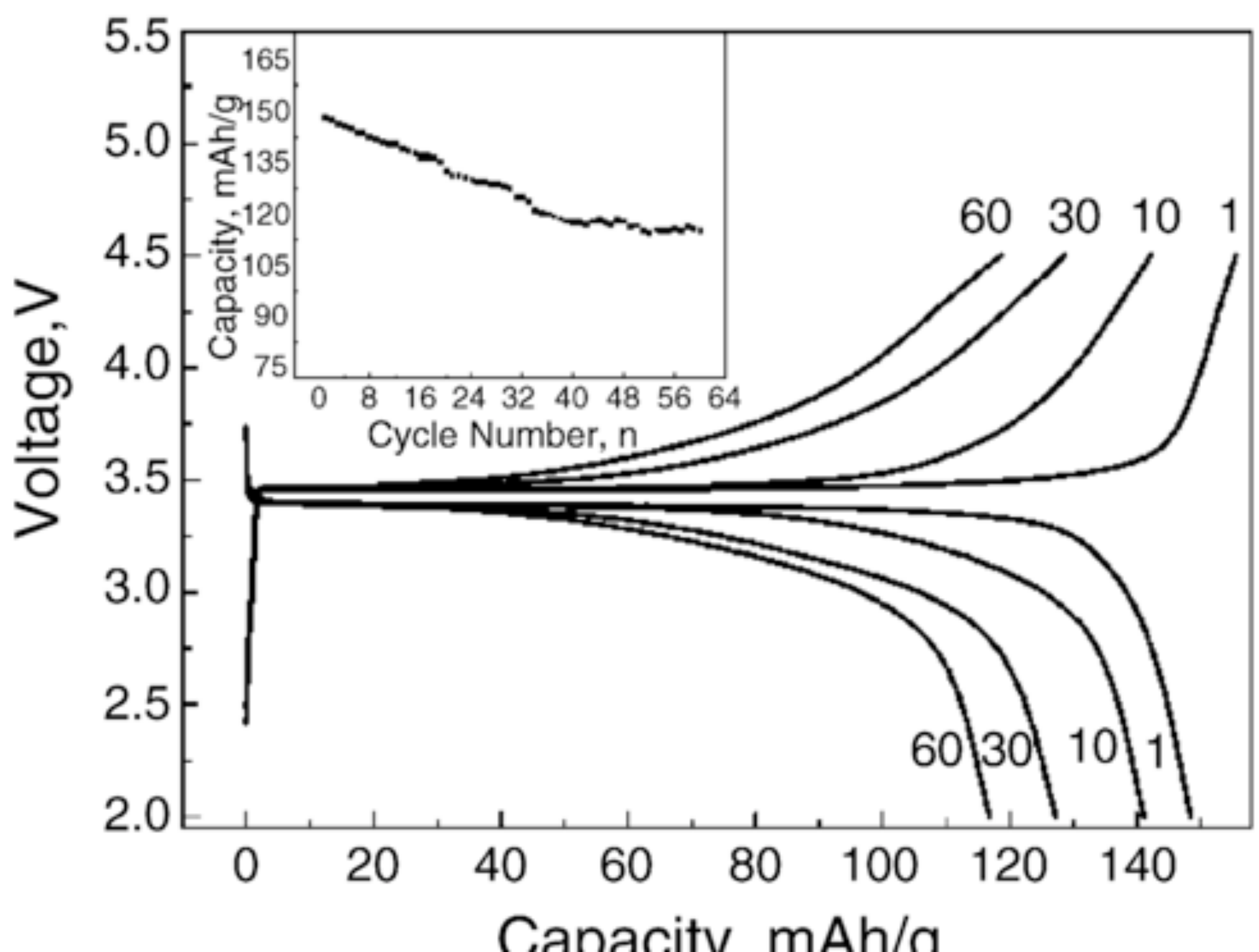


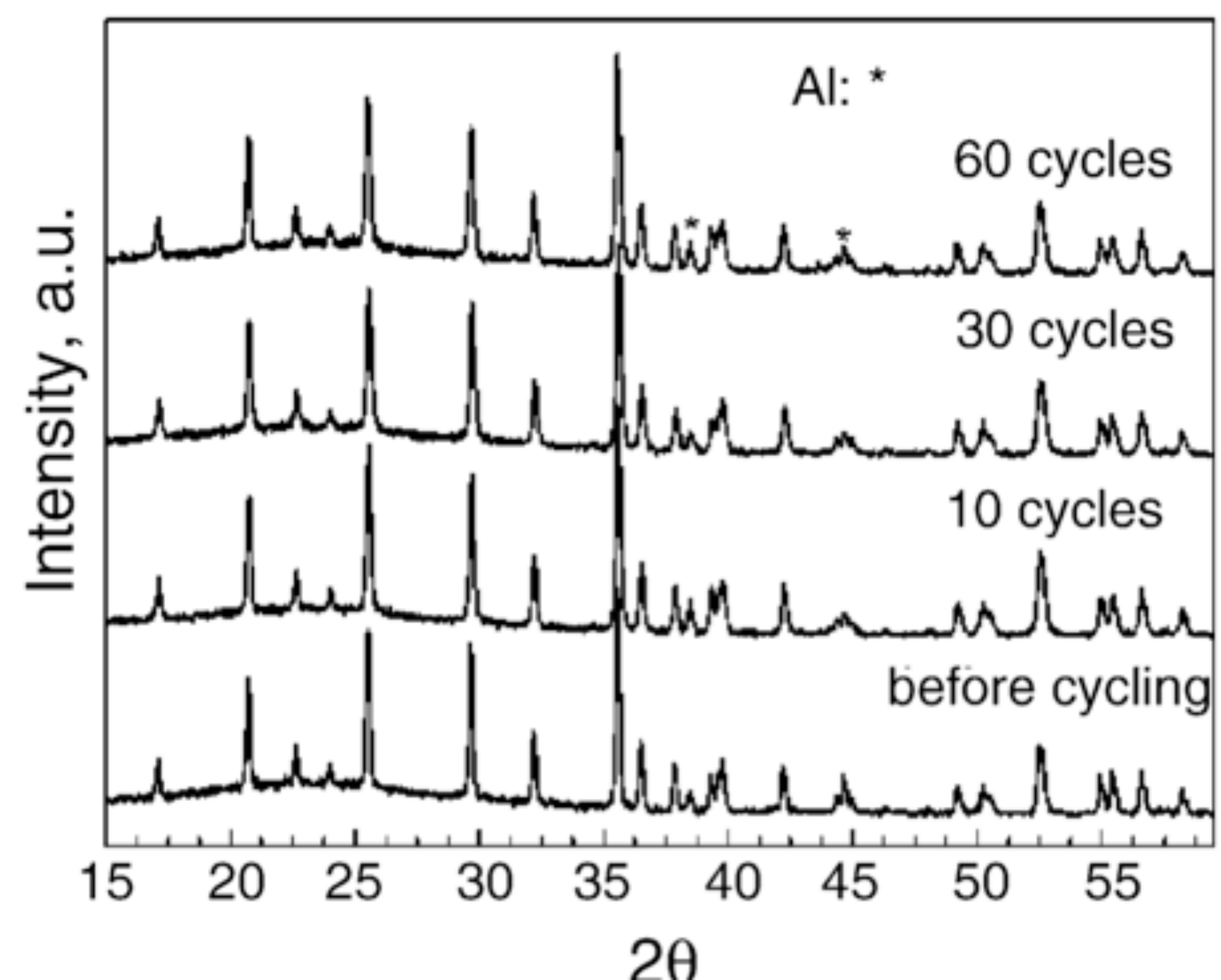
Intercalation Dynamics Experimental Observations

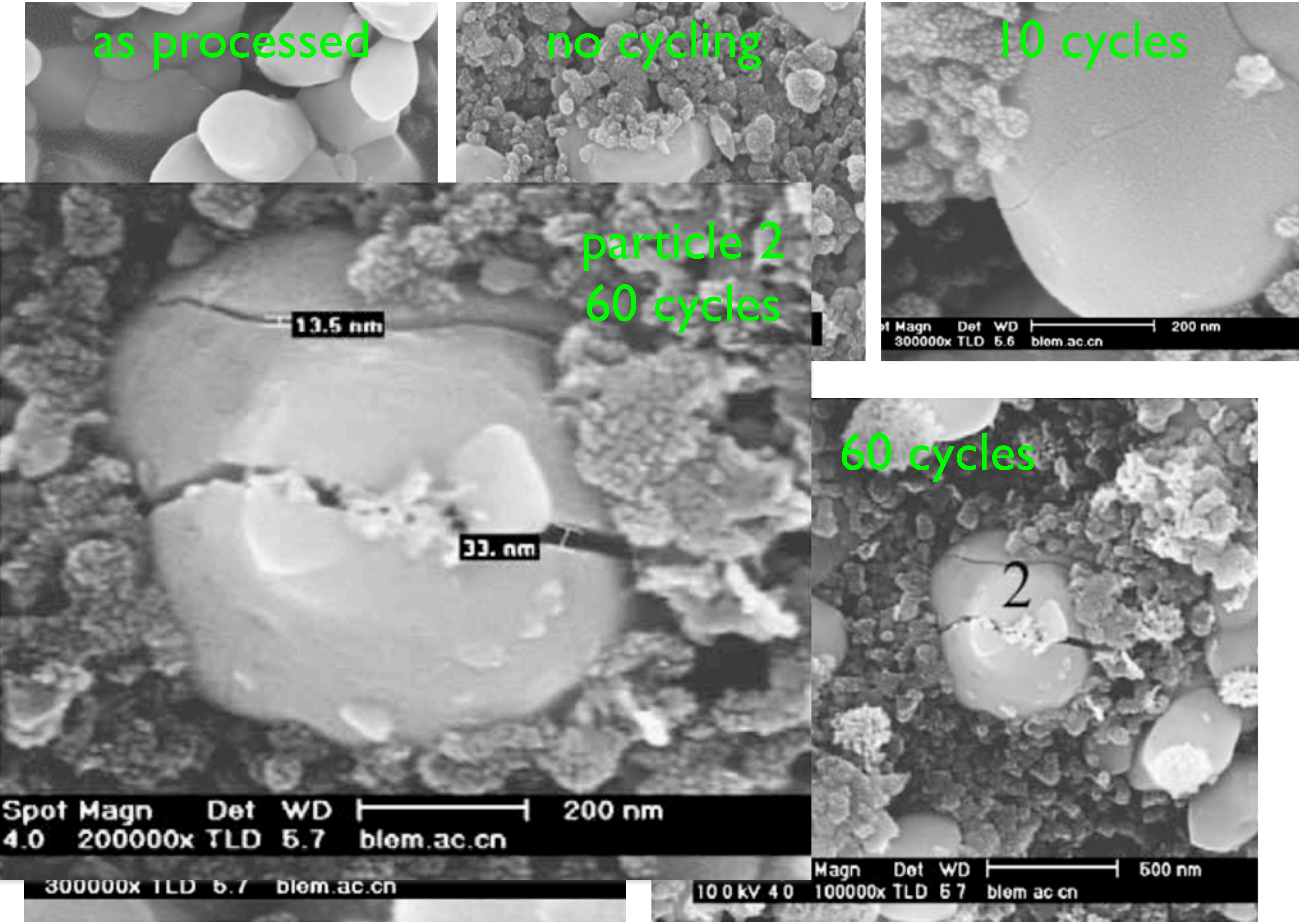


Experimental Evidence

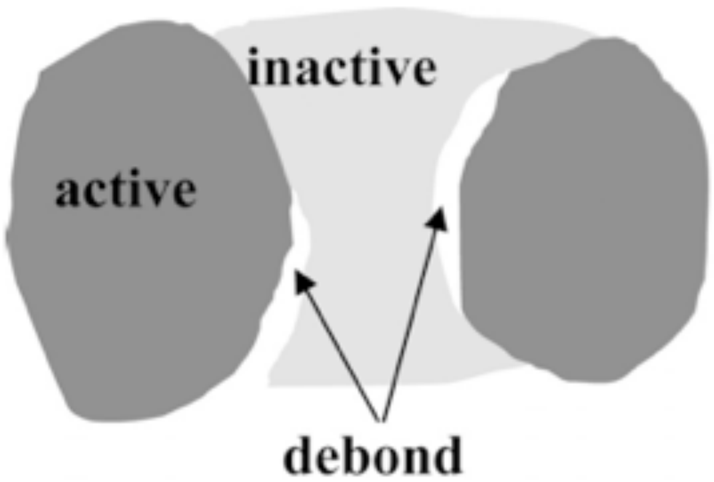
cathode contains carbon black (15%), $LiFePO_4$ (75%), and PvdF (10%). Anode is metallic lithium. Electrolyte is EC:DMC = 1:1, with 1 mol/L of $LiPF_6$. Separator is trilayer PP+PE+PP (Celgard 2340).





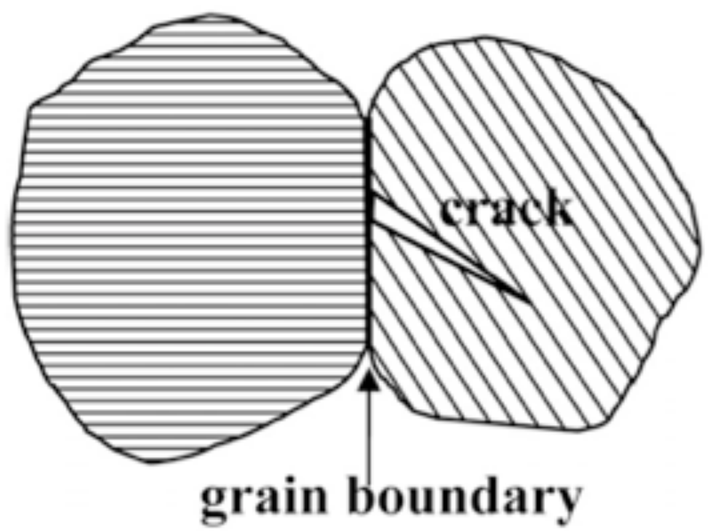

as processed
no cycling
10 cycles
particle 2
60 cycles
13.5 nm
33. nm
Spot Magn Det WD 200 nm
4.0 200000x TLD 5.7 blem.ac.cn
Magn Det WD 200 nm
300000x TLD 5.6 blem.ac.cn
60 cycles
2
Magn Det WD 500 nm
10.0 kV 4.0 100000x TLD 5.7 blem ac cn
300000x TLD 5.7 blem.ac.cn

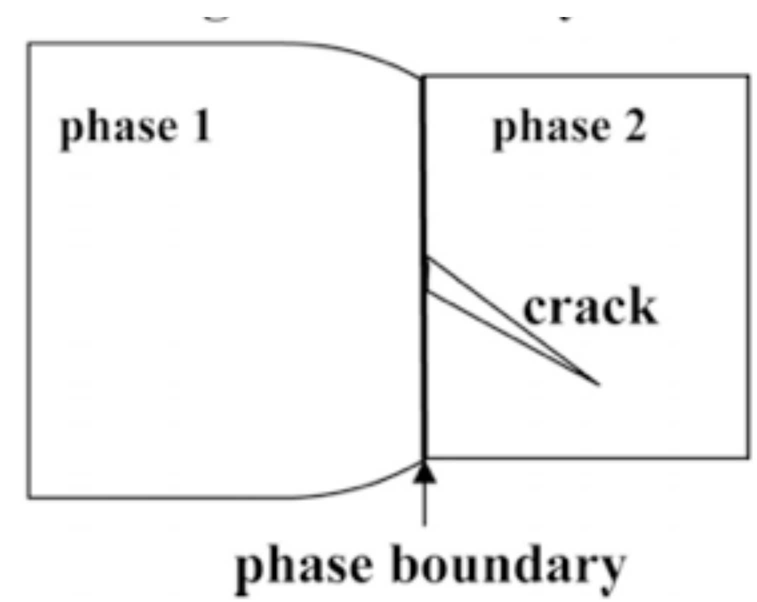
Fracture Mechanics in Battery Materials



Likely to occur
in crystallographically
anisotropic materials

Likely to occur
during delithiation





accumulated energy for fracture

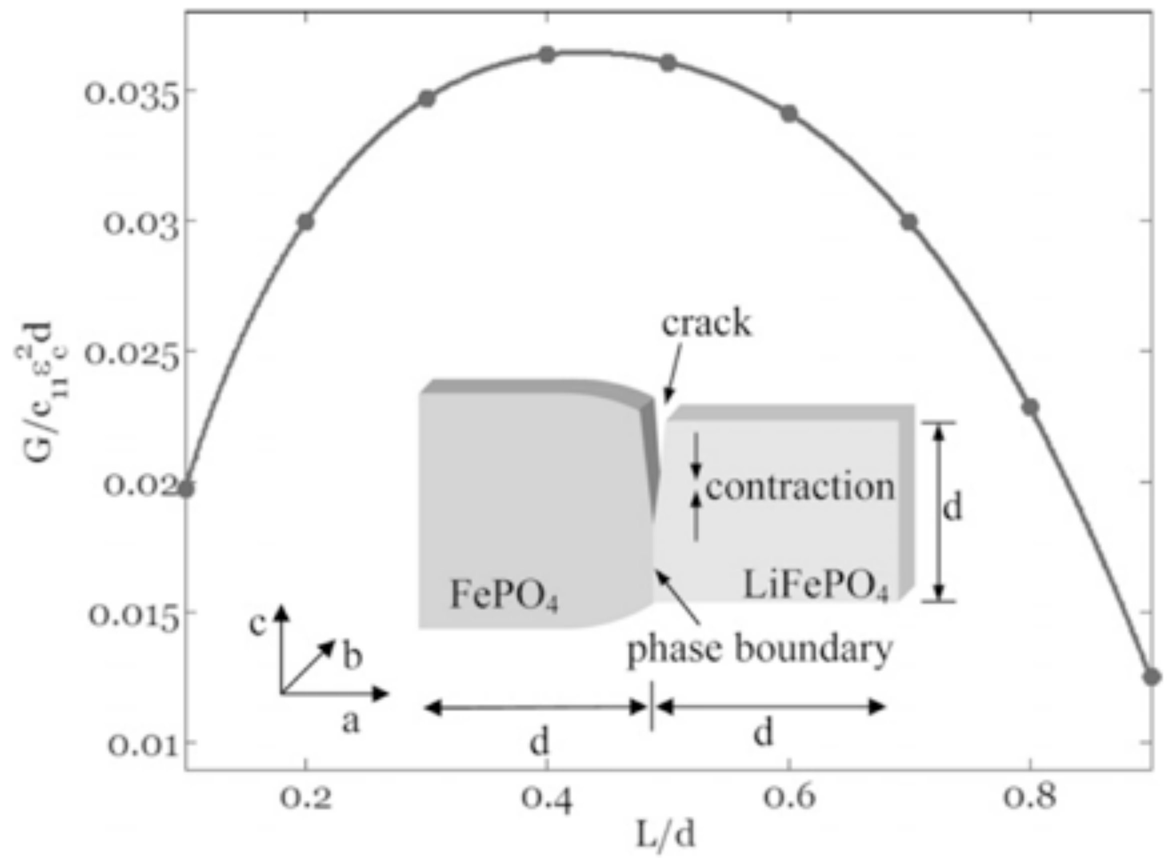
$$G = Z\sigma\varepsilon a = ZE\varepsilon^2 a$$

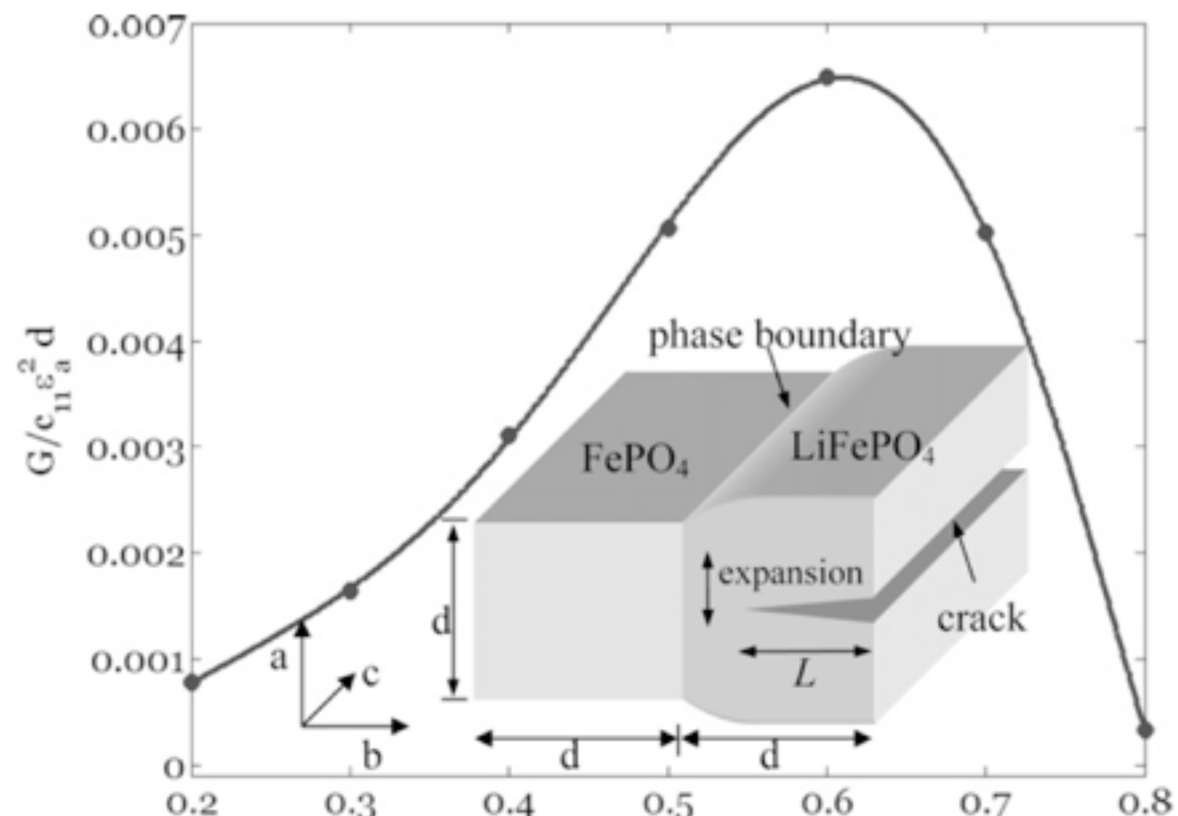
Fracture occurs if:

$$G \geq 2\gamma$$

Likely to occur
in two-phase
materials

Stresses and Cracks in $LiFePO_4$



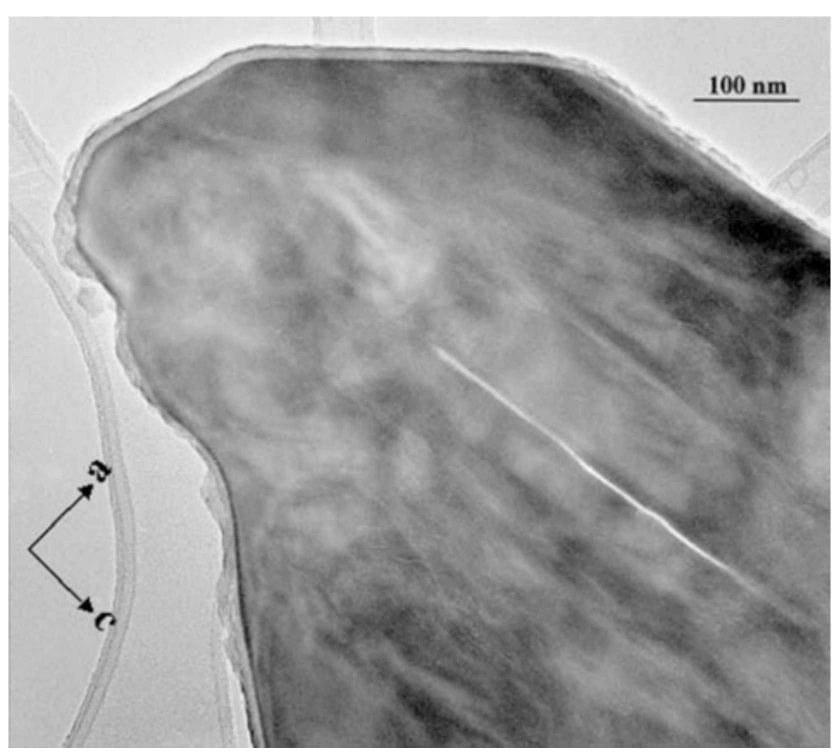


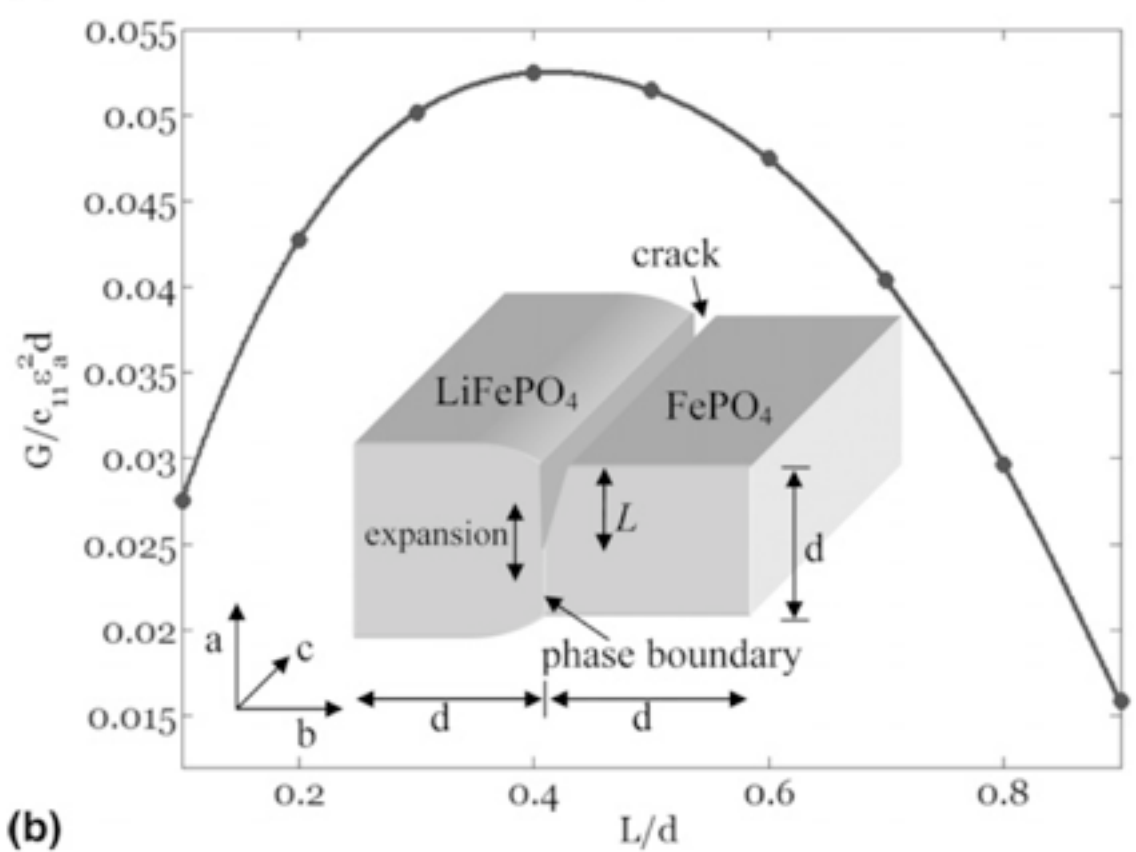
(a)

$$\varepsilon_a = 5.03\%$$

$$\varepsilon_b = 3.7\%$$

$$\varepsilon_c = -1.9\%$$





(b)

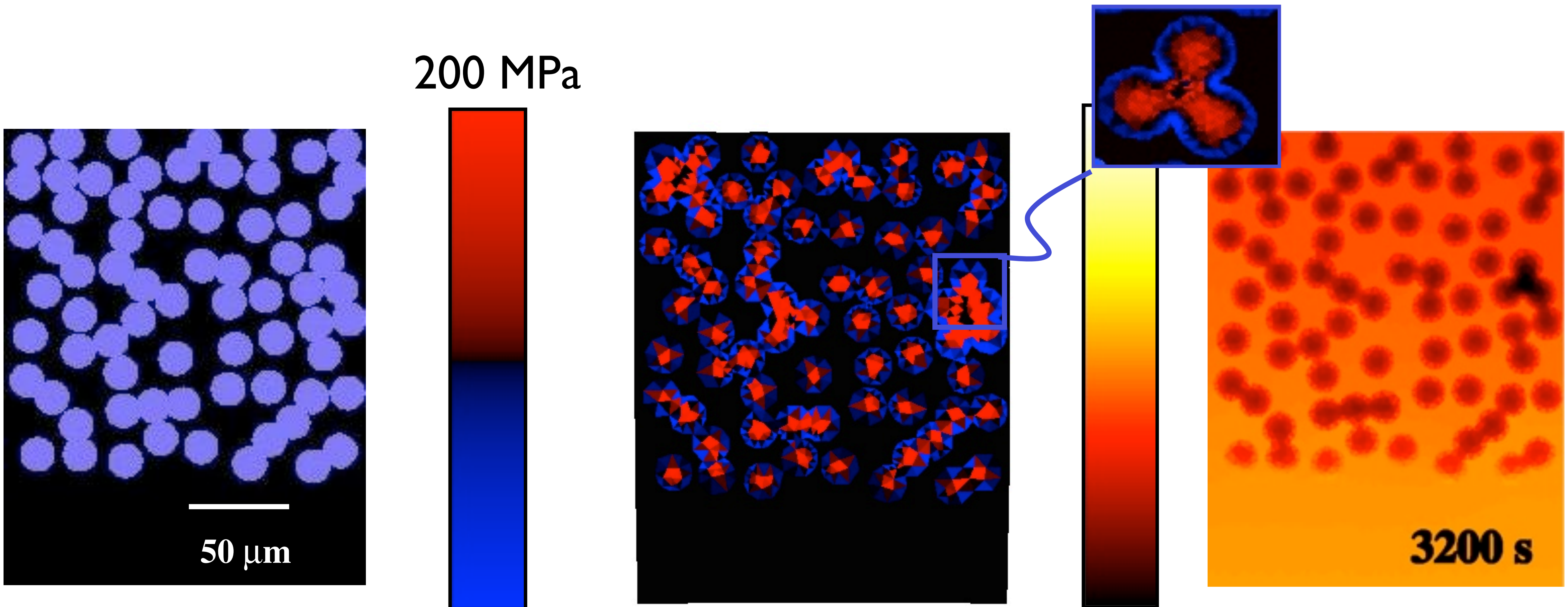
Volumetric Changes in Battery Materials

Delithiated		Lithiated		Volume change	
Chemical Formula	Volume (cm³/Ah)	Chemical Formula	Volume (cm³/Ah)	cm³/Ah	(%)
$Li_{0.45}CoO_2$	1.34	$LiCoO_2$	1.31	–0.03	–2.0
$Li_{0.30}NiO_2$	1.05	$LiNiO_2$	1.09	0.04	3.2
$FePO_4$	1.53	$LiFePO_4$	1.64	0.11	6.5
Mn_2O_4	1.46	$LiMn_2O_4$	1.57	0.11	7.3
$Li_4Ti_5O_{12}$	1.64	$Li_7Ti_5O_{12}$	1.64	0.00	0.0
C (graphite)	1.19	LiC_6	1.34	0.15	11.6

Lithium-storage compound	Limiting composition	Volume strain DV/V_0	Linear strain [a] DL/L_0	Potential vs. Li/Li^+
Li-extraction				
$LiCoO_2$	$Li_{0.5}CoO_2$	+1.9 %	+0.6 %	4.0 V
$LiFePO_4$	$FePO_4$	–6.5 %	–2.2 %	3.4 V
$LiMn_2O_4$	Mn_2O_4	–7.3 %	–2.5 %	4.0 V
$LiNiO_2$	$Li_{0.3}NiO_2$	–2.8 %	–0.9 %	3.8 V
Li-insertion				
C (graphite)	1/6 LiC_6	+13.1 %	+4.2 %	0.1 V
$Li_4Ti_5O_{12}$	$Li_7Ti_5O_{12}$	0.0 %	0.0 %	1.5 V
Si	$Li_{4.4}Si$	+311 %	+60 %	0.3 V
b-Sn	$Li_{4.4}Sn$	+260 %	+53 %	0.4 V

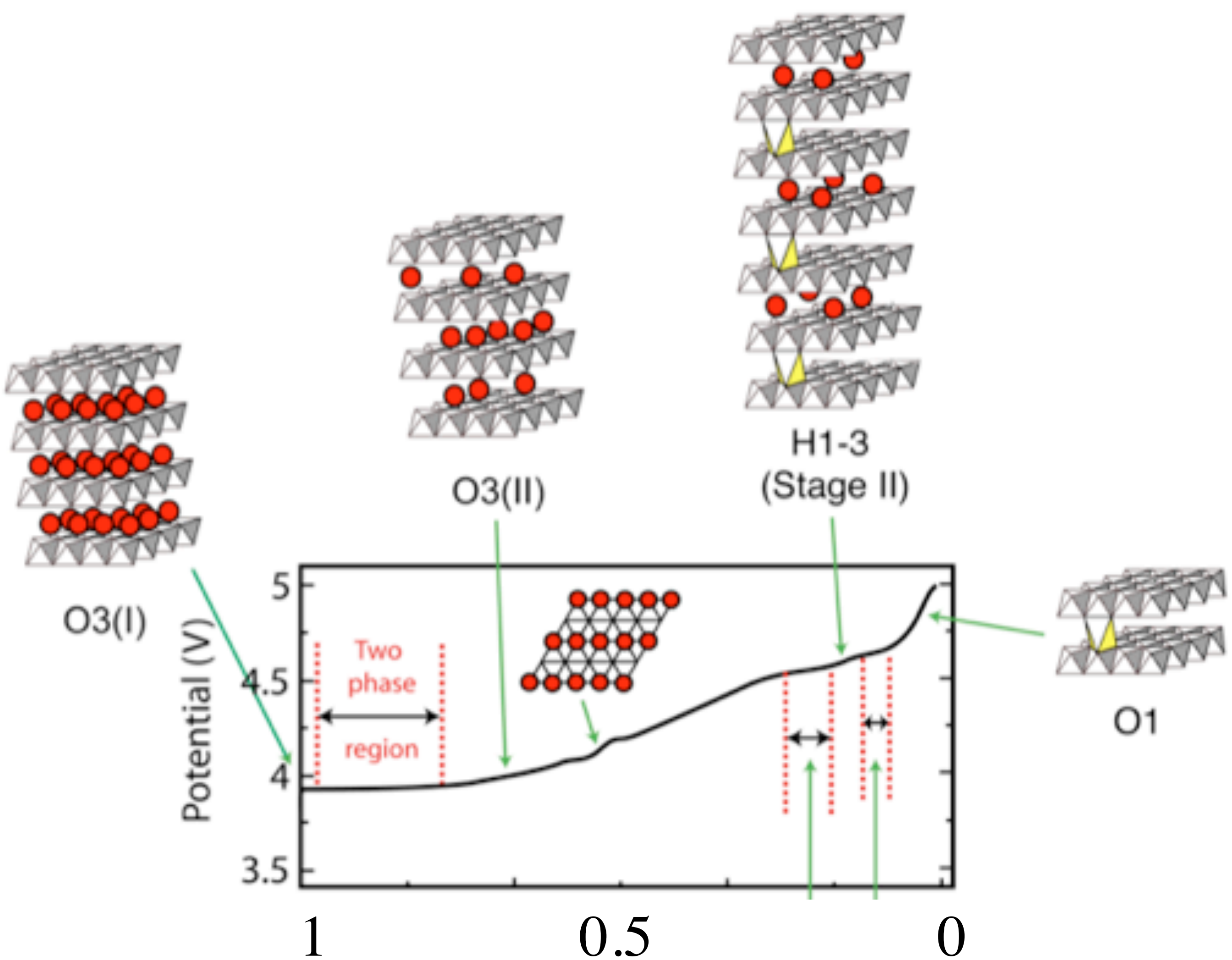
[a] Assuming isotropic expansion/contraction.

Galvanostatic Discharge Stresses

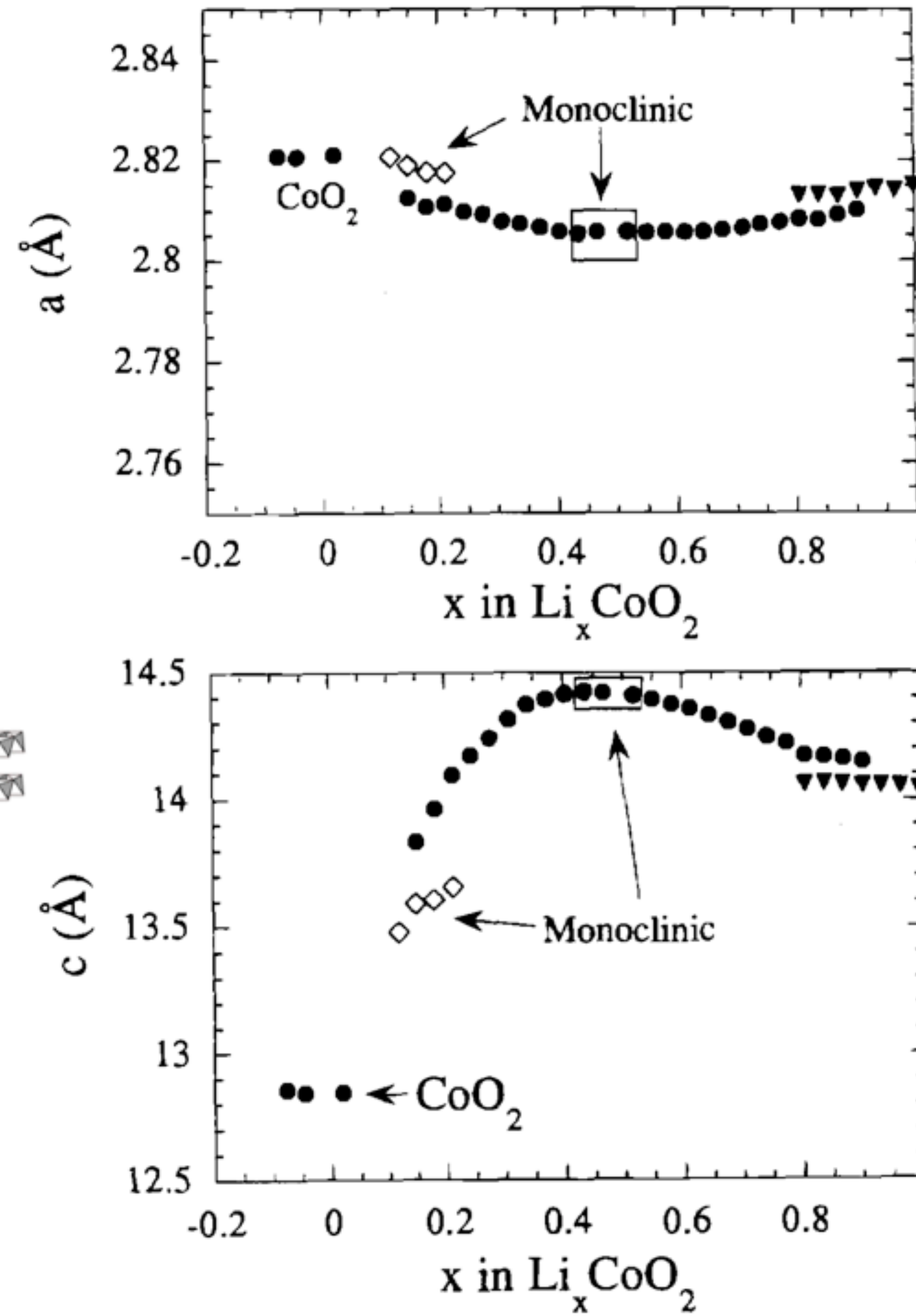


cathode microstructure 200 MPa hydrostatic stresses 0.9 lithium concentration

$LiCoO_2$

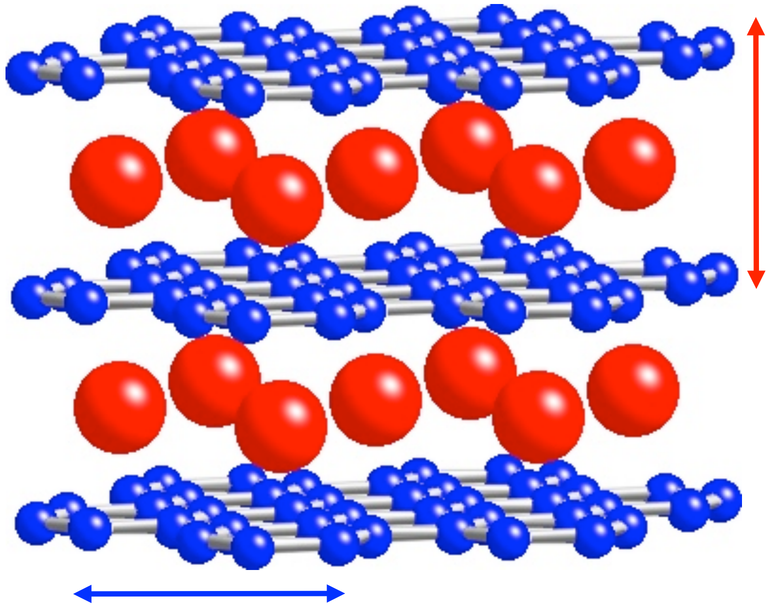


O3(I)
O3(II)
H1-3
(Stage II)
O1
Potential (V)
5
4.5
4
3.5
Two
phase
region
1
0.5
0



a (Å)
2.84
2.82
2.8
2.78
2.76
Monoclinic
CoO2
-0.2
0
0.2
0.4
0.6
0.8
1
x in LixCoO2
c (Å)
14.5
14
13.5
13
12.5
Monoclinic
CoO2
-0.2
0
0.2
0.4
0.6
0.8
1
x in LixCoO2

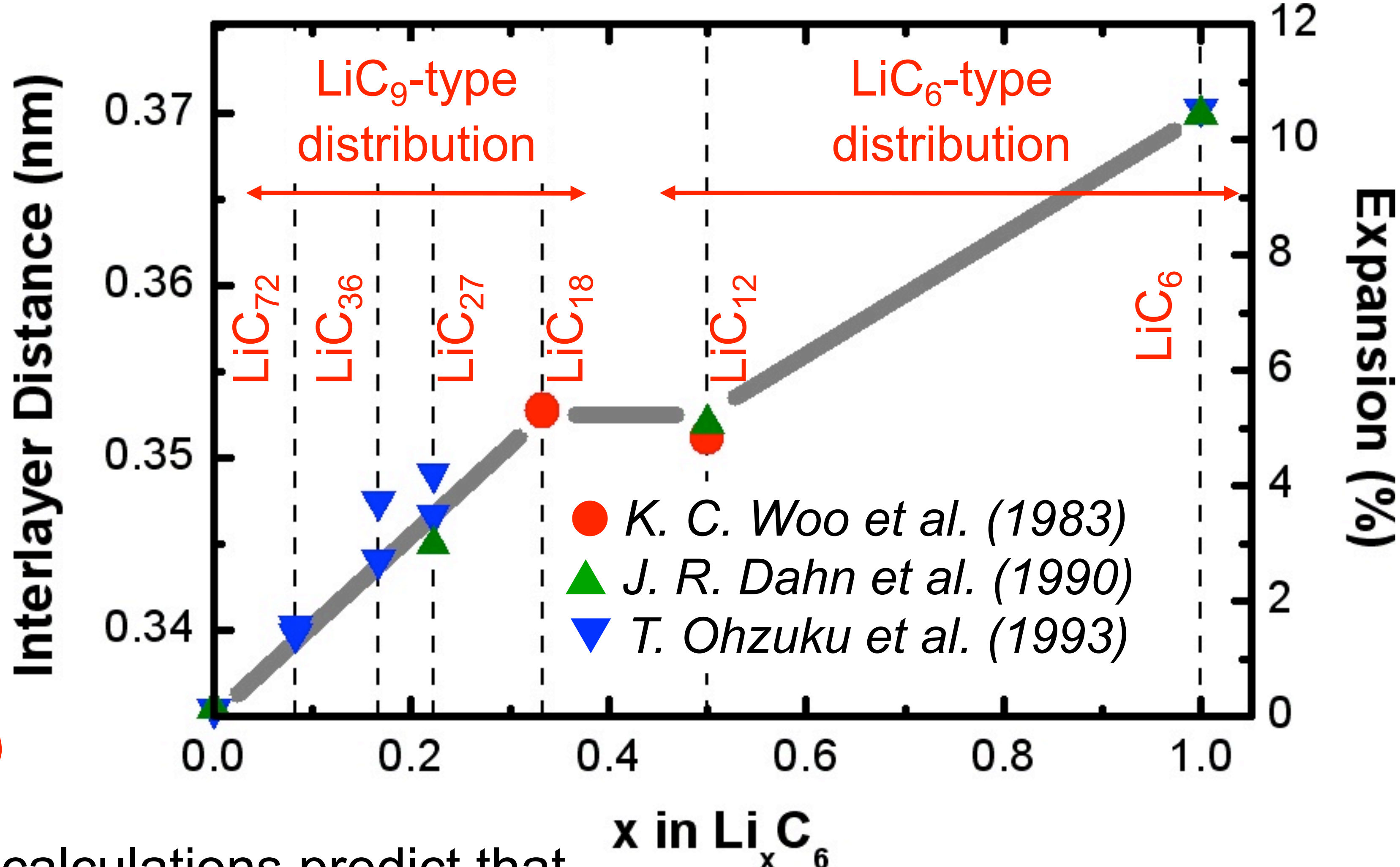
Lithium Graphite Intercalation Compounds



Through-layer
Expansion +10.4%
Modulus 34 - 37 GPa

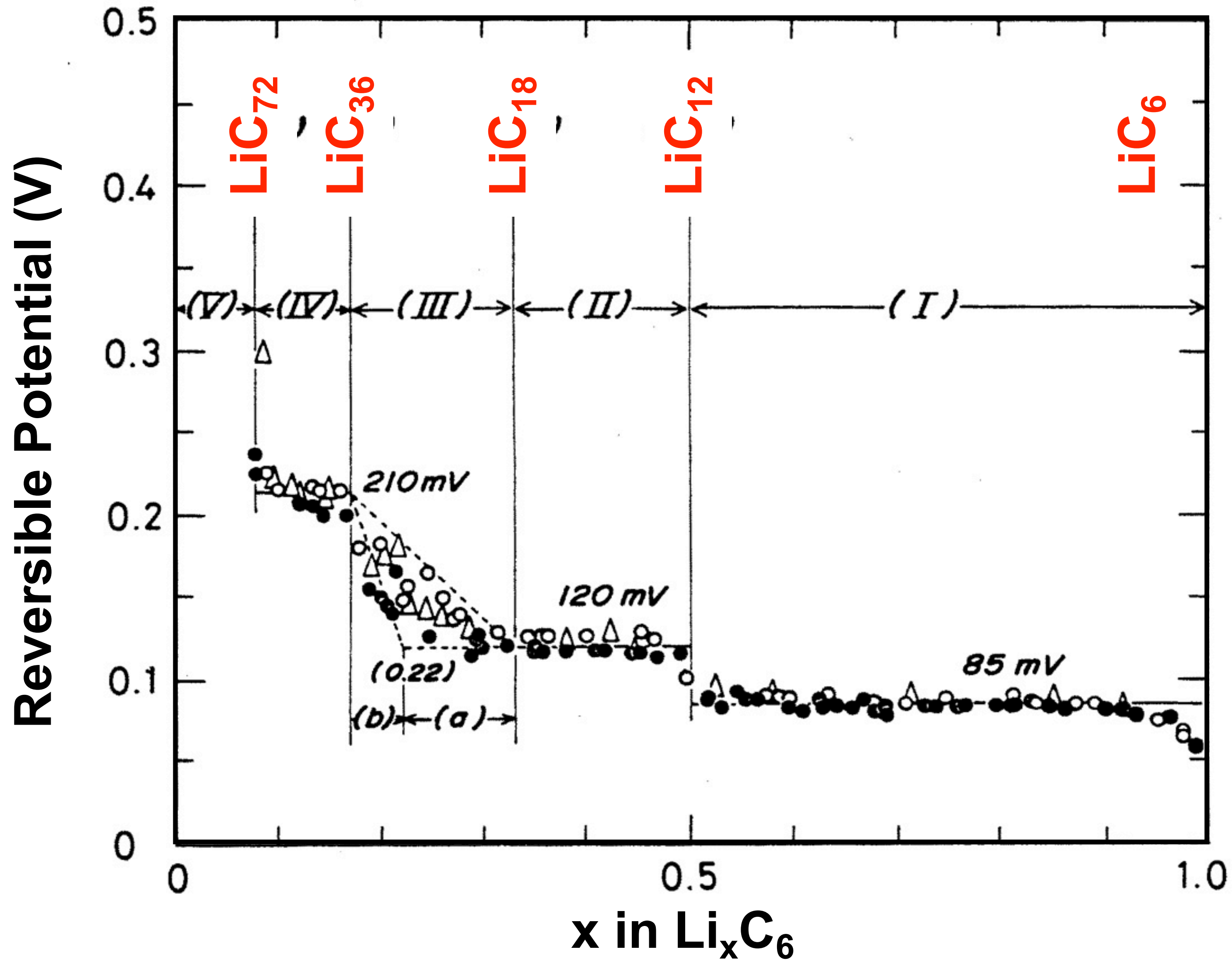
In-layer
Expansion +1.2%
Modulus >1,000 GPa

Low density (2.27 g/cm³)
Low voltage (0.1 - 0.2 V vs. Li)



First-principles calculations predict that
Li intercalation increases through-layer modulus by 60 - 80%
K. R. Kganyago and P. E. Ngoepe, Phys. Rev. B, 68, 205111 (2003)

Electrochemical Properties of Li-GIC



T. Ohzuku et al., J. Electrochem. Soc., 140, 2490 (1993)

- Low potential versus Li-metal (0.1 - 0.2 V)
- Electrically controllable compositions (amounts of ions stored)

Overall System Expansion/Contraction

Electrochemical charging reaction for cell	Cell voltage	Net volume change	Net linear change [a]
$LiCoO_2 + 3C \rightarrow Li_{0.5}CoO_2 + 0.5LiC_6$	3.9 V	+6.9 %	+2.2 %
$LiFePO_4 + 6C \rightarrow FePO_4 + LiC_6$	3.3 V	+1.7 %	+0.5 %
$LiMn_2O_4 + 6C \rightarrow Mn_2O_4 + LiC_6$	3.9 V	+1.4 %	+0.4 %
$LiNiO_2 + 4.2C \rightarrow Li_{0.3}NiO_2 + 0.7LiC_6$	3.7 V	+5.5 %	+1.7 %
$LiCoO_2 + 1/6\ Li_4Ti_5O_{12} \rightarrow Li_{0.5}CoO_2 + 1/6\ Li_7Ti_5O_{12}$	2.5 V	+0.9 %	+0.3 %
$LiFePO_4 + 1/3\ Li_4Ti_5O_{12} \rightarrow FePO_4 + 1/3\ Li_7Ti_5O_{12}$	1.9 V	–3.3 %	–1.1 %
$LiMn_2O_4 + 1/3\ Li_4Ti_5O_{12} \rightarrow Mn_2O_4 + 1/3\ Li_7Ti_5O_{12}$	2.5 V	–3.6 %	–1.2 %
$Li_7Ti_5O_{12} + 18C \rightarrow Li_4Ti_5O_{12} + 3LiC_6$	1.4 V	+5.5 %	+1.8 %

[a] Assuming isotropic expansion/contraction.