Investigations of Energy Interfaces and Interphases With Spatially-resolved Tools

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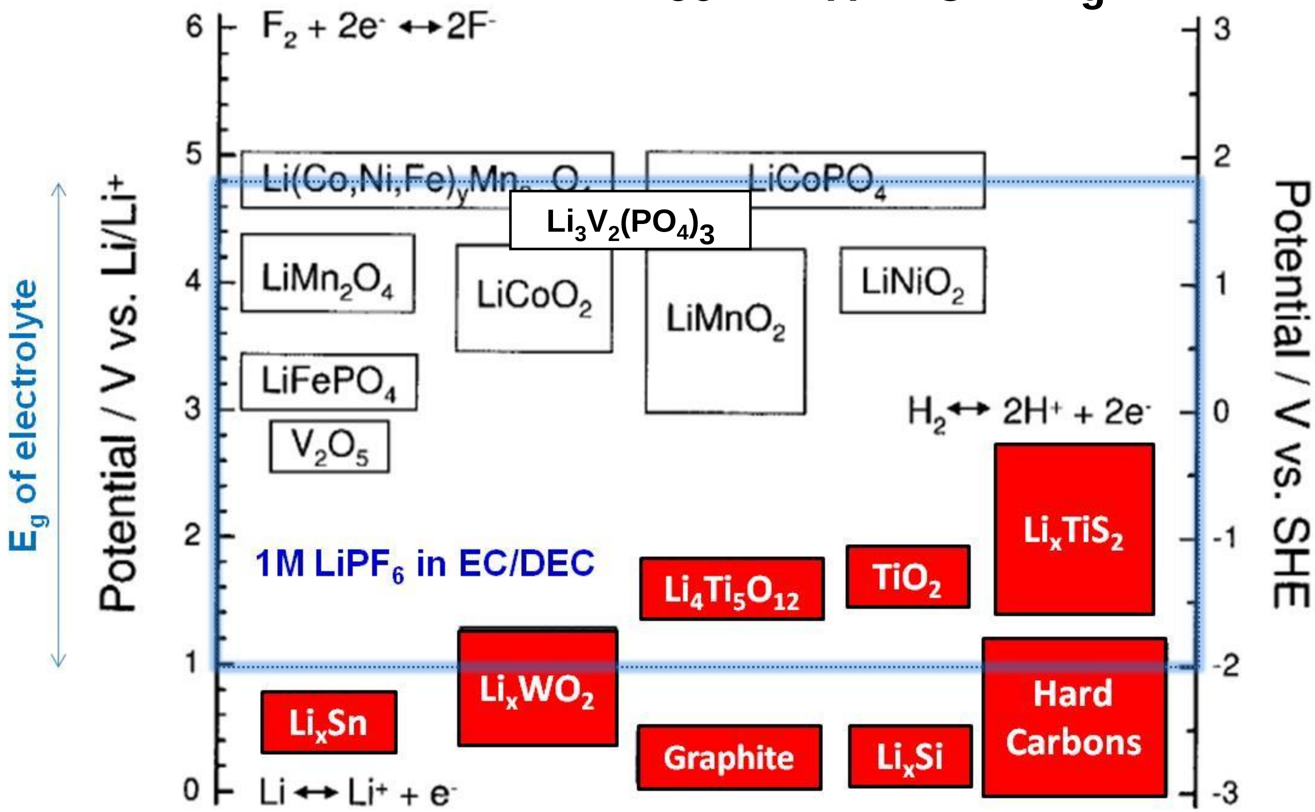
September 17, 2017

Challenges for Energy Storage

$eV_{oc} < \mu_A - \mu_C < E_g$



Energy Density
Power Density
Stability
Electrolytes
Safety
Cost

Energy = Capacity (Q) x Voltage (V) — **How FAR on one charge**

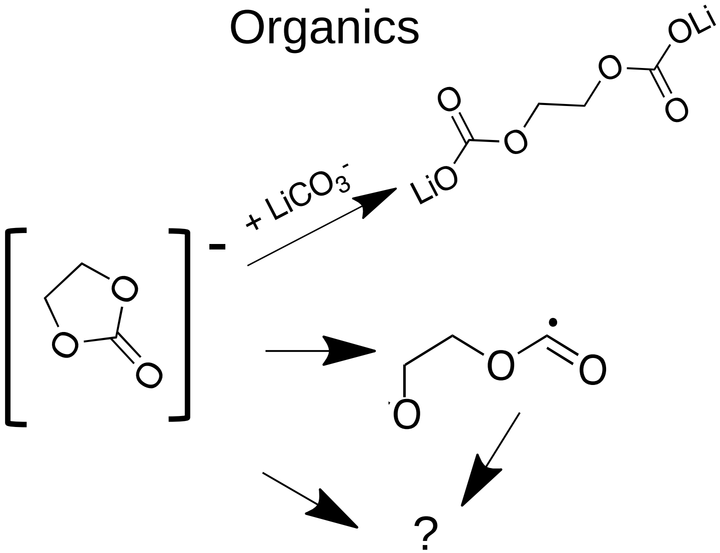
Power = Current (A) x Voltage (V) — **How FAST on one charge**

Goodenough and Kim *Chem. Mater.* **2010**, *22* (3), 587.

Challenges for Energy Storage

SEI layer formation at interface.

Organics



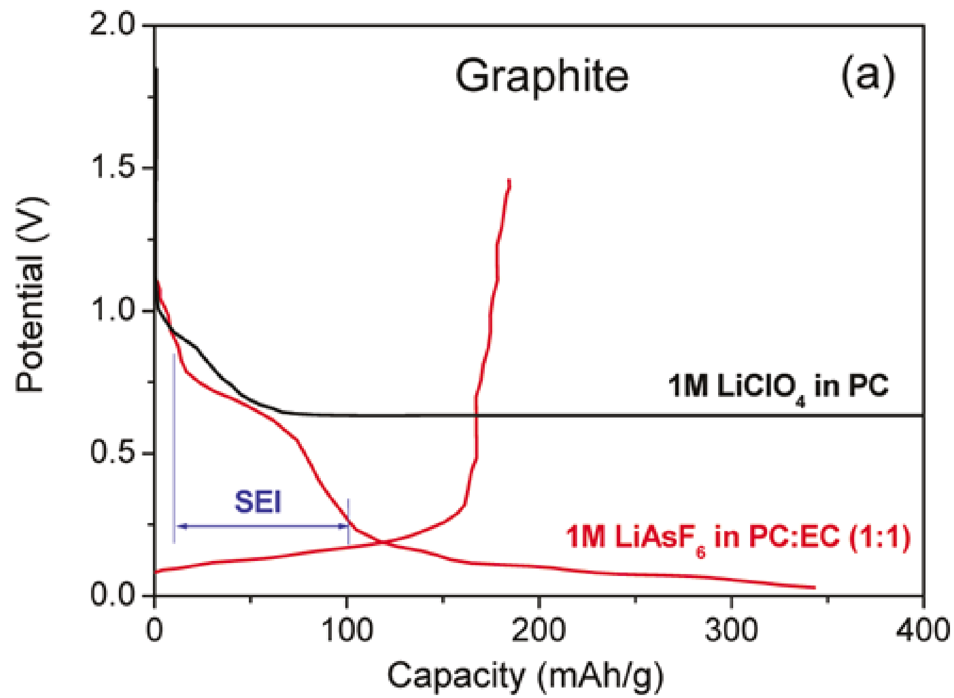
Inorganics

$$LiPF_{6(sol.)} \xrightarrow{\Delta} LiF_{(insol.)} + PF_{5(gas)}$$

SEI is both beneficial and detrimental

Surface reactivity changes dramatically with
Composition, particle size, potential

Complex amorphous mixtures form:
Active and/or passive towards e- and Li+



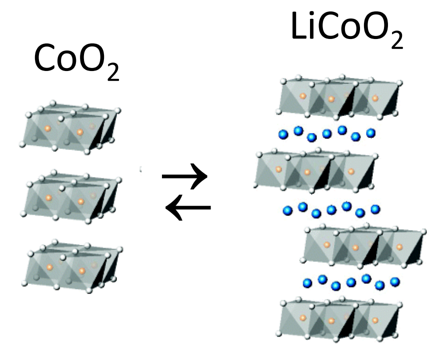
Goodenough and Kim *Chem. Mater.* **2010**, *22* (3), 587.

Basic Charge Storage Mechanisms

Insertion/intercalation reactions

$$MO_n + x\,Li^+ + x\,e^- \rightleftarrows Li_xMO_n$$

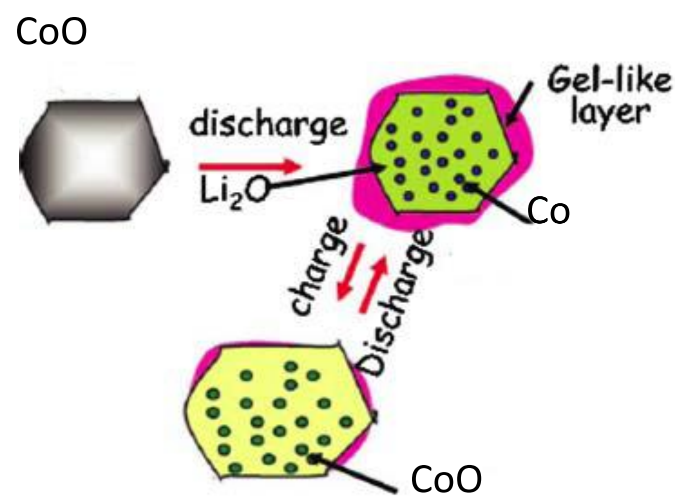
Ex: $Co^{4+}O_2 + x\,Li^+ + x\,e^- \rightleftarrows Li_xCo^{4+}{}_{1-x}Co^{3+}{}_xO_2$



Conversion/displacement reactions

$$M^{2n+}O_n + 2n\,Li^+ + 2n\,e^- \rightleftarrows M^0 + n\,Li_2O$$

Ex: $Co^{2+}O + 2\,Li^+ + 2\,e^- \rightleftarrows Co^0 + Li_2O$

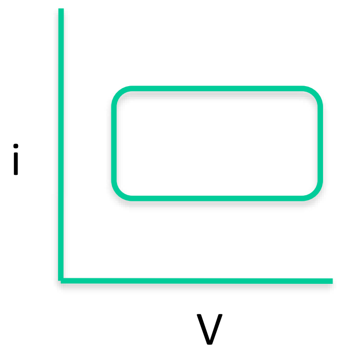
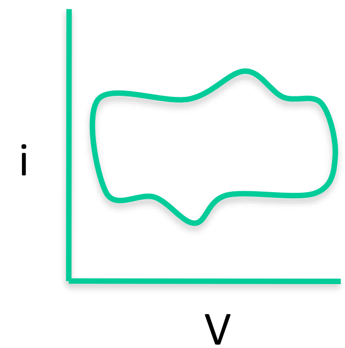
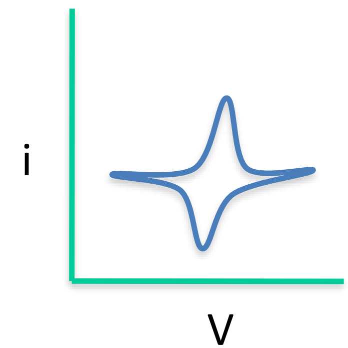
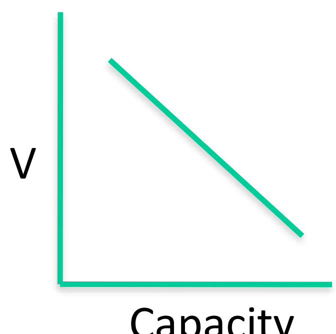
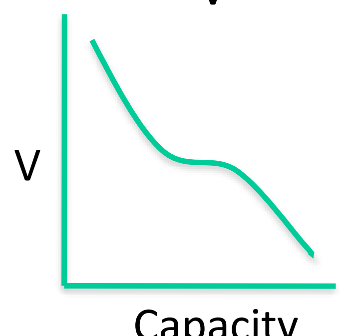
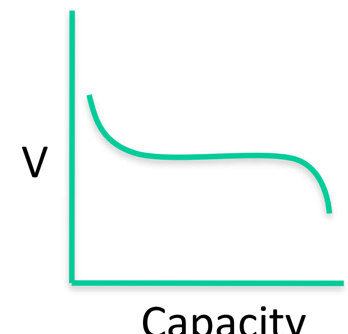


Several Factors Influence Mechanistic Pathways

Morphology, Shape, Size, Defect chemistry, Phase Stability, Crystallinity

Charge separation and transfer processes not fully understood!

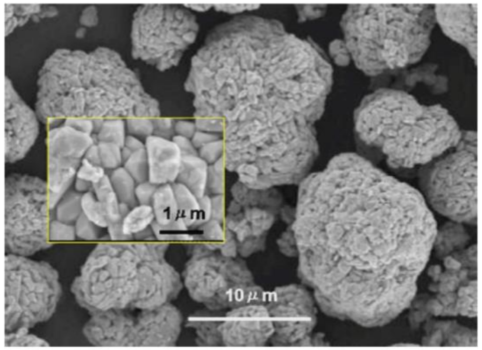
Charge Storage Processes

	Capacitor	*Pseudocapacitor (Batt-Cap)*	*Battery*
Current-scan rate relationship	$i = \frac{dV}{dt} * C_{dl} * A = \nu * C_{dl} * A$	$i = \frac{dV}{dt} * C_{\Phi} = \nu * C_{\Phi}$ + $i = 0.4958 \mathrm{nFAc} \left(\frac{\mathrm{D} \alpha \mathrm{nF} \nu}{\mathrm{RT}} \right)^{1/2}$	$i = 0.4958 \mathrm{nFAc} \left(\frac{\mathrm{D} \alpha \mathrm{nF} \nu}{\mathrm{RT}} \right)^{1/2}$
Informal definition	Surface double layer capacitance (non-Faradaic process)	Surface charge transfer (Faradaic process)	Diffusion controlled charge transfer (Faradaic process)
Cyclic voltammetry			
Galvanostatic discharge			

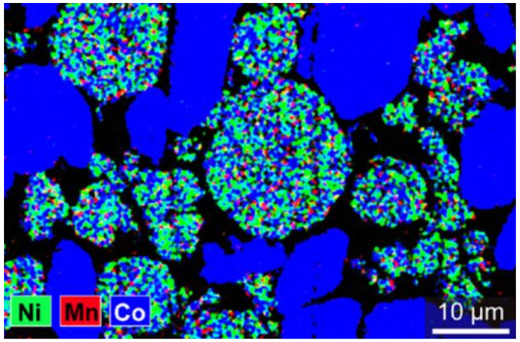
Typical Electrode Materials

Chemically Complex

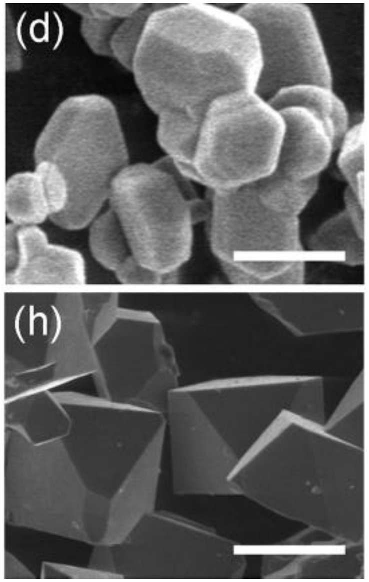
Li($Co_{1/3}Ni_{1/3}Mn_{1/3}$)O_2 Particles[1]



$LiCoO_2$/Li($Co_{1/3}Ni_{1/3}Mn_{1/3}$)O_2 Composite Electrode[2]

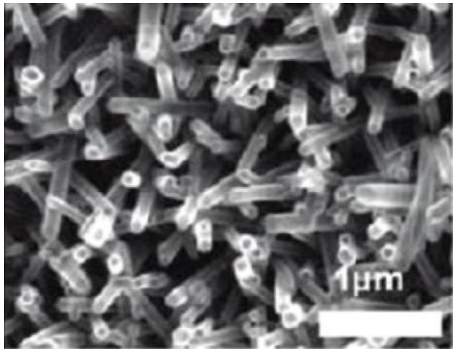


Li($Ni_{0.8}Co_{0.1}Mn_{0.1}$)O_2 Nanoparticles[3]

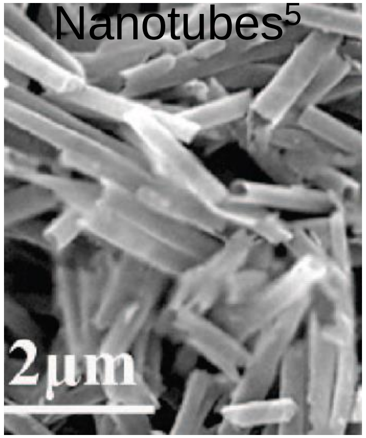


Geometrically Complex

Silicon Nanowires[4]

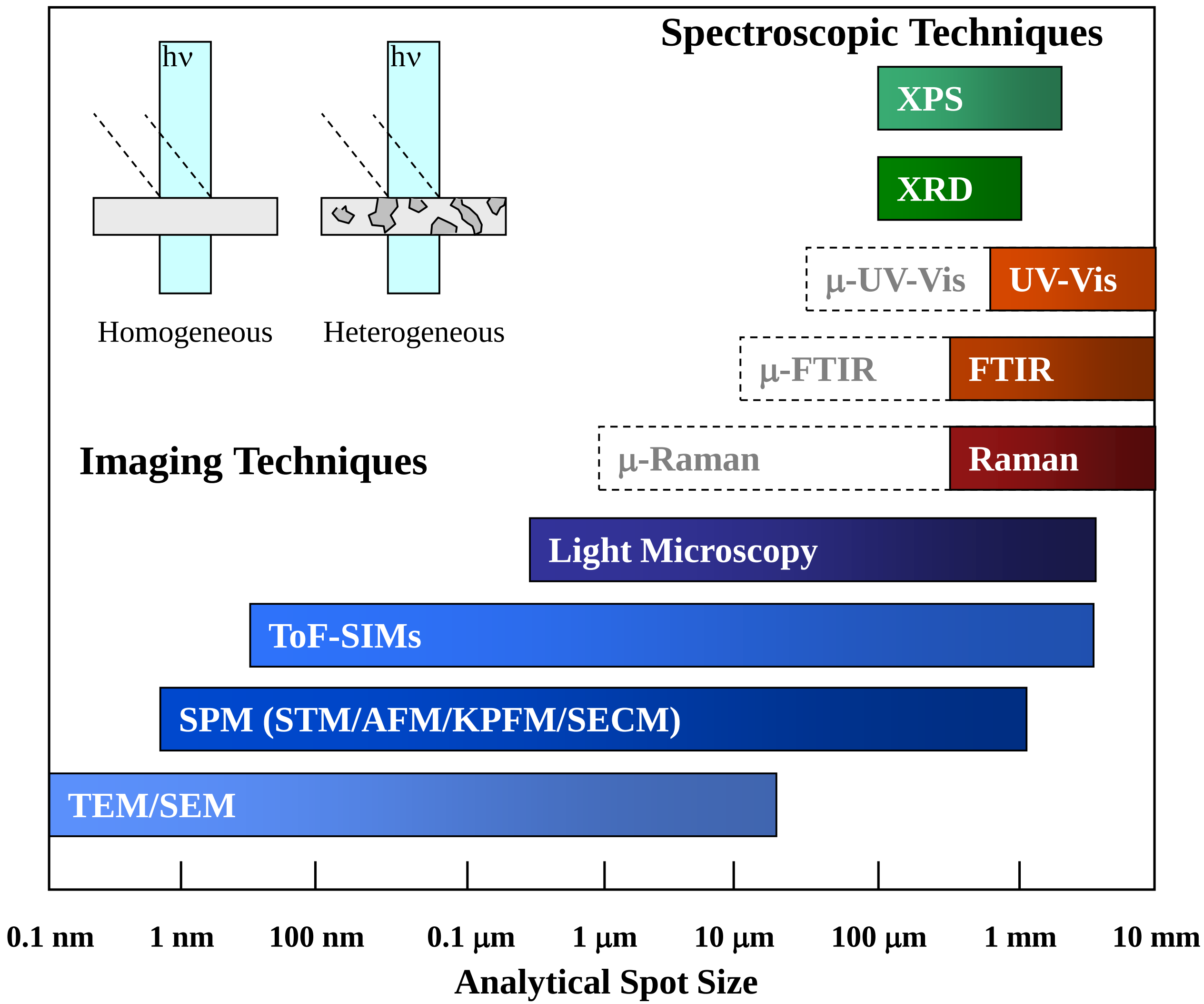


$LiCoO_2$ Nanotubes[5]



1. Yoshizawa, H.; Ohzuku, T. *J. Power Sources* **2007**, *174*, 813.
2. Liu, Z.; et al. *J. Power Sources* **2013**, *227*, 267.
3. Kim, Y. *ACS Appl. Mater. Interfaces* **2012**, *4*, 2329.
4. Song, T.; Hu, L.; Paik, U. *J. Phys. Chem. Lett.* **2014**, *5*, 720.
5. Cheng, F.; Tao, Z.; Liang, J.; Chen, J. *Chem. Mater.* **2008**, *20*, 667.

Materials Challenges In Characterization



Limitations and Biases

Ordered Materials

Homogeneous Materials

Ensemble Averaged

Ex situ Environment

Slow Data Acquisition

Modern Advantages

Localized Interrogation

2D & 3D Mapping

In situ Environment

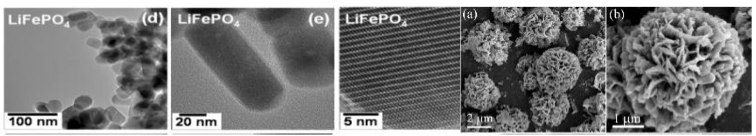
Fast Data Acquisition

Overview of Research Efforts

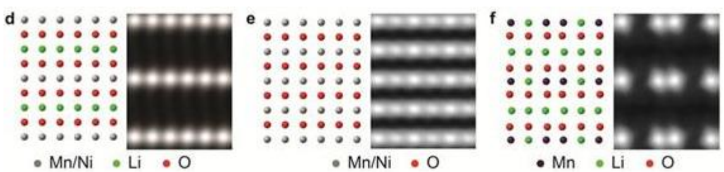
T1: Materials

New Materials & Model Interfaces

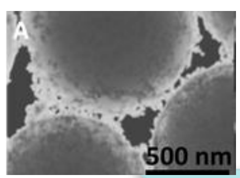
synthesis of model prototypes that climb the ladder of complexity.



surface chemistry & composition affects rate, capacity and stability



particle-particle interactions influence transport



Driven by Synthetic Developments

devices

films

composites

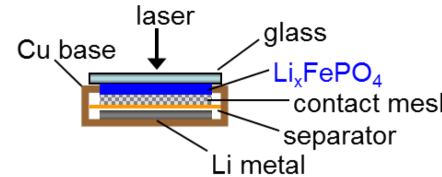
single crystals

model systems

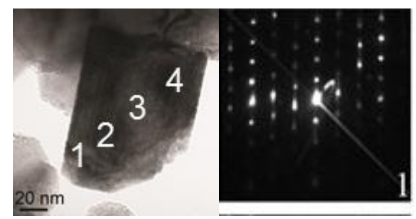
T2: Mechanisms

Ion Coupled Charge Transfer Dynamics

measurement of interfacial mechanisms

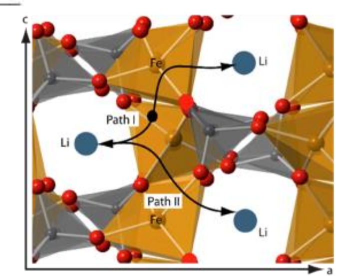


in situ Raman cell setup



direct probes of morphology and phases

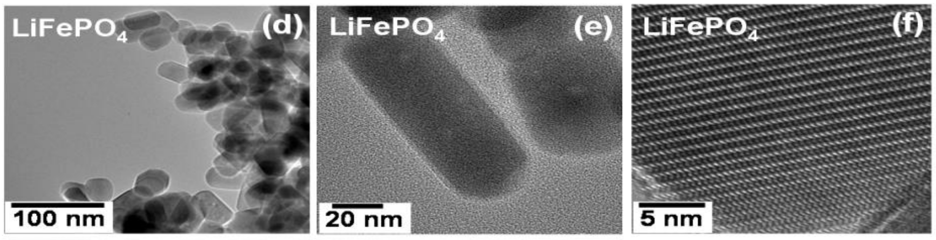
accurate electronic structure, kinetics & thermodynamics



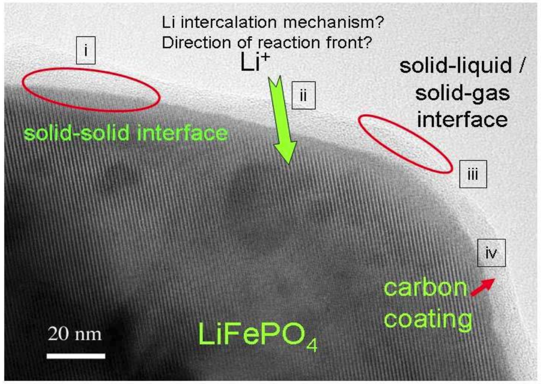
Driven by Characterization & Theory Developments

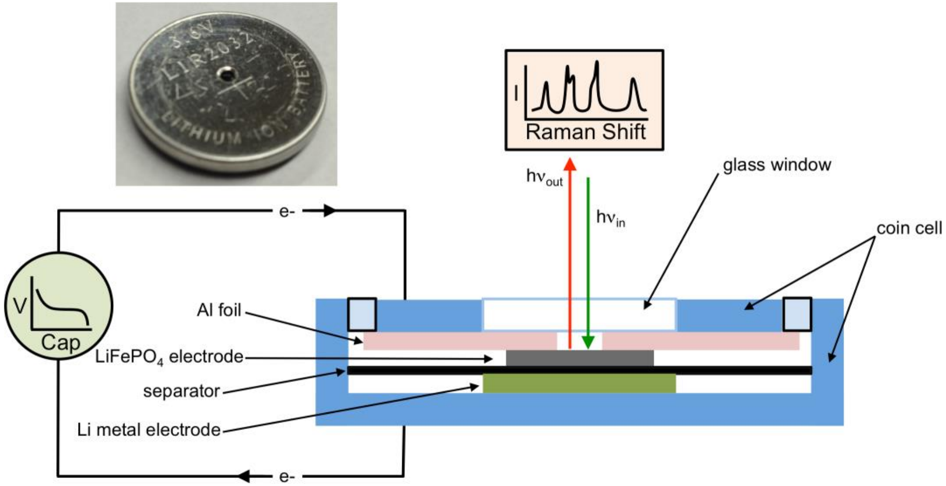
High Resolution Studies of Model Materials

$LiMPO_4$ Size & Composition Library



$LiMPO_4$ Interfaces





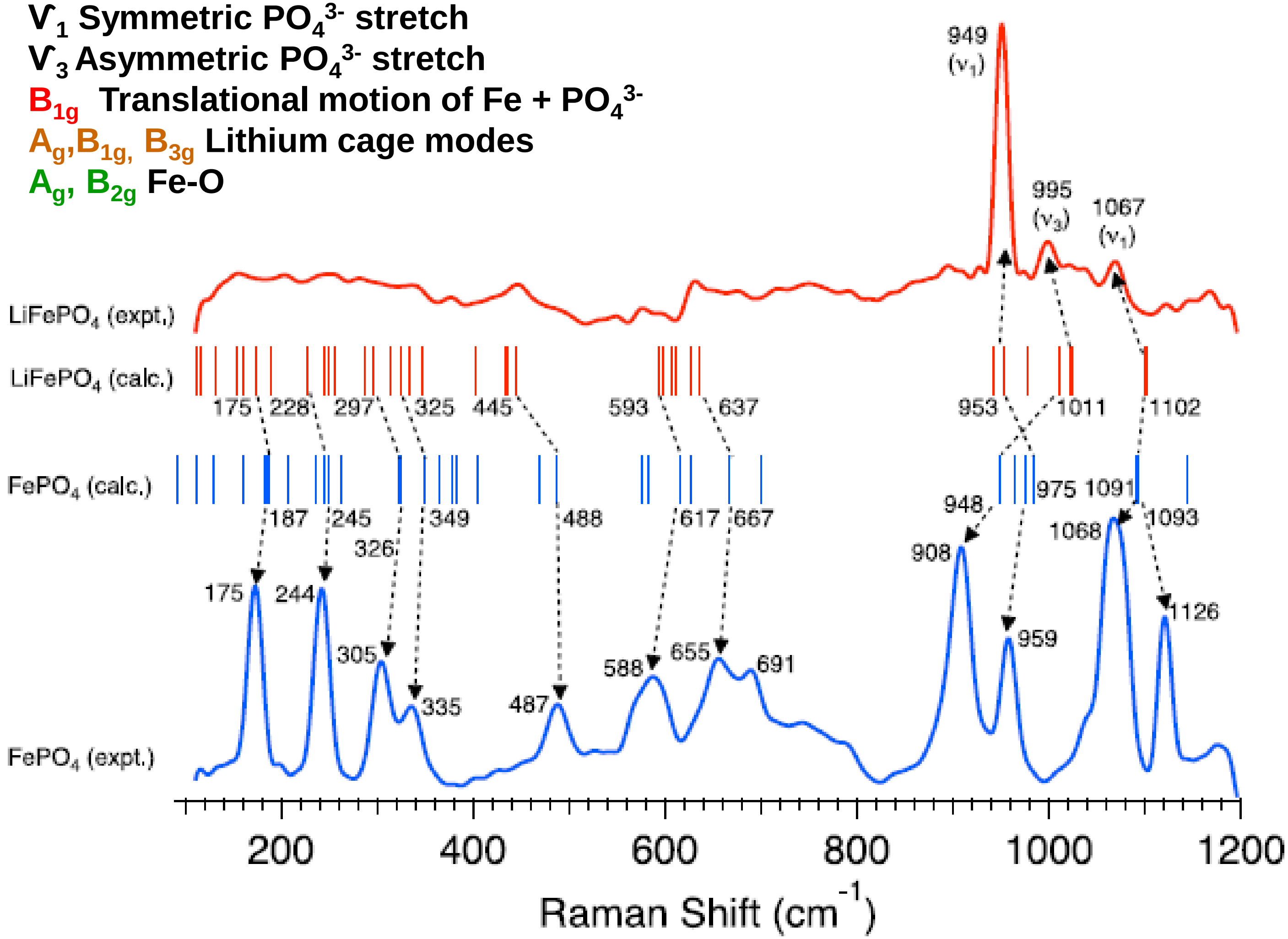
Above: In situ spectroelectrochemical Raman studies Li^+ insertion/deinsertion in olivines.

<u>Studies allow us to understand:</u>

- kinetics and energetics of how size, morphology, and configuration influence Li^+-coupled charge transfer, volume expansion/contraction processes, and phase formation mechanisms
- which factors govern charge transfer rates within and across model nanostructures and interfaces
- theoretical principles underlying all of the above

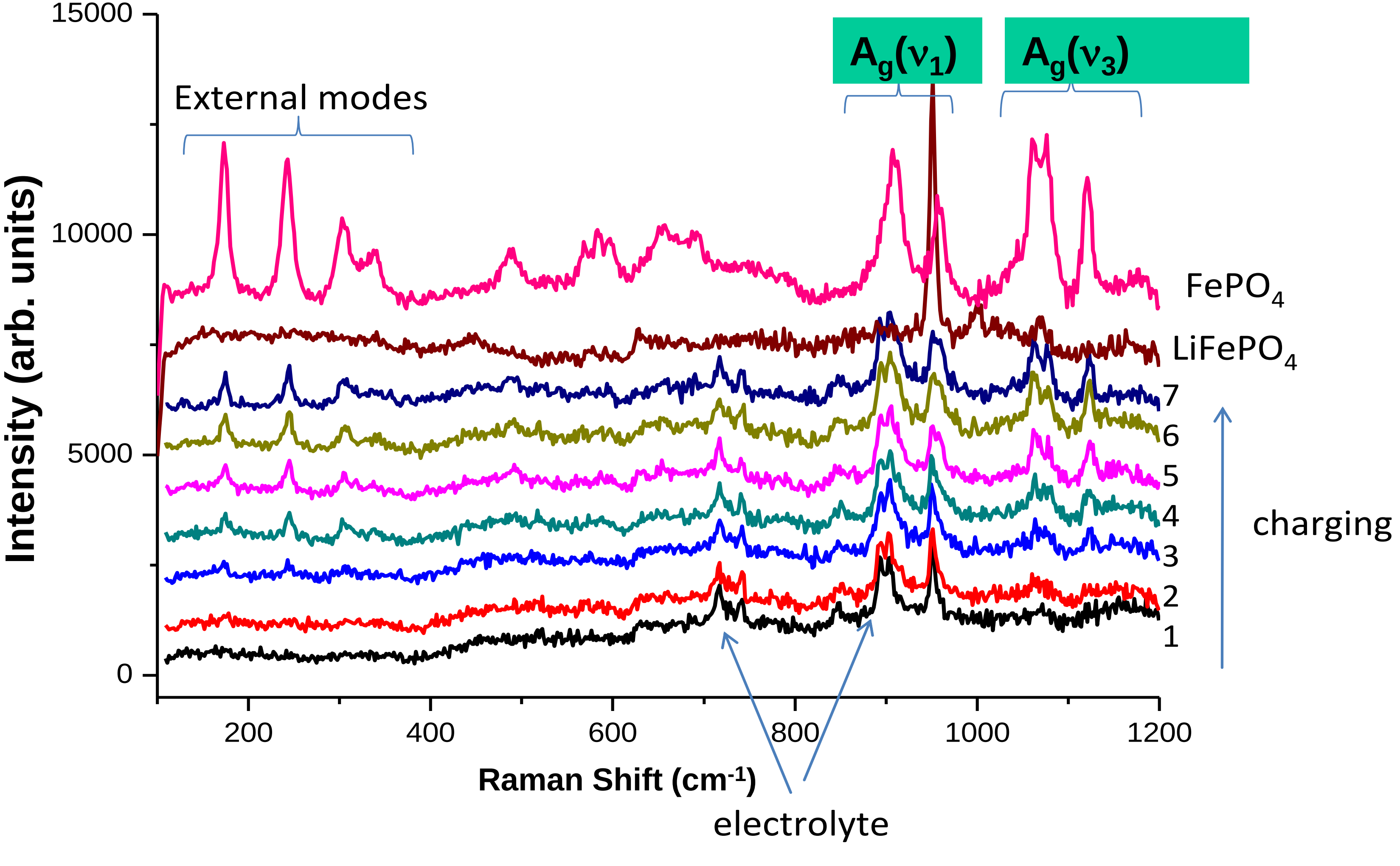
Raman Spectra: Experiment vs. Theory

ν_1 Symmetric PO_4^{3-} stretch
ν_3 Asymmetric PO_4^{3-} stretch
B_{1g} Translational motion of Fe + PO_4^{3-}
A_g, B_{1g}, B_{3g} Lithium cage modes
A_g, B_{2g} Fe-O



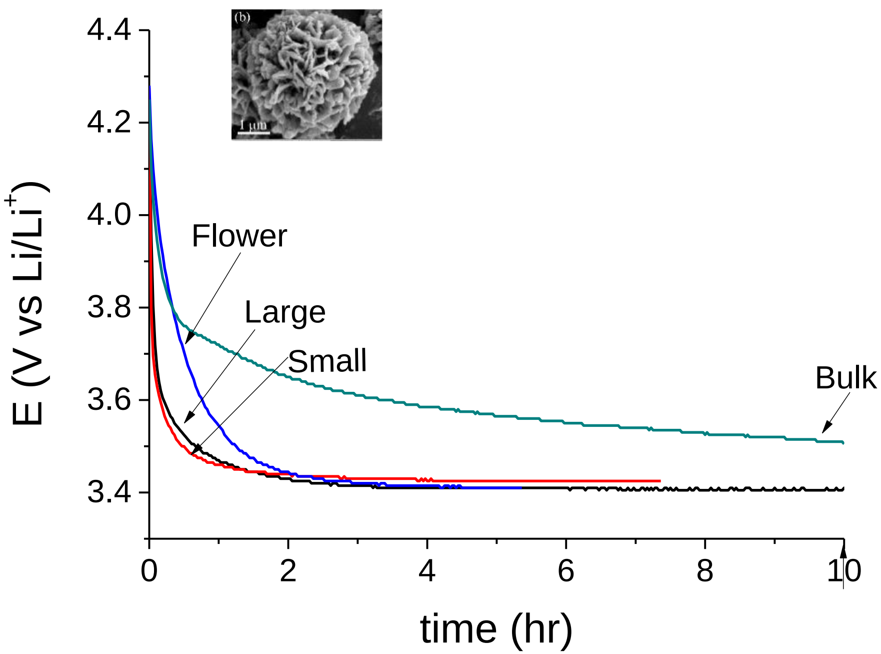
J. Wu et al. *Nanotechnology* **2013,** *24,* 424009

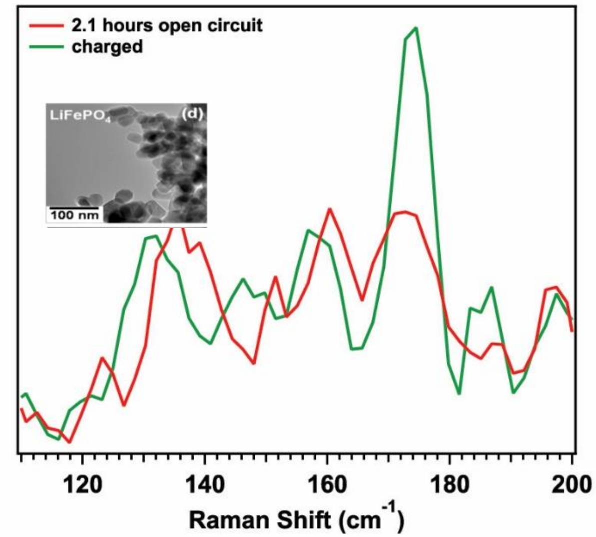
In Situ Raman of Lithium Insertion

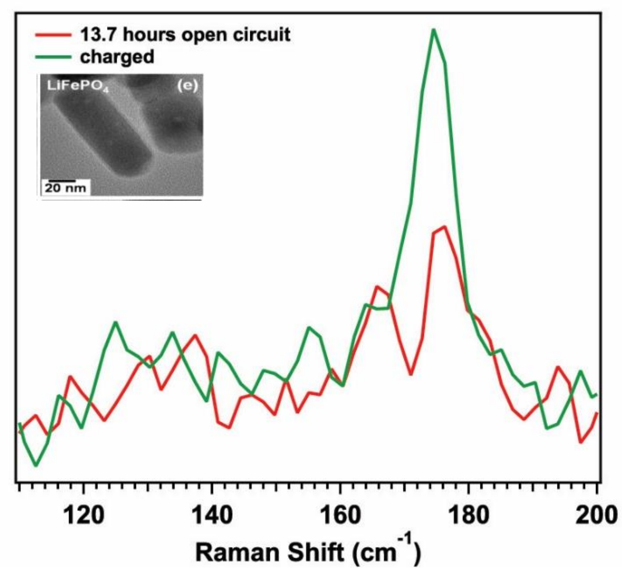


J. Wu et al. *Nanotechnology* **2013,** *24***,** 424009

In Situ Raman of Self-Discharge of $FePO_4$



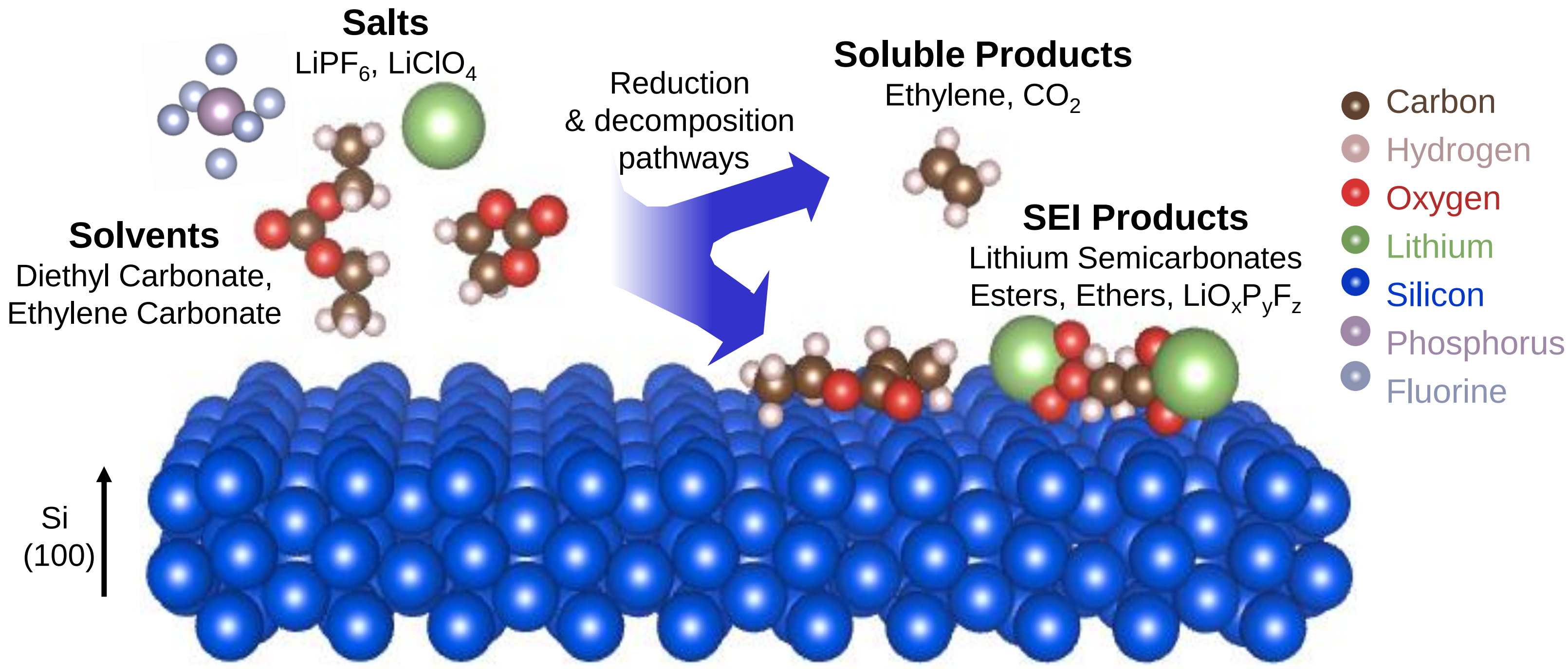




Sample	Self-Discharge Time
Small (30 nm W 100 nm L)	2 hr
Large (230 W nm 300 nm L)	14 hr
Flower (3 μM porous)	5 hr
Bulk LFP > 1 μM	> 15 hr

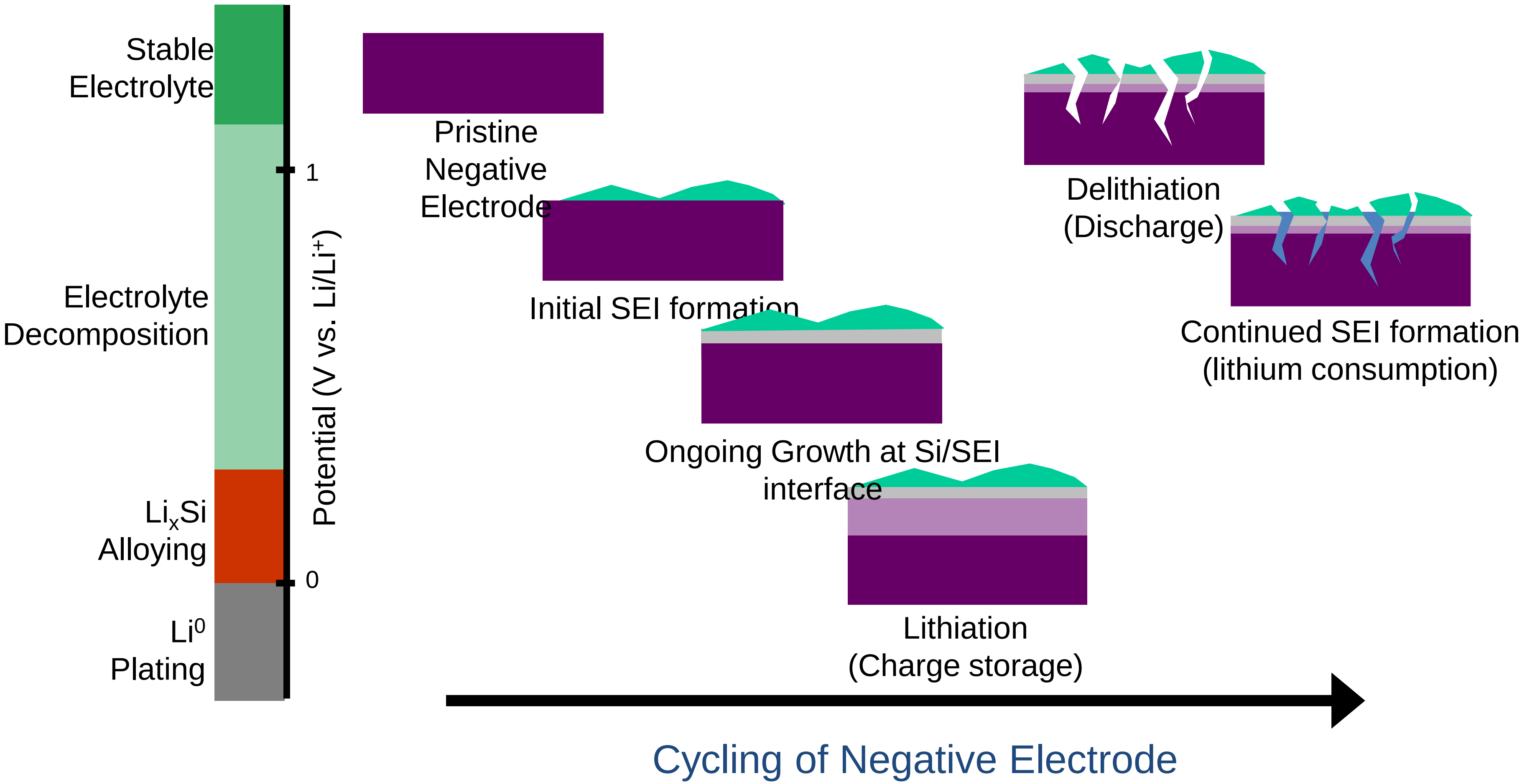
J. Wu et al. *Nanotechnology* **2013,** *24,* 424009

The Solid Electrolyte Interphase on Model Systems



- Model Systems
  - c-Si wafer electrodes, DC-sputtered a-Si, PE-CVD a-Si, Nano a-Si
- Accurate Analytical Characterization
  - Kinetically stable compounds – take extra precaution investigating

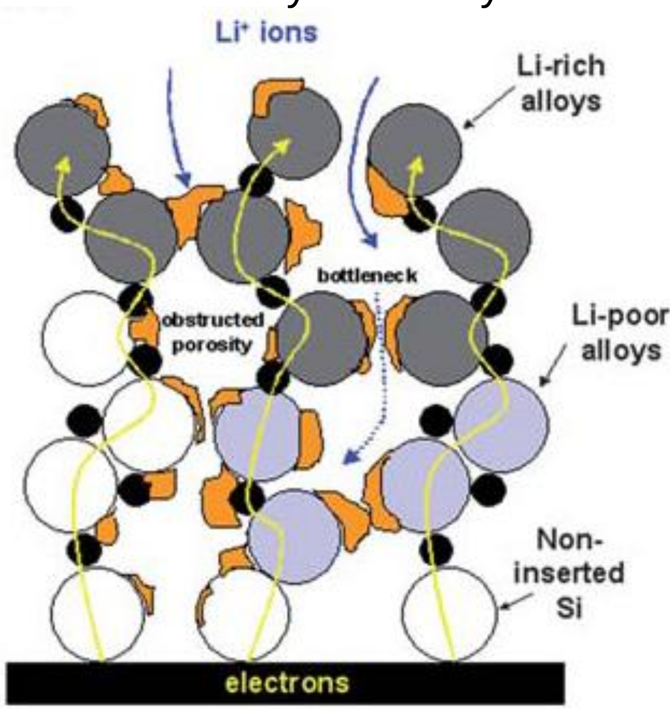
Silicon Electrode Degradation with Cycling



Wang, J. et al., *J. Power Sources* (2011)
Deshpande, R. et al., *J. Electrochem. Soc.* (2012)

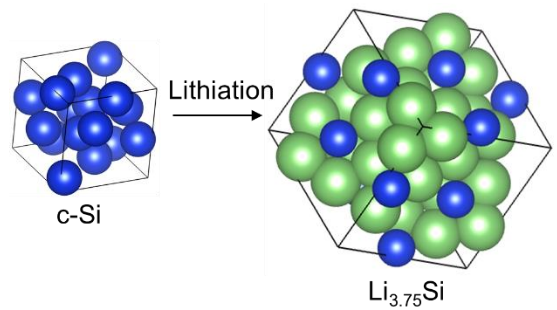
Sources of Li-ion Consumption & Degradation

Electrode Architecture and Porosity/Tortuosity



Y. Oumellal et al *J. Mater. Chem.* (2011)

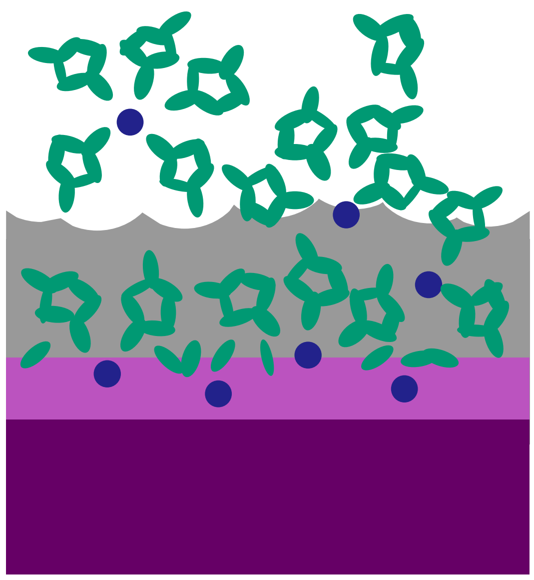
Swelling/Volume Expansion



Cracking

Interfacial Chemistry

- Surface Passivation
- Ion Transport
- Solvation/desolvation barriers

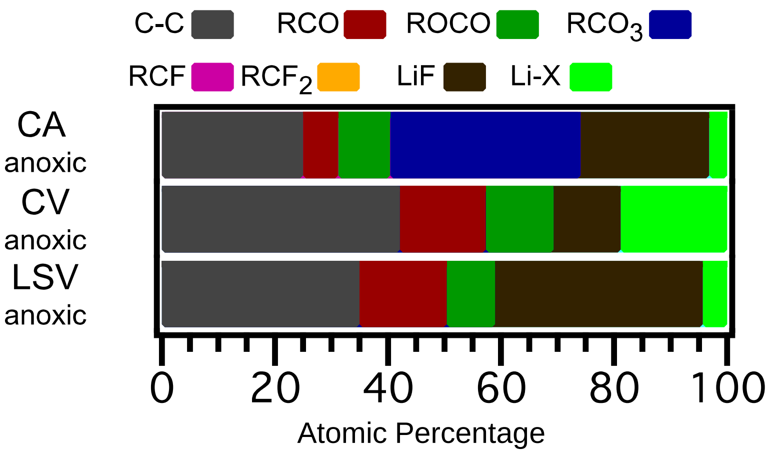


Solvent

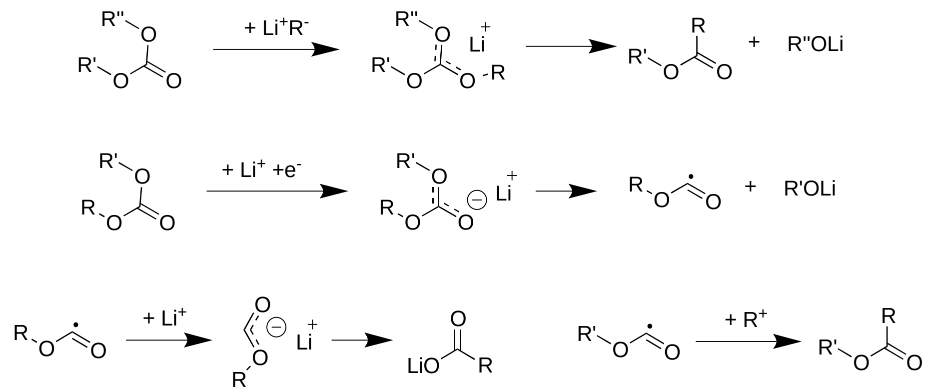
Li^+

SEI Formation Reaction Mechanisms on Si (100)

Composition by Functionality

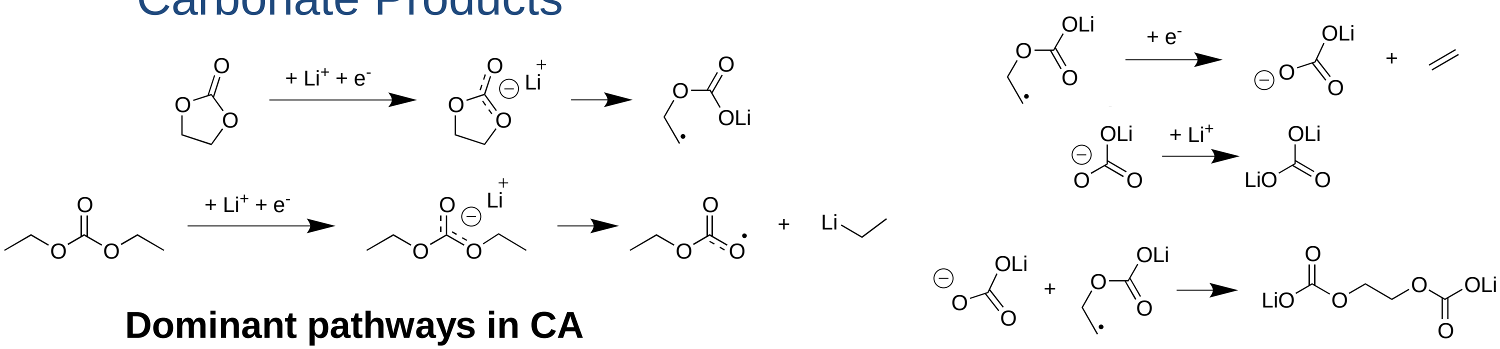


Ester & Ether Products



Dominant pathways in CV and LSV

Carbonate Products

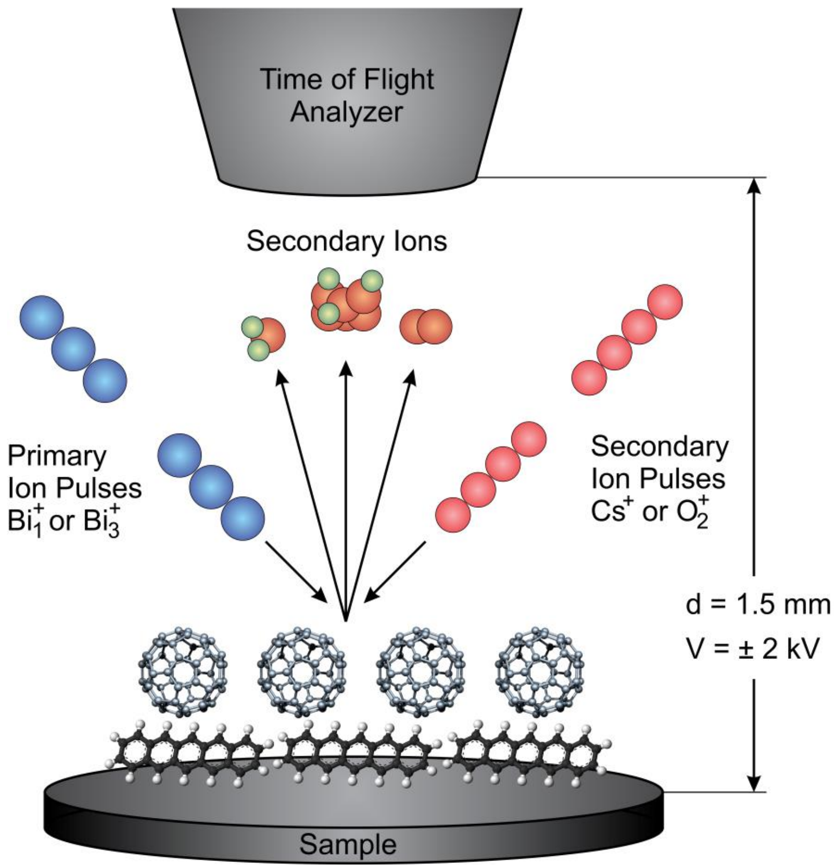


Dominant pathways in CA

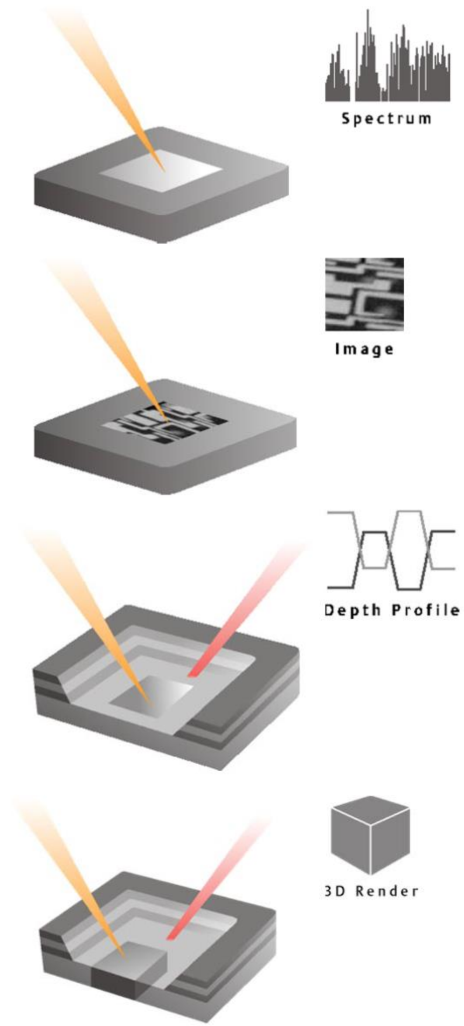
Schroder et al. *J. Phys. Chem. C.*, **2012**, *116*, 19737.

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS)

- The TOF-SIMS Principle



- **Surface Spectroscopy**
  - elemental and molecular
  - ppm sensitivity
  - < 1 nm surface sensitivity
  - > 10000 mass resolution
- **Surface Imaging**
  - lateral resolution < 100 nm
  - parallel mass detection
- **Depth Profiling**
  - depth resolution < 1 nm
  - thin layers 1 nm to > 10 nm
- **3D Analysis**
  - parallel mass detection
  - high lateral resolution
  - high depth resolution

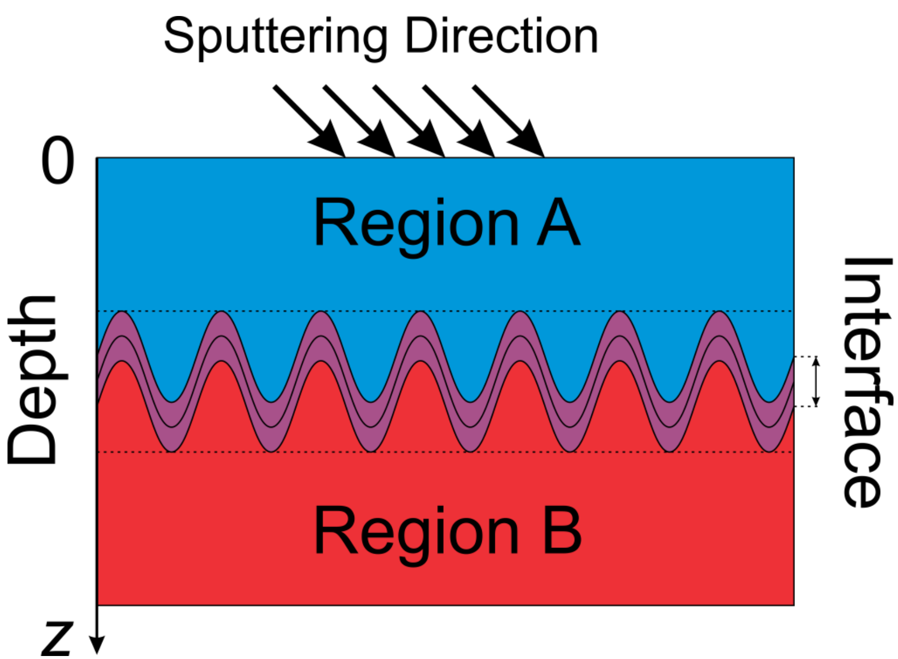


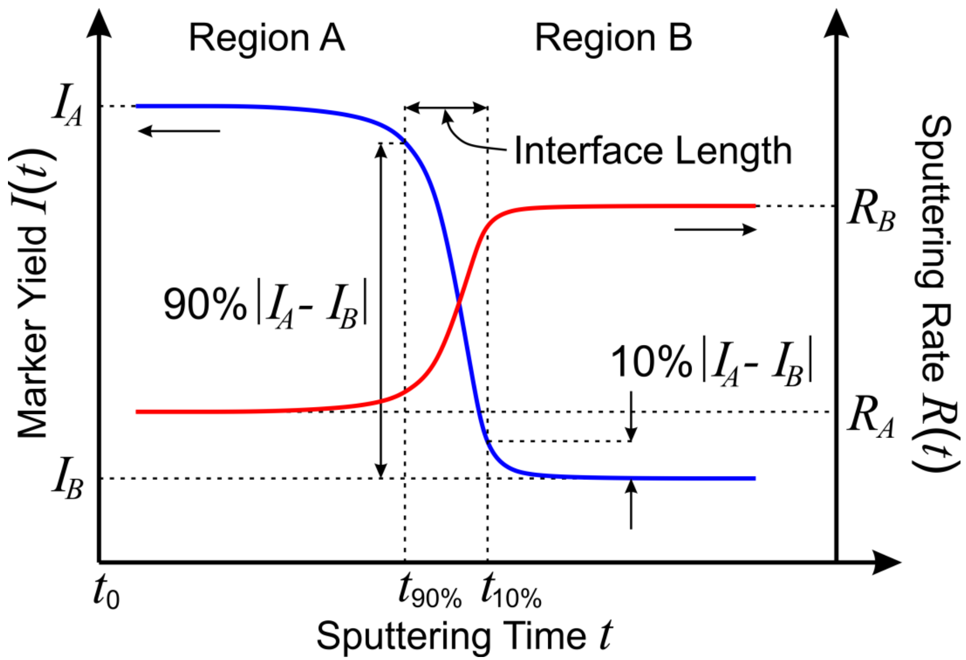
TOF.SIMS[5], ION-TOF GmbH

TOF-SIMS Depth Profiling

- Bilayer interface consists of mixing
- Interface depth profile adds corrugation and sputtering effects

$$R(t) = \left|\frac{I(t) - I_B}{I_A - I_B}\right| R_A + \left|\frac{I(t) - I_A}{I_A - I_B}\right| R_B \longrightarrow z(t) = \int_{t_0}^{t} dt' R(t')$$





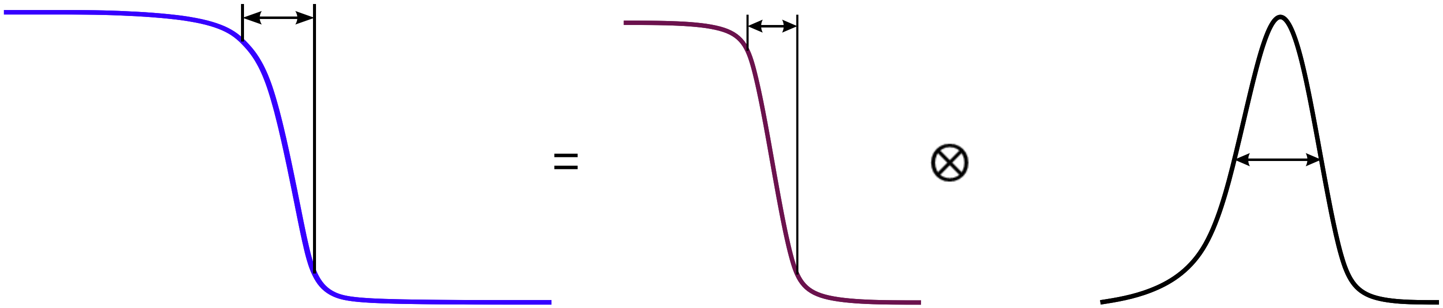
ACS Nano **7 (10)**, 9268 (2013)

TOF-SIMS Depth Profiling

- Mixing-Roughness-Information (MRI) Model

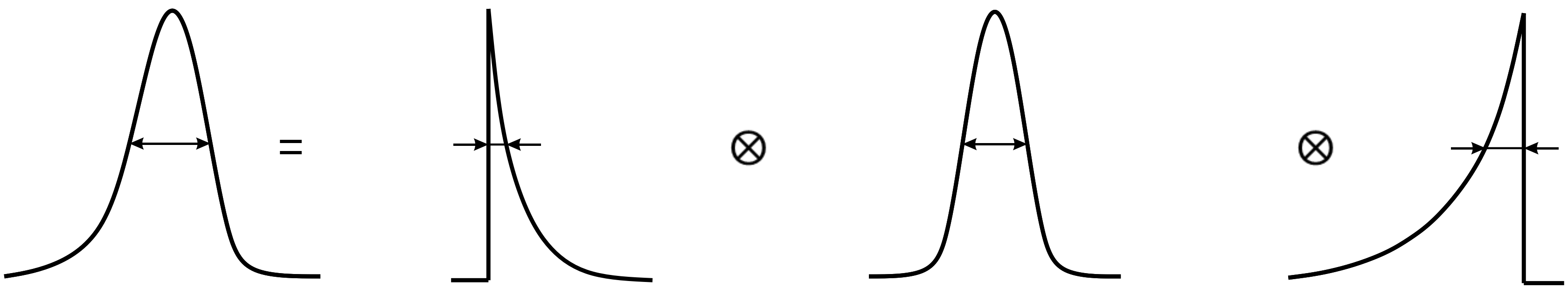
Real Interface = Mixing (Fabrication)

Measured Interface = Real Interface ⊗ Depth Resolution Function (DRF)



$$(\Delta z_{meas})^2 = (\Delta z_{real})^2 + (\Delta z_{DRF})^2$$

DRF = Mixing (Sputtering) ⊗ Roughness (Corrugation) ⊗ Information



$$(\Delta z_{DRF})^2 = (\Delta z_{mix})^2 + (\Delta z_{corr})^2 + (\Delta z_{inf})^2$$

Surf. Interface Anal. **27**, 825–834 (1999)

TOF-SIMS Depth Profiling

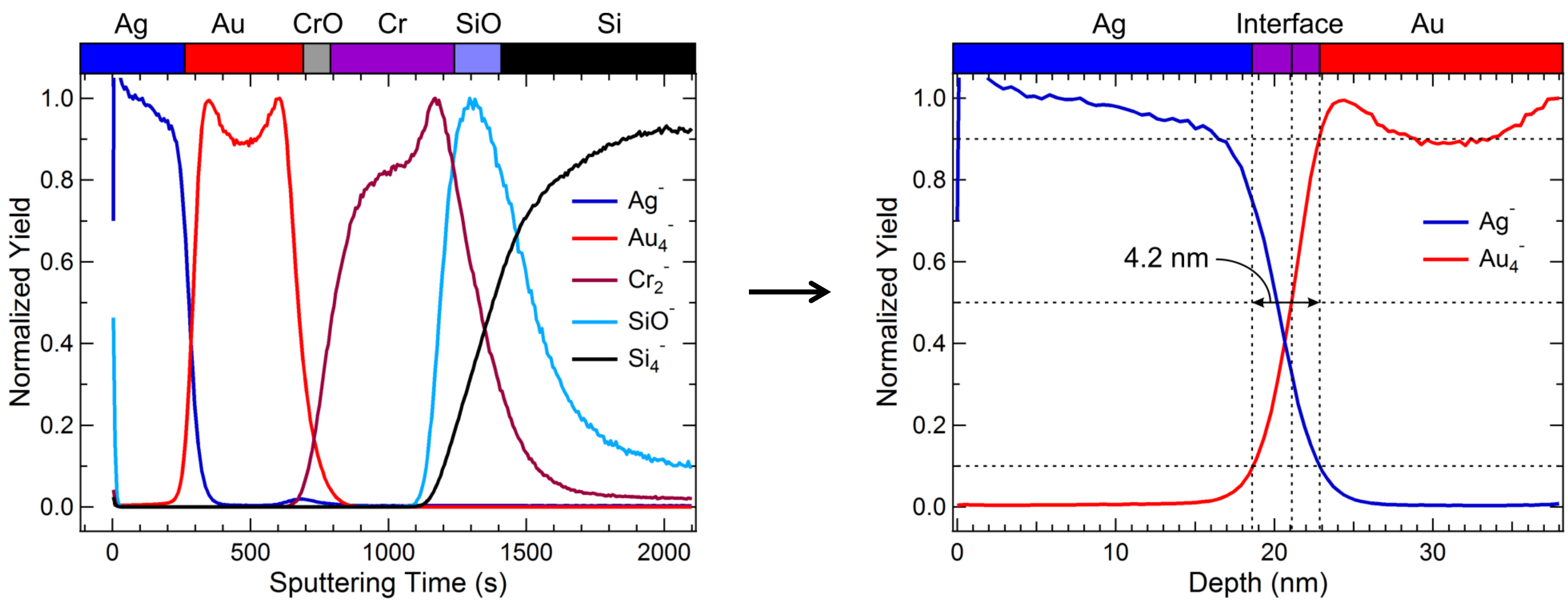
- According to the MRI model the measured depth profile contains:

  Mixing = Fabrication ⊗ Sputtering

  Roughness (Corrugation) = Initial (Underlayer) ⊗ Deposition ⊗ Sputtering

  Information = secondary ion depth of origin

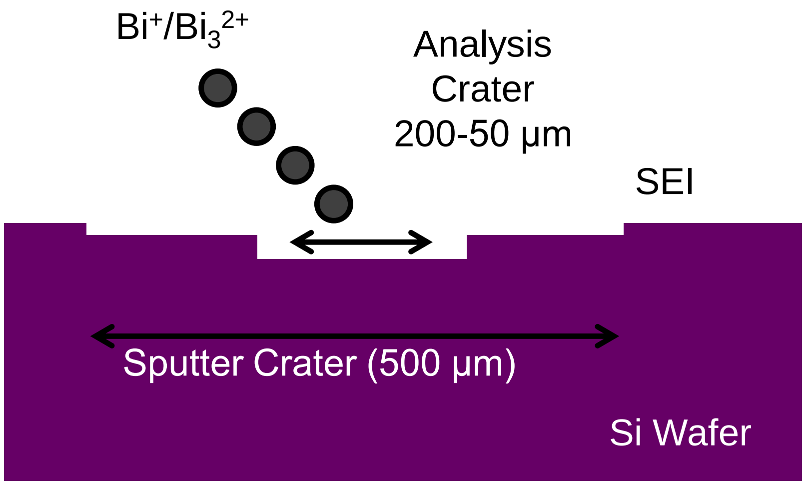
- $Si/SiO_2/Cr(10nm)/Au(20nm)/Ag(20nm)$ sputtered with Bi_3^+ (30 kV) and Cs^+ (250 V)



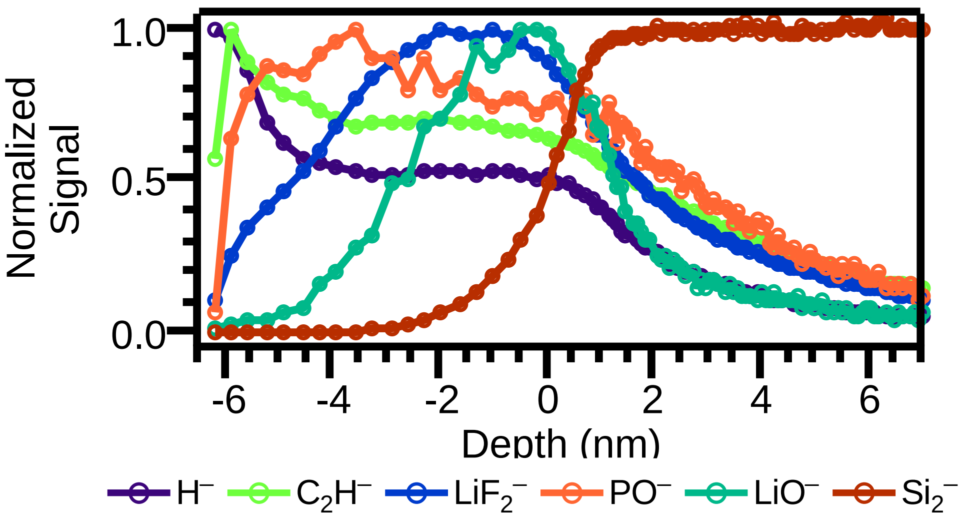
Thin Solid Films **250**, 56 (1994)

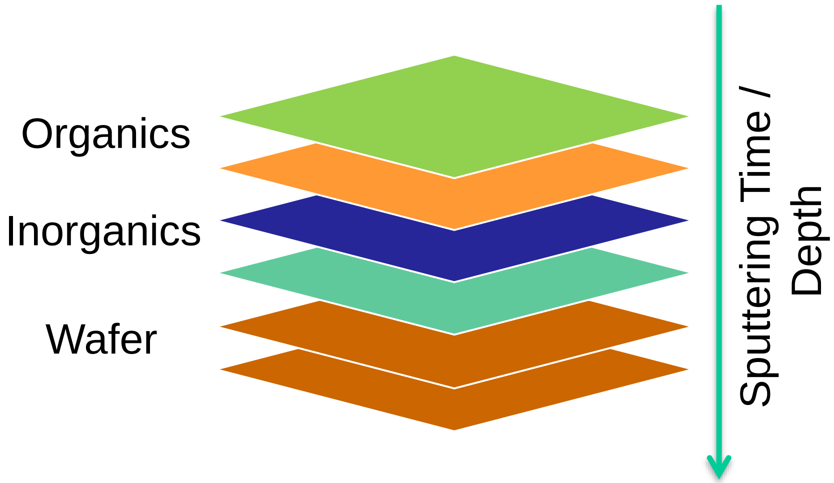
TOF-SIMS Depth Profiling

Analysis Craters

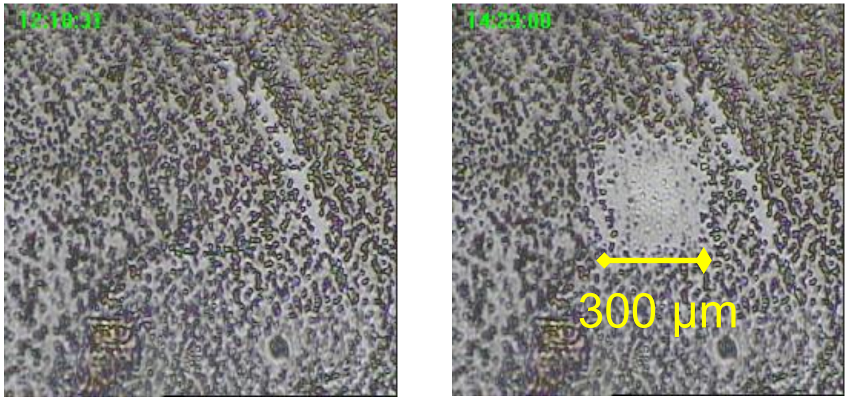


Depth Profile



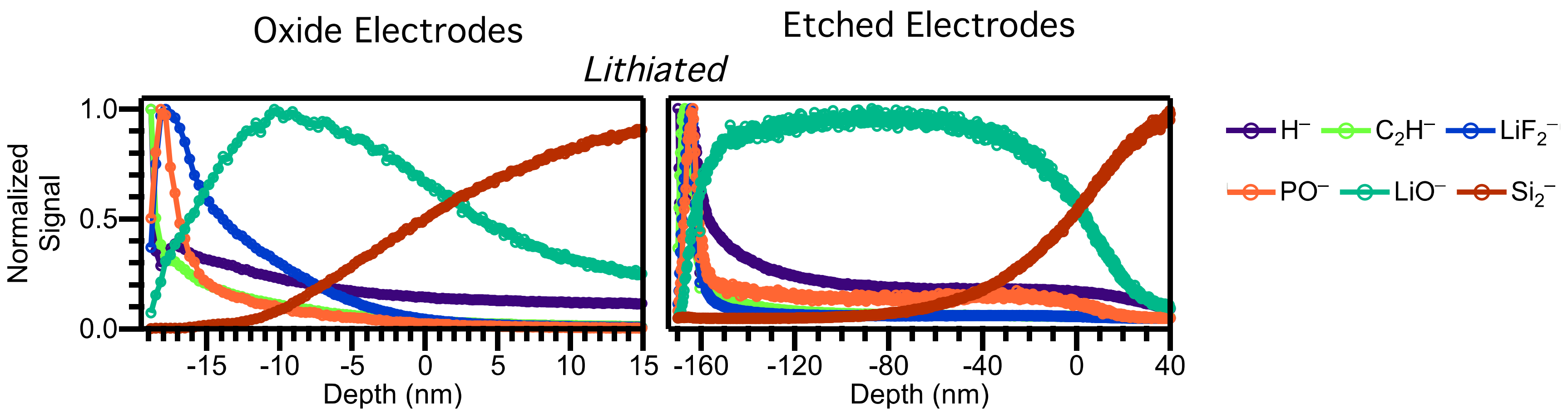


Pre- and Post-Sputtering

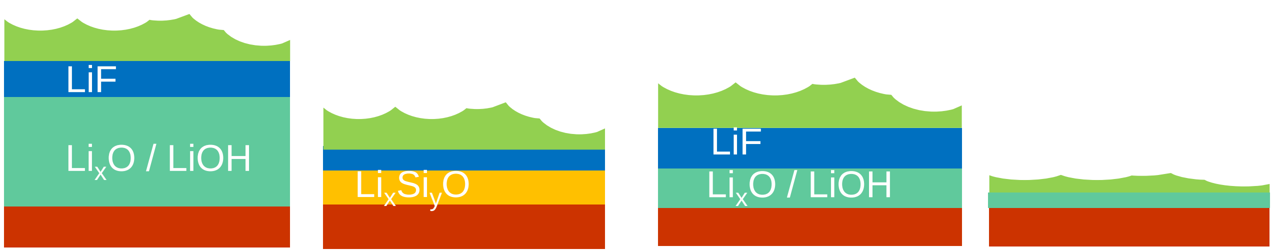


Schroder et al., *ACS Appl. Mater. Inter.* (2014)

Depth Profiling and SEI Structure Si



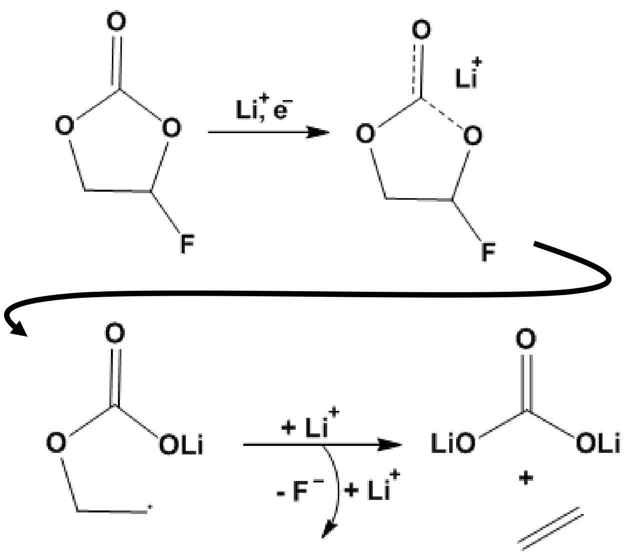
Conclusions about SiOx effects on SEI



Etched vs. Oxide **Lithiated vs. Delithiated**

Schroder et al., *ACS Appl. Mater. Inter.* (2014)

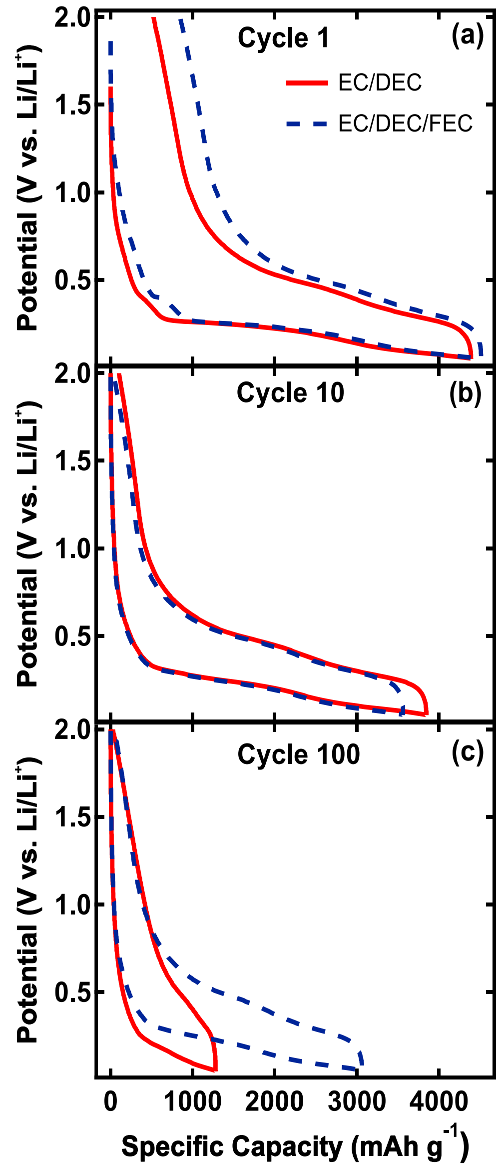
SEI on a-Si with FEC Co-Solvent

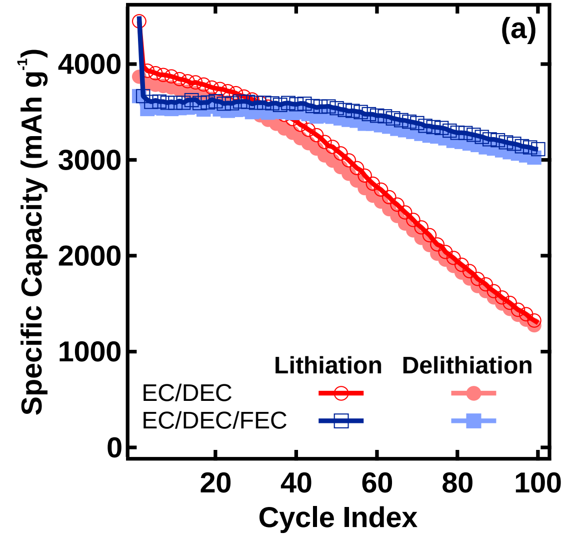


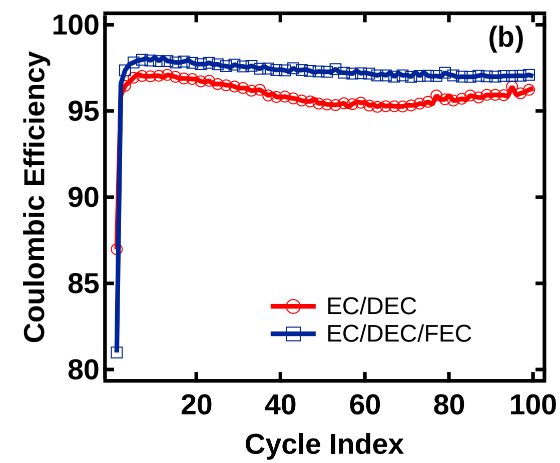
Etching Reaction

$$(CF_2)_n + O_2 \rightarrow CO_2 + 2F^-$$
$$SiO_X + XF^- \rightarrow SiF_X + X/2O_2$$

LiF formation

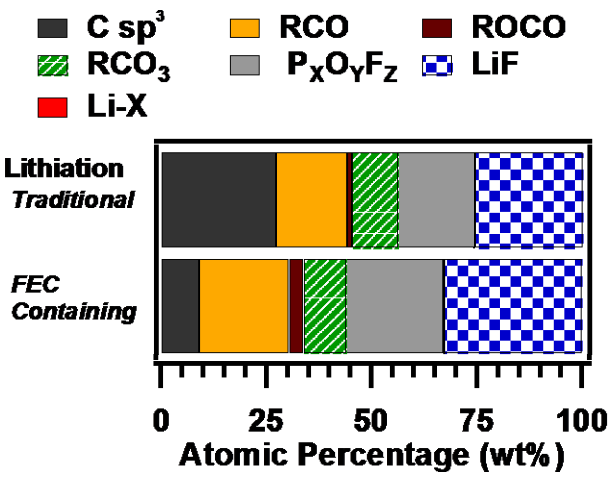


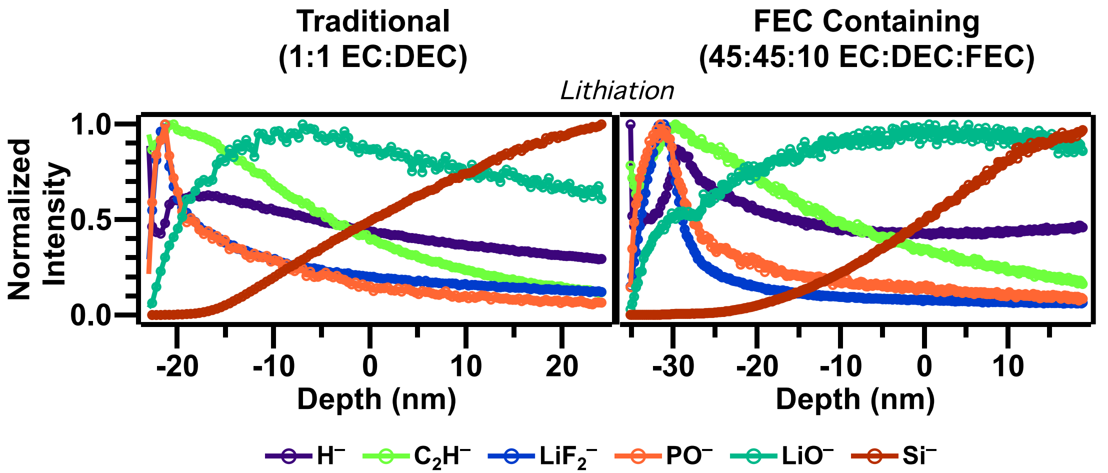




Schroder et al., *Chem. Mater.* **2015**, *27*, 5531.

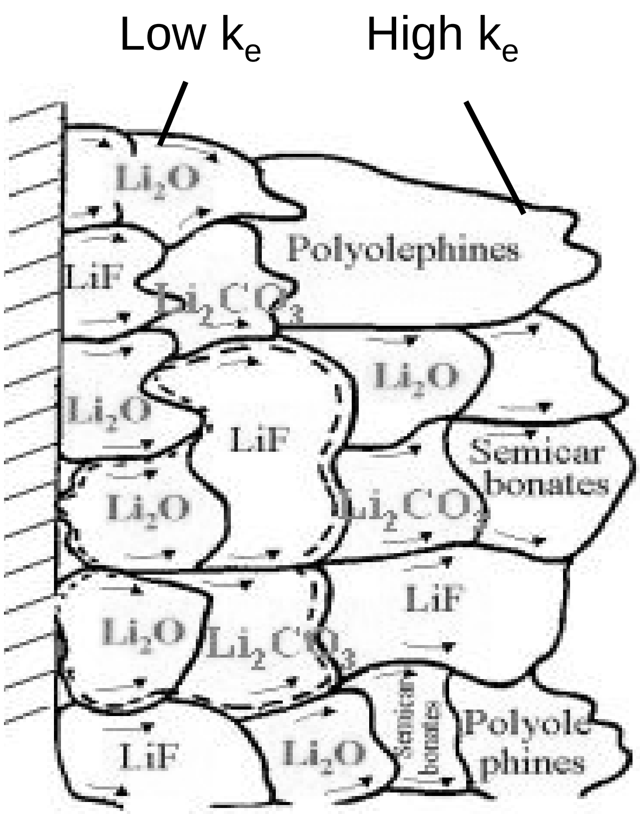
XPS and TOF-SIMs of a-Si Thin Films with FEC





Schroder et al., *Chem. Mater.* **2015**, *27*, 5531.

Kinetic Stability Theory of SEI Structure



What about surface?

Desolvation?

$$F(e^-) \overset{?}{>} E^0_{SEI}$$

Structure and Composition of SEI determined by rate:

$$e^- + S \xrightarrow{k_e} product$$

Peled E., Golodnitsky D. and Ardel G., *J. Electrochem. Soc.* (1997)
Besenland et al., *J. Power Sources* (1995)
Aurbach et al. *J. Electrochem. Soc.* (1994)

Summary SEI on Anodes

Interfacial layers form on anodes due to both spontaneous and electrochemically driven decomposition processes

SEI on anodes is heavily influenced by solvent, carbon, LiF formation, HF and LiOx and LiOH

SEI composition on Si influenced by potential, surface chemistry and environmental exposure

- **SEI is porous that allows transport of solvated Li ions**
- **SEI is dynamic and has graded composition of Inorganics & Organics**
- **SEI is thick on non-oxide covered anode surfaces**
- **SEI is thick with FEC cosolvent, enriched with LiF on outer surface**
- **Quasireversible shuttle mechanism between LiF and Li_2O increase CE**

$$SiO_X + xF^- \rightarrow SiF_X + (x/2)O_2$$

$$2LiF_{(s)} \leftrightarrow 2Li^+_{(sol)} + F_{2\,(sol)} + 2e^-$$

$$2Li_2O_{(s)} \leftrightarrow 4Li^+_{(sol)} + O_{2\,(sol)} + 4e^-$$

$$S_{Li_2O} = \sqrt[3]{\frac{K_{SP}}{4}} = \sqrt[3]{\frac{[O]([Li]_{Li_2O} + [Li]_{LiF})^2}{4}}$$

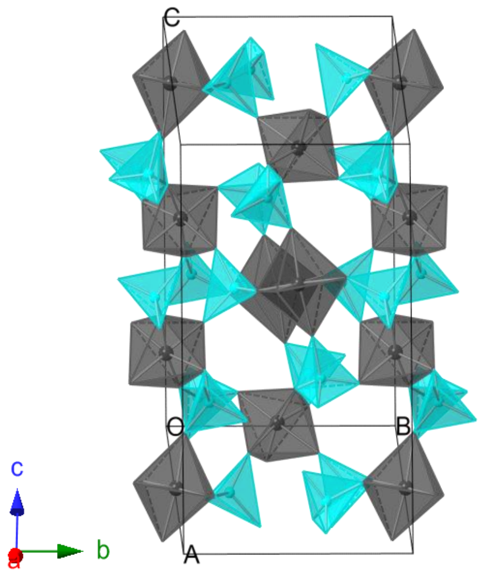
SEI library needed to understand parameter space

New High Capacity $Li_3V_2(PO_4)_3$

$$V^{4.5+}_2(PO_4)_3 + 3\,Li^+ + 3\,e^- \rightarrow Li_3V^{3+}_2(PO_4)_3$$

Gravimetric Capacity: 197 mAh/g

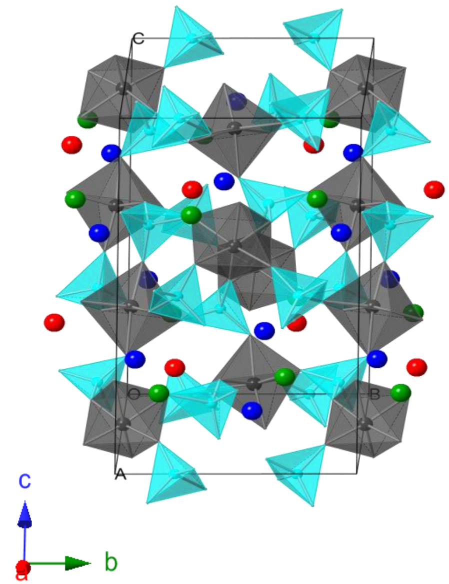
$V_2(PO_4)_3$



discharge →

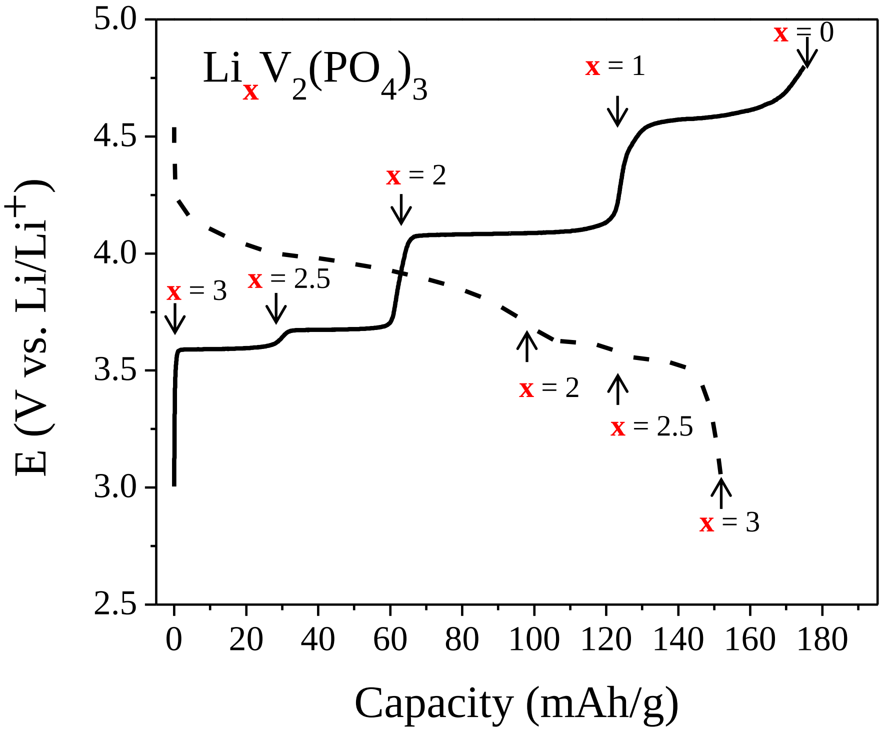
← **charge**

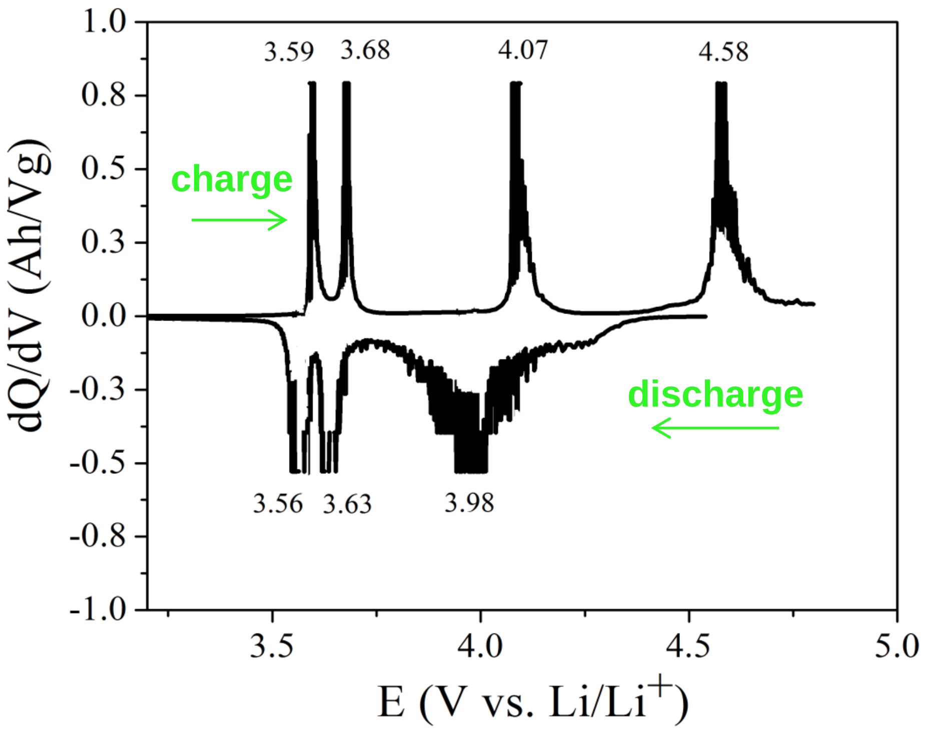
$Li_3V_2(PO_4)_3$



Electrochemistry of $Li_3V_2(PO_4)_3$

$$Li_3V^{+3}{}_2(PO_4)_3 \rightarrow 3\ Li^+ + 3\ e^- + V^{+4.5}{}_2(PO_4)_3$$

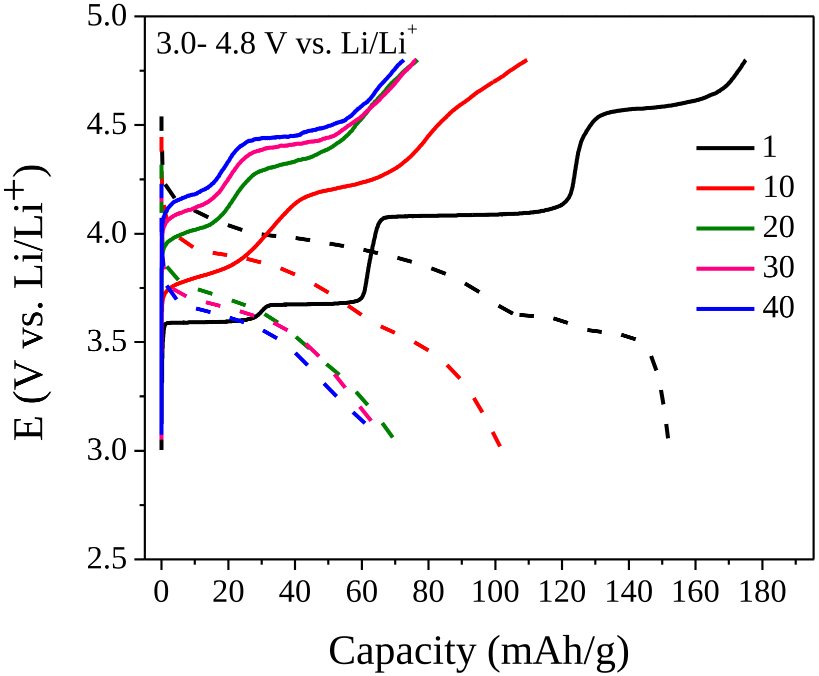




C/20 rate (1C = full charge over 1 hr)

3.0-4.8 V vs. Li/Li^+

Severe Capacity Fade of $Li_3V_2(PO_4)_3$



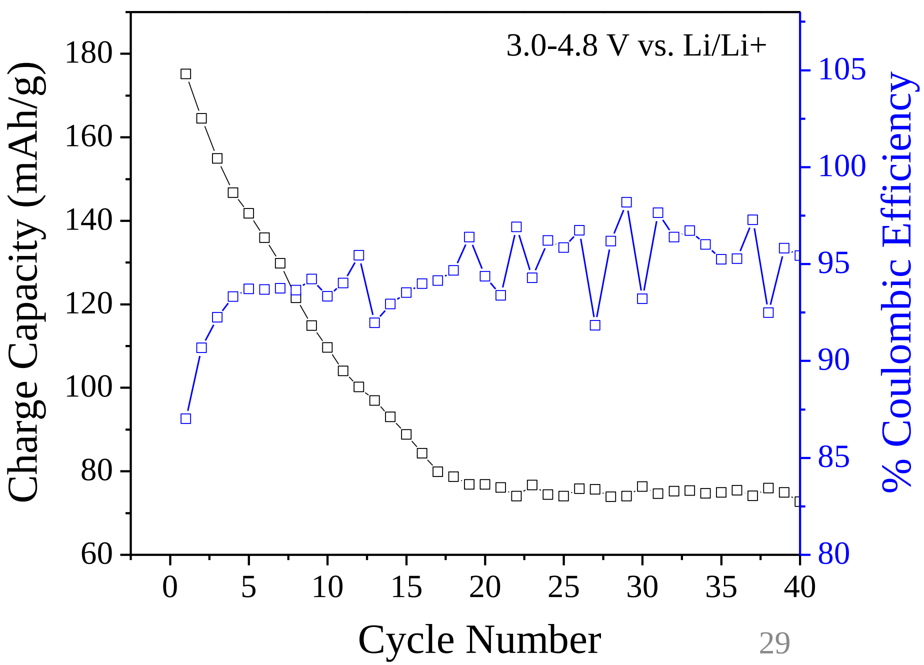
• **Sloping of voltage plateaus**

• **Increasing overpotential with cycle number**

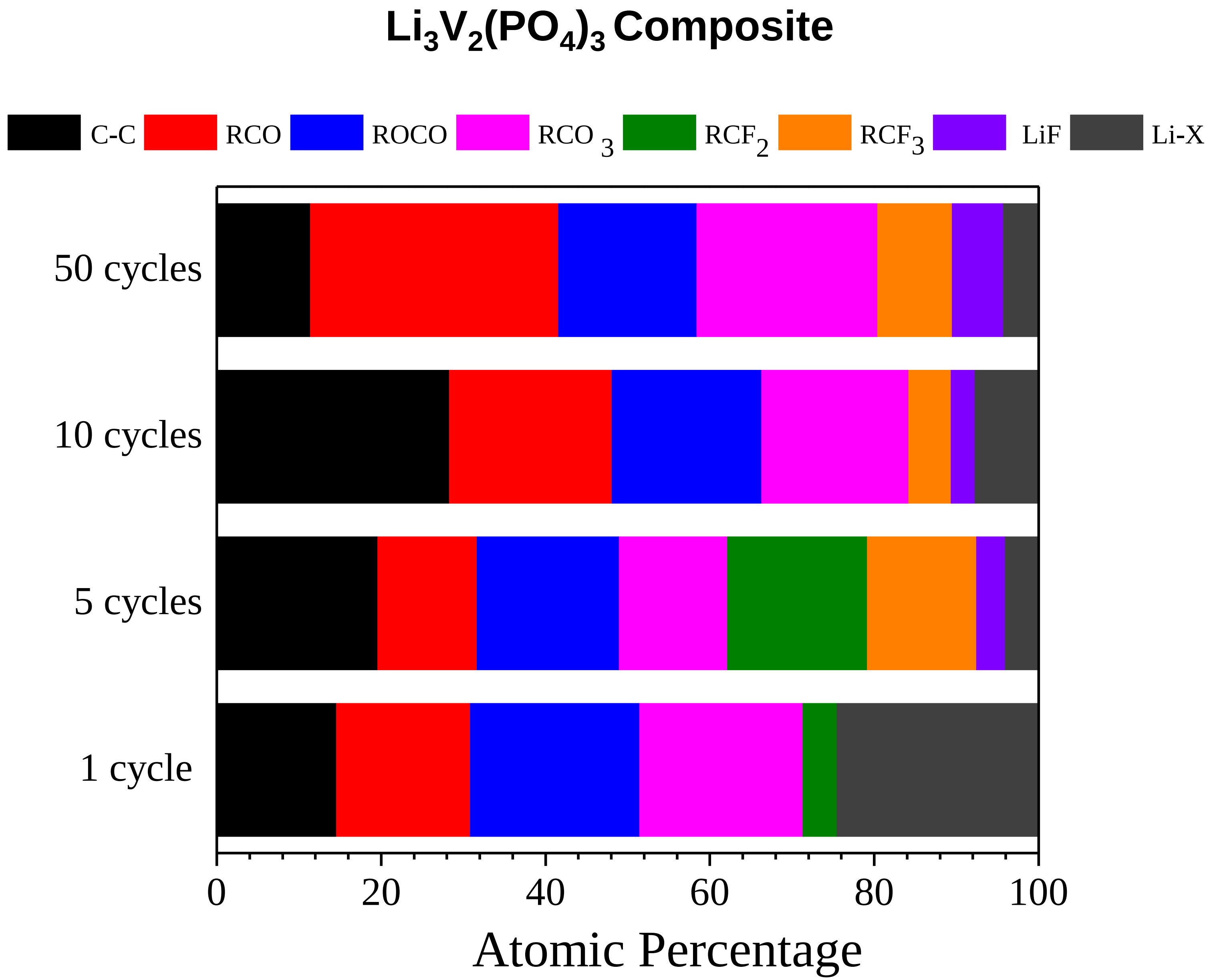
• **Rapid drop in capacity with cycle number**

• **Initial low coulombic efficiency indicative of the formation of passivation film**

• **(Coulombic efficiency) $qc=Q_d/Q_c$**



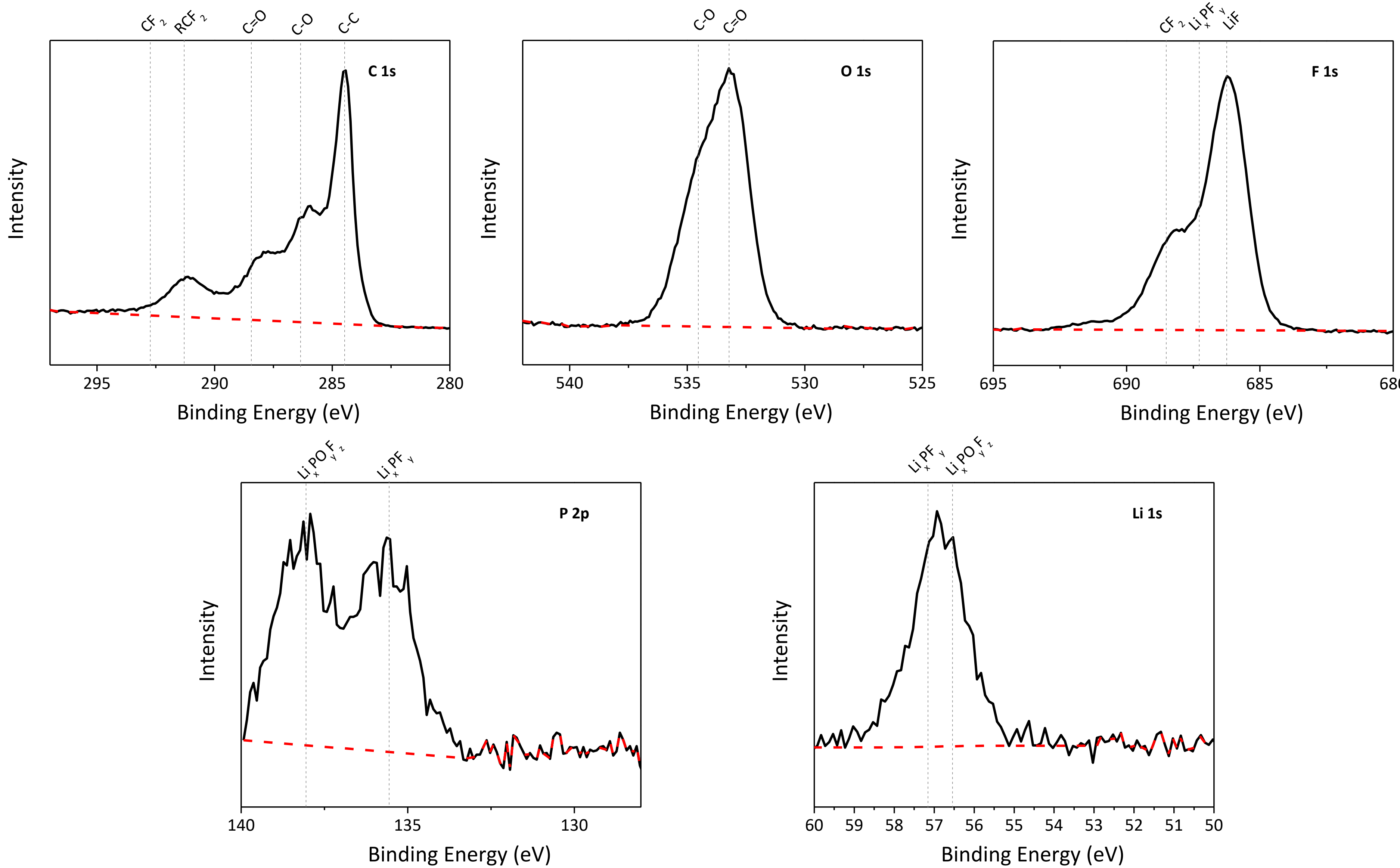
SEI Compositions (Cycled to 4.8 V)



Electrochemical SEI formation on Carbon

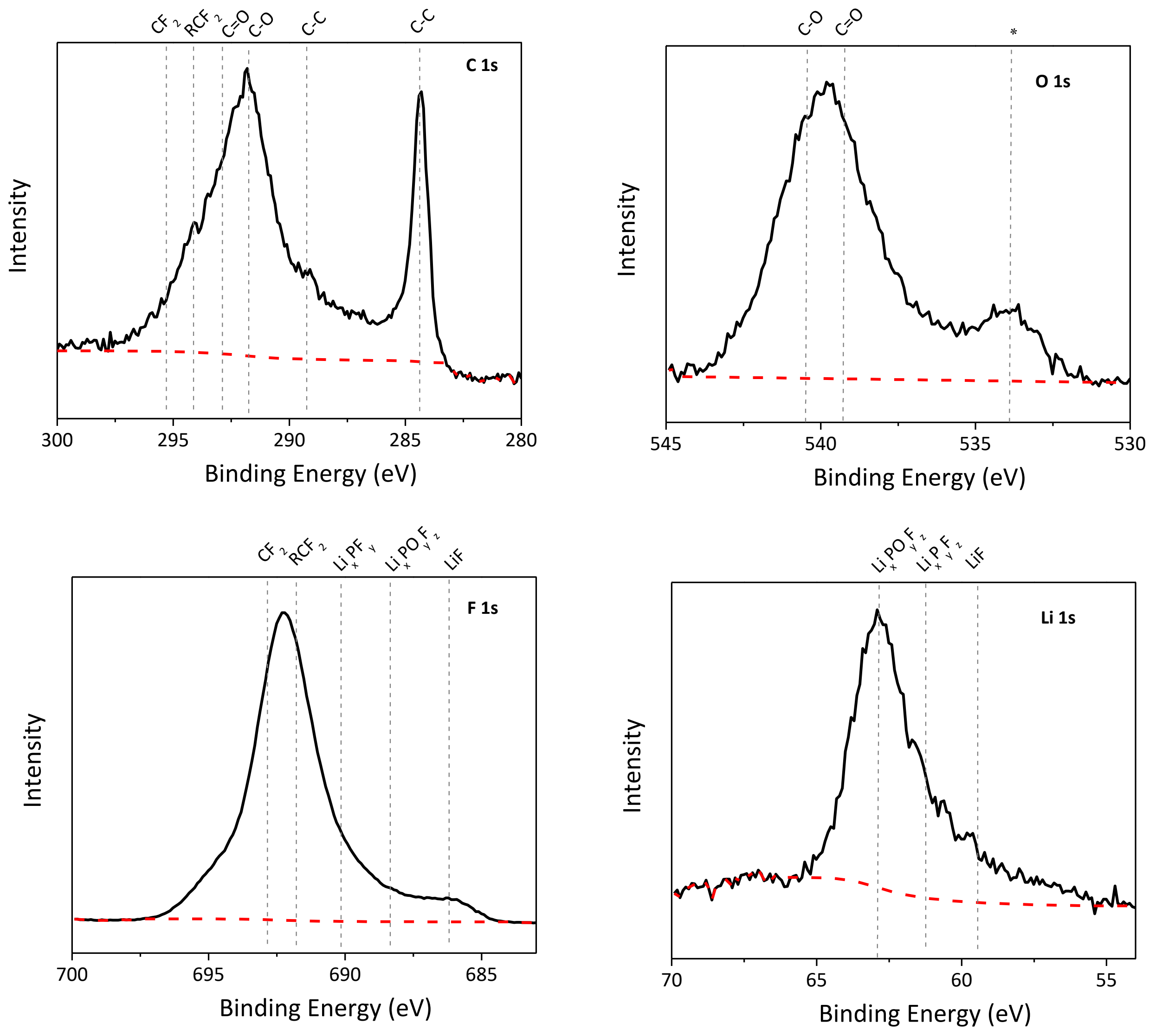
One Cycle (3-4.8 V vs Li/Li+)

Super P Carbon

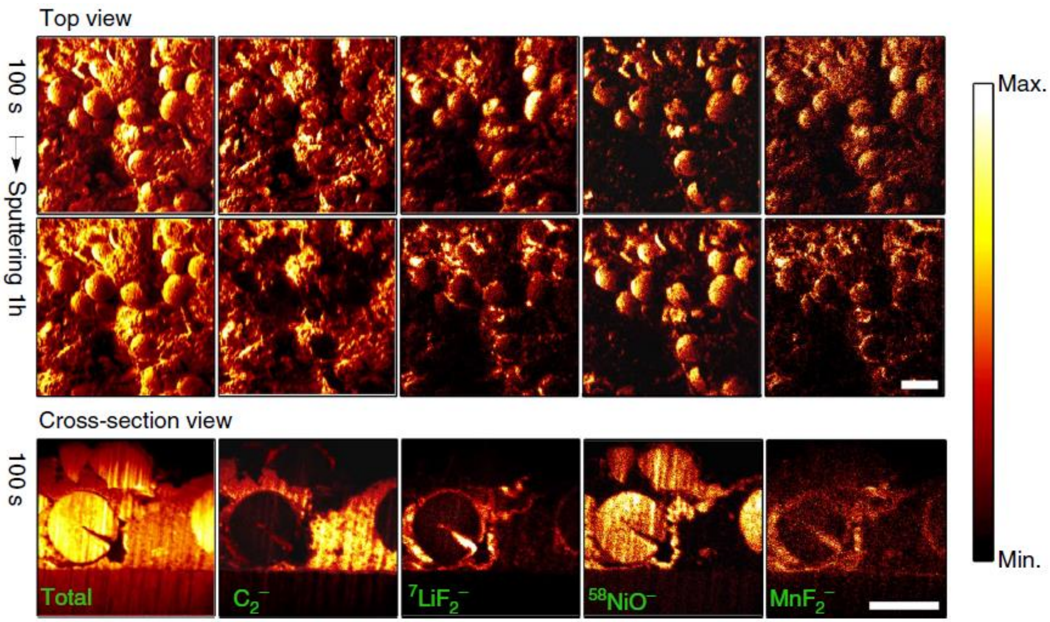


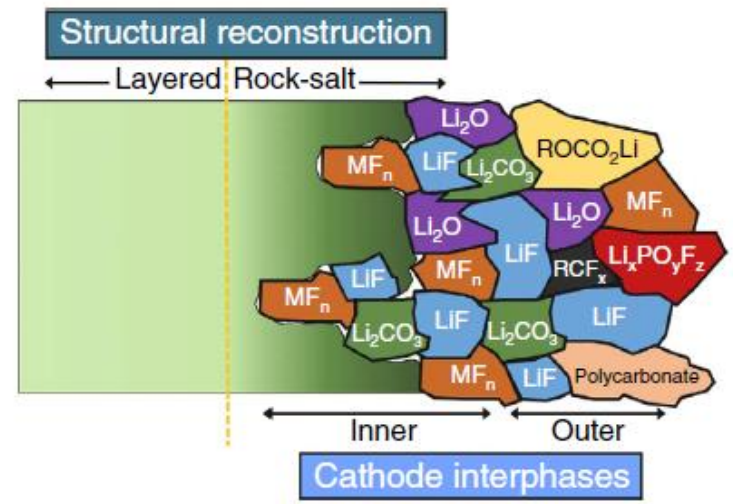
Spontaneous SEI formation on Carbon

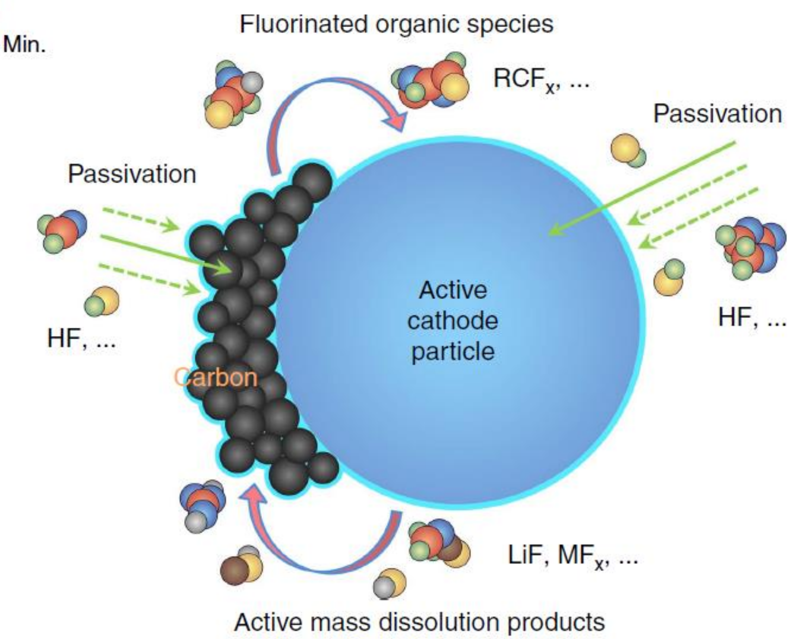
Super P Carbon soaked in electrolyte



Spill-over Mechanism for SEI formation on NMC Cathodes







Dynamic behavior of cathode interphases driven by conductive carbon. The cathode-electrolyte interphase, initially formed on carbon with no electrochemical bias applied, readily passivates the cathode particles through mutual exchange of surface species

DOI: 10.1038/ncomms14589

Summary SEI on LVP Composite Electrodes

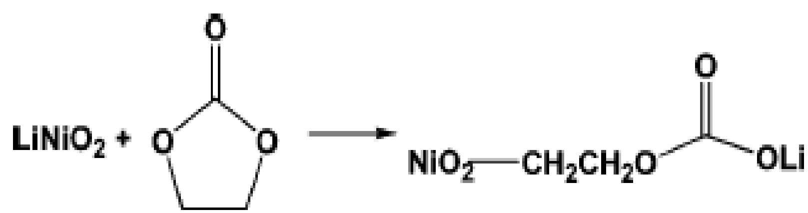
SEI on cathode: alkoxides, ethers, esters, lithium carboxylates, carbonate, difluoroalkanes, alkyl lithium, lithium salts (at both 4.2 & 4.8 V vs. Li/Li^+)

Difficult to interpret whether the SEI's chemical composition is evolving (quantitatively) with increasing cycle number

Carbon additive is responsible for SEI formed spontaneously and electrochemically on composite LVP cathodes

O in PO_4 has a lower basicity or nucleophilicity as compared to Li_xMO_y cathodes and do not form SEI spontaneously as has been proposed for lithium metal oxides

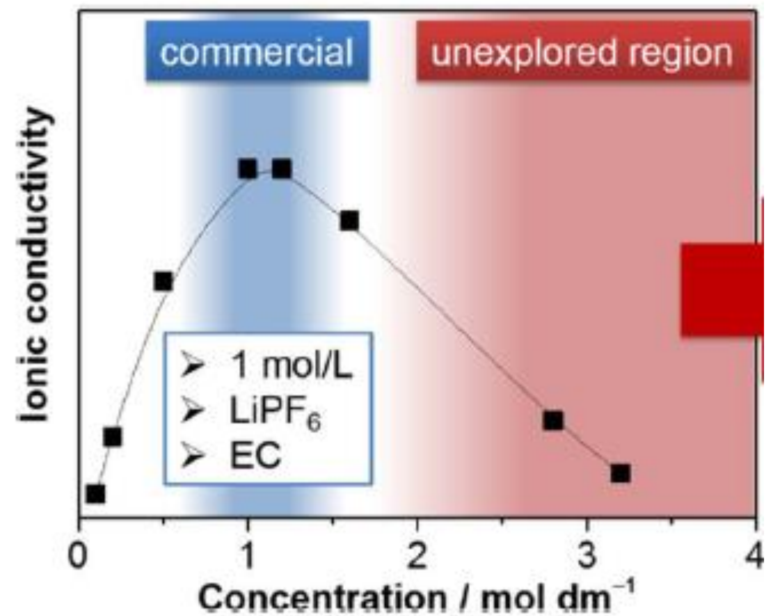
$$Li_yMO_x + ROCO_2R' \rightarrow Li_{y-1}MO_xR + R'OCO_2Li$$



Superconcentrated Electrolytes

Highly concentrated electrolyte: anything more concentrated than **standard electrolyte**: 1 M $LiPF_6$ in EC/DMC (DEC, EMC)

- high ionic conductivity
- protects Al current collector
- non-viscous
- forms stable SEI due to EC



What do concentrated electrolytes offer?

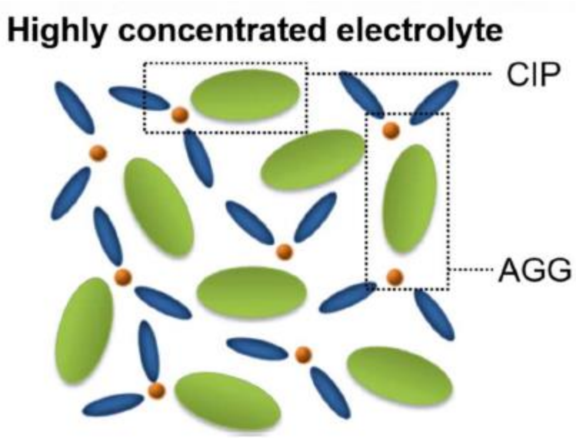
- higher oxidative/reductive stability
- lower vapor pressure
- thermal stability
- good SEI without EC (?)
- low flammability
- fast electrode reactions (?)

Disadvantages

- lower ionic conductivity
- higher viscosity
- high cost

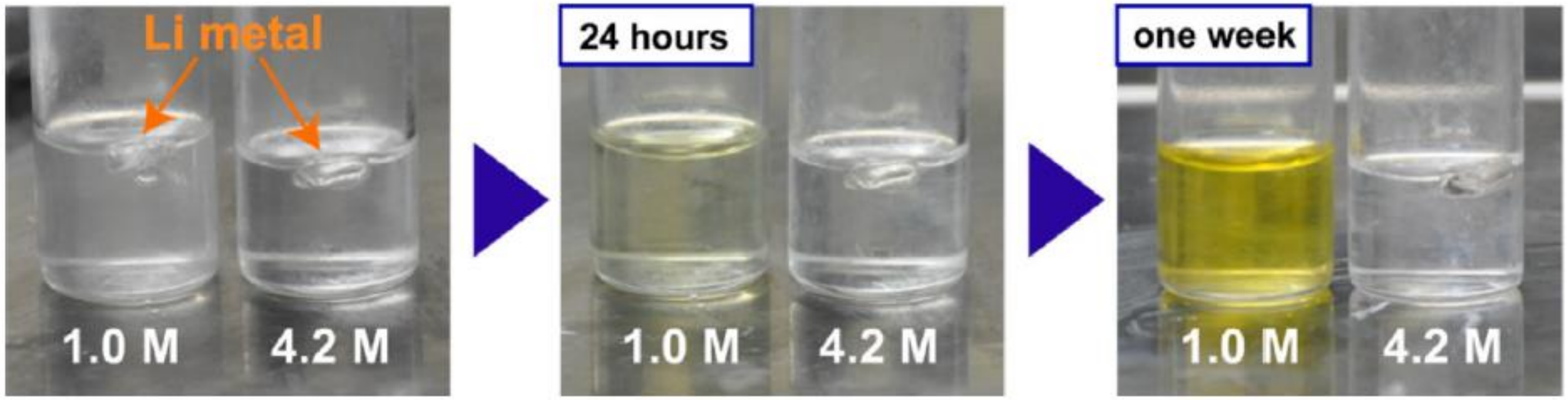
Superconcentrated Electrolytes: Hypothesis?

Highly concentrated electrolyte solutions:
enhanced ionic association; no free solvent molecules →
change in solvent physicochemical properties



- Suppress active material dissolution ($LiMn_2O_4$)
- Better CEI and SEI chemistry – enhanced stability of electrode/electrolyte interface
- Higher potentials for solvent and electrolyte oxidation
- Lower potentials for solvent and electrolyte reduction

Reactivity of lithium metal foil and LiTFSI/AN solutions



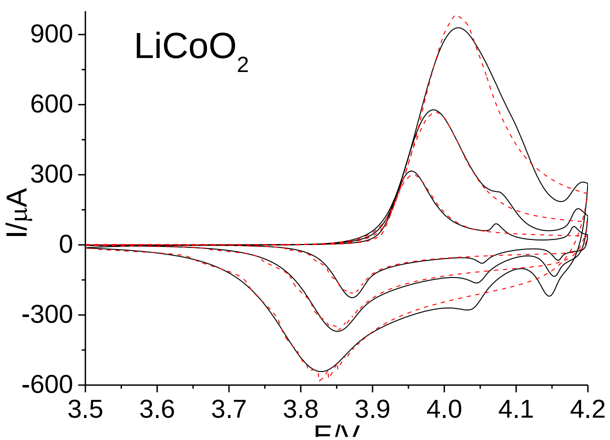
Y. Yamada *et al*/J. Am. Chem. Soc. **2014**, *136,* 5039−5046

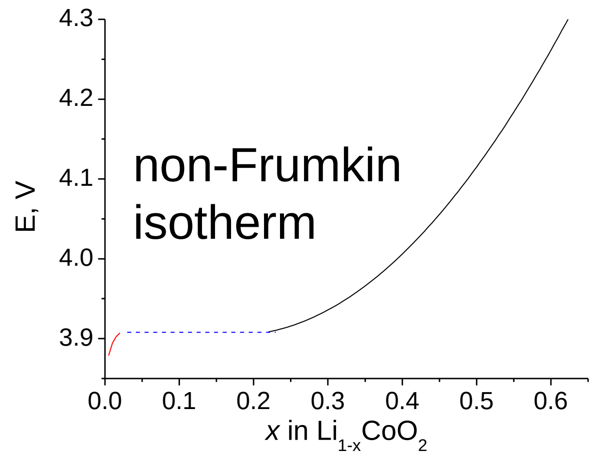
Cyclic Voltammetry to measure k_s and D_{app}

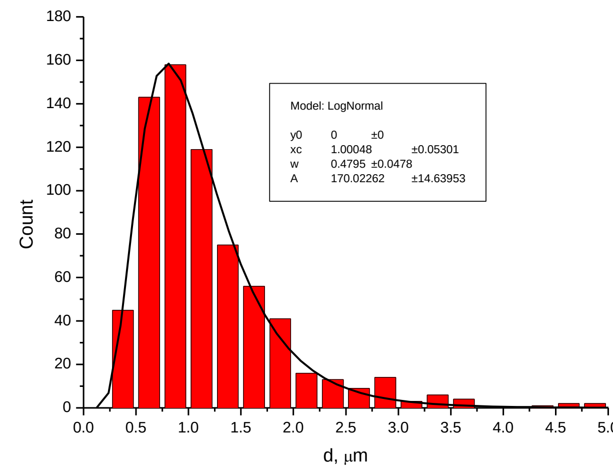
Simple Butler-Volmer formalism

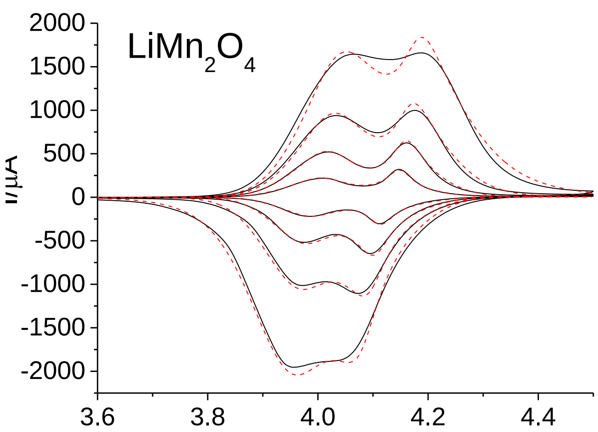
$$I(E) = SF \cdot 10^6 \cdot \frac{\rho \cdot n_{Li}}{M_r} \cdot k_s \cdot \left\{ \theta \cdot \exp\left[\frac{(1-\alpha)F(E-E_0(\theta))}{RT}\right] - (1-\theta) \cdot \exp\left[-\frac{\alpha F(E-E_0(\theta))}{RT}\right] \right\}$$

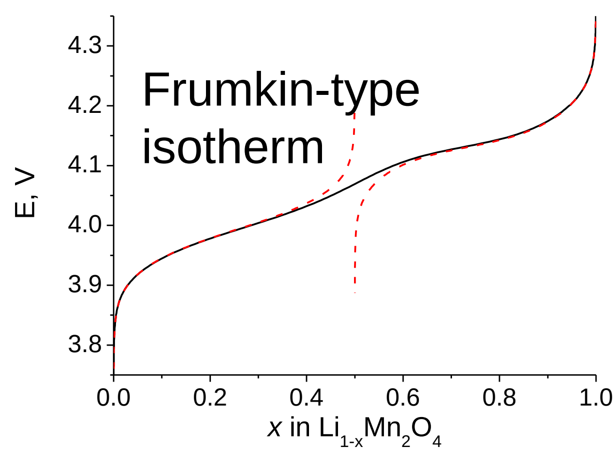
$$E(\theta) = E_0(\theta) + \frac{RT}{F}\ln\left(\frac{1-\theta}{\theta}\right) = E_{eq} + \frac{RT}{F}\ln\left(\frac{1-\theta}{\theta}\right) + \frac{RT}{F}\cdot[g_1(0.5-\theta) + g_2(0.5-\theta)^2 + g_3(0.5-\theta)^3 + g_4(0.5-\theta)^4 + g_5(0.5-\theta)^5]$$







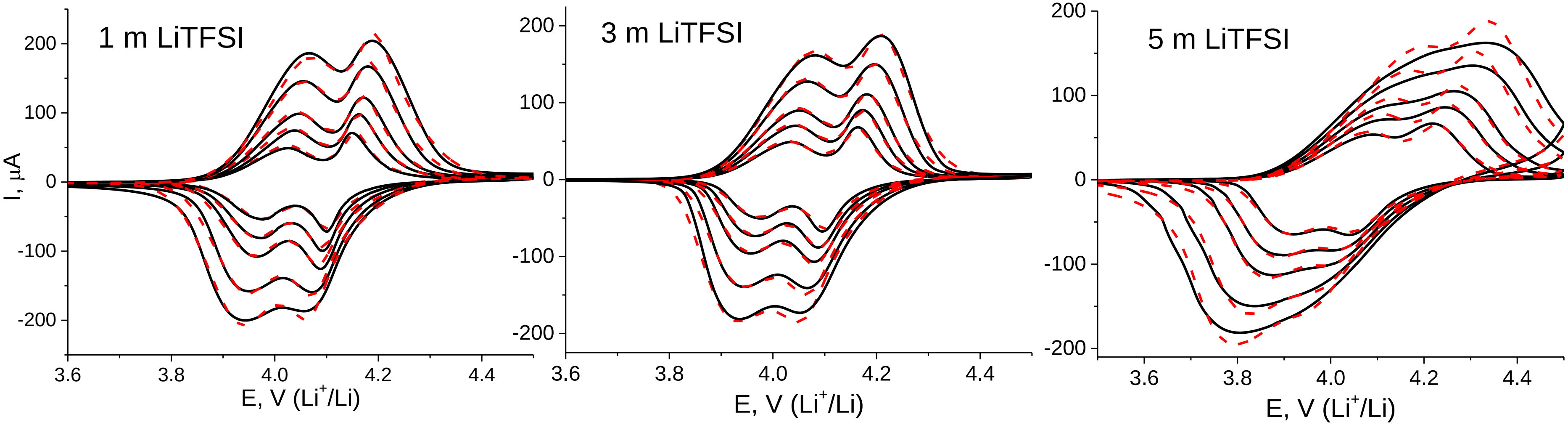


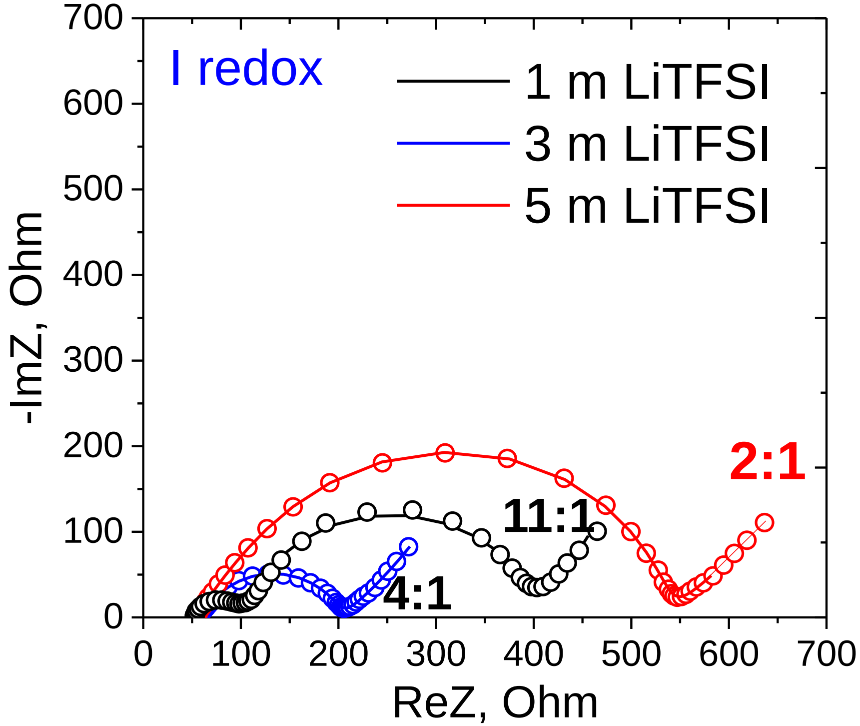


single value of D_{eff} and apparent k_s

V. Nikitina et al MSU

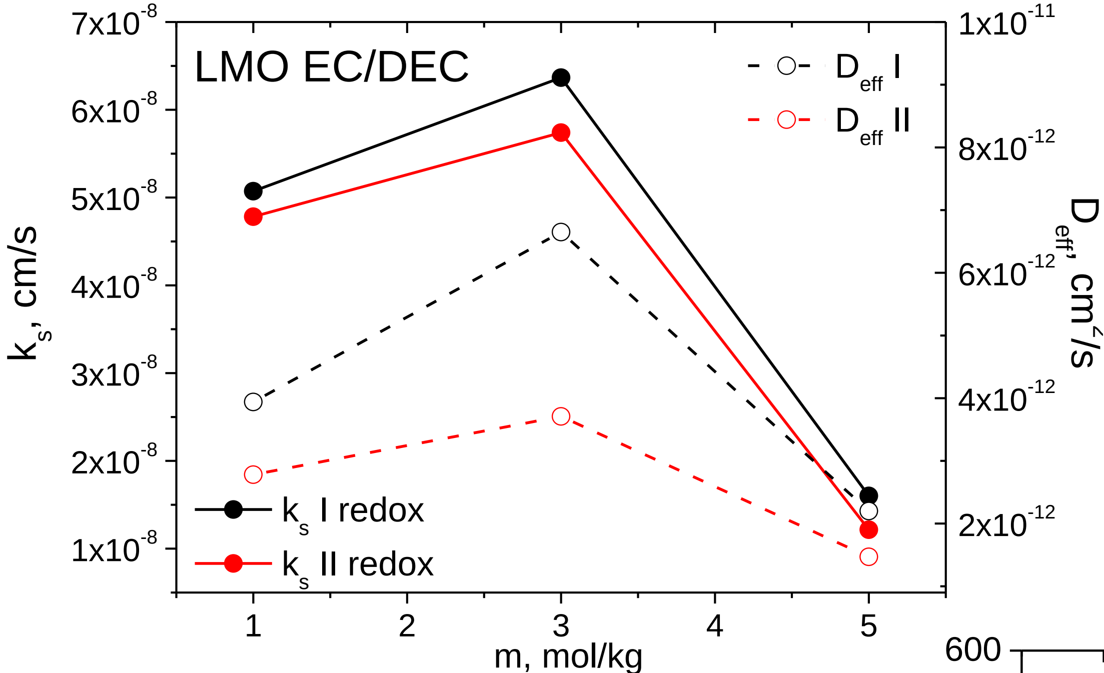
Highly Concentrated EC/DEC Solutions: $LiMn_2O_4$

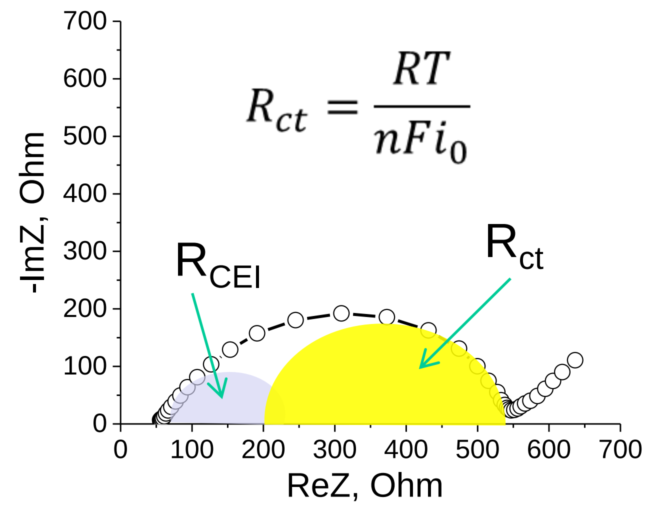




- **At higher concentrations Mn dissolution is suppressed – decrease in R_{ct}**
- **For concentrations > 4 M sharp increase in R_{ct}: resistive F-containing SEI forms**

V. Nikitina et al MSU





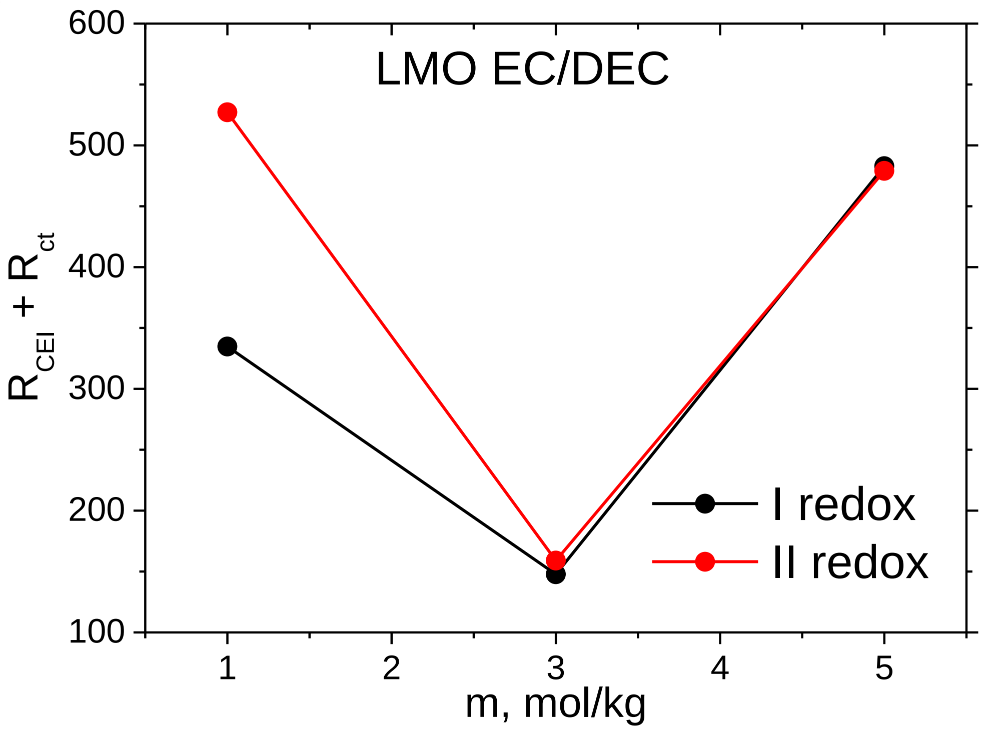
- From **1 M to 3 M**:

slight increase in k_s and D

- From **3 M to 5 M:**

drop in k_s and D (0.5 order of magnitude)

- Impossible to separate R_{CEI} and R_{ct} unambiguously



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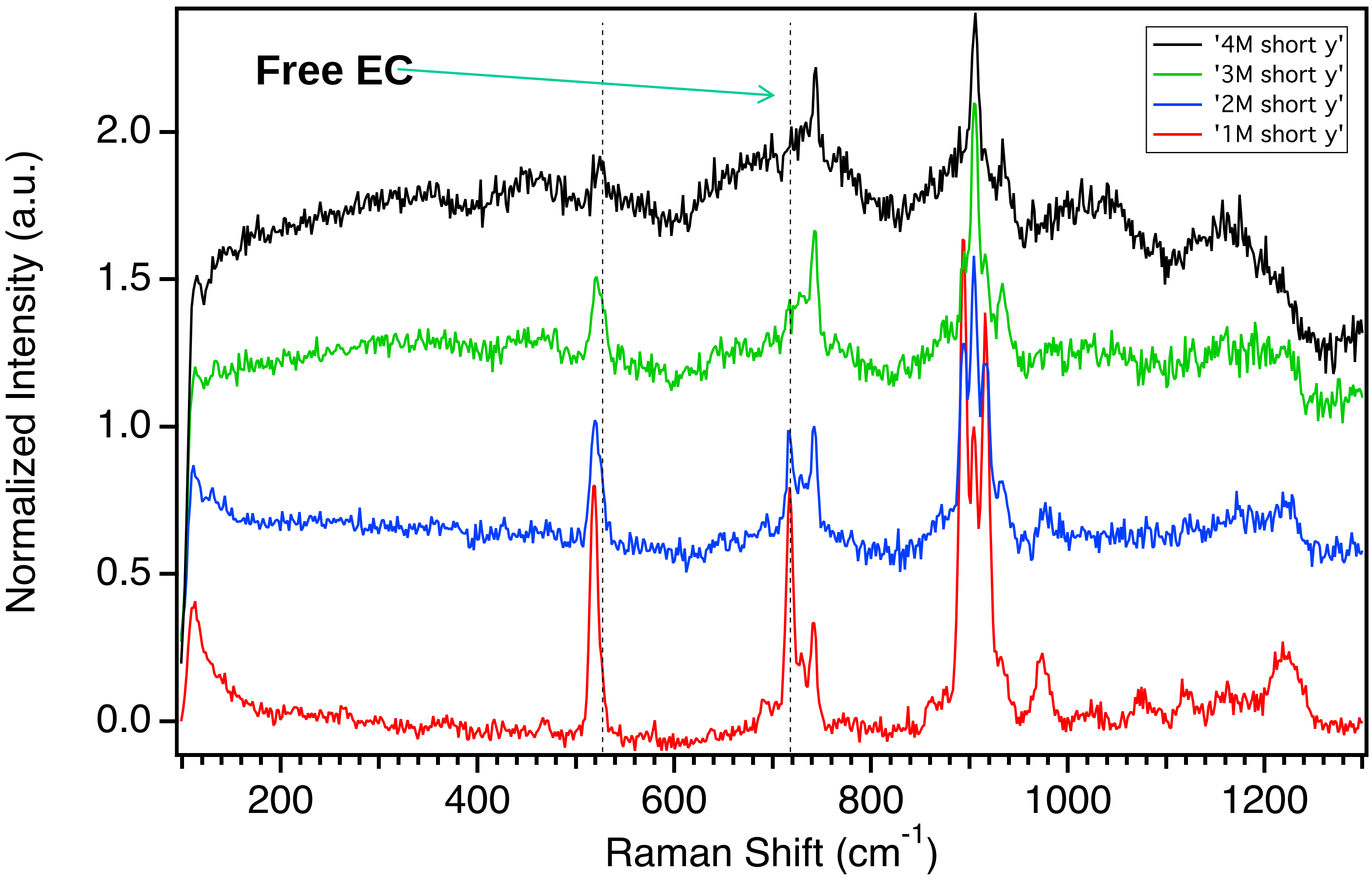
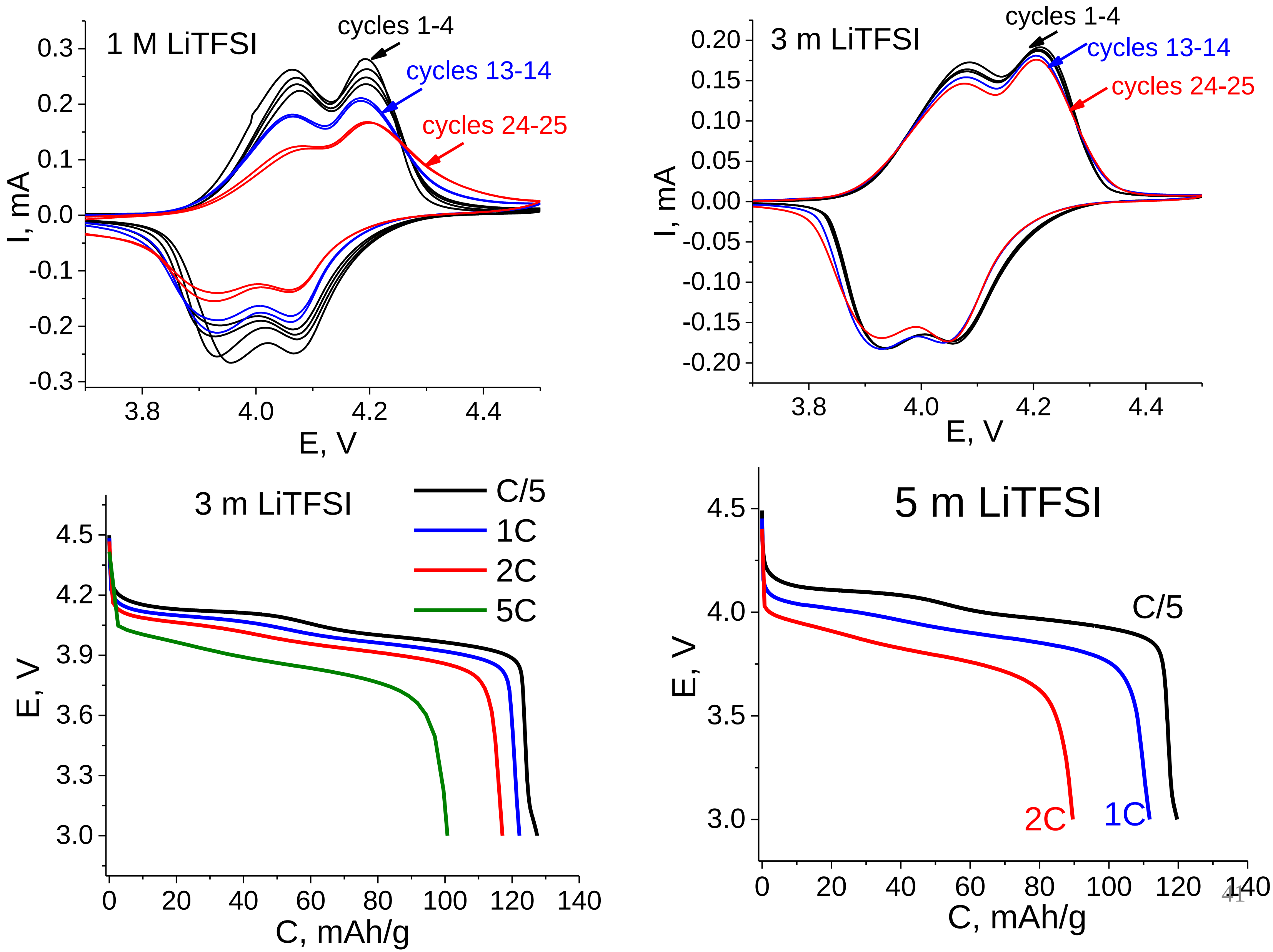
LiTFSI in EC/DEC

Free EC disappears with the increase in salt concentration



Cycling Stability and Rate Capability



Overall Summary

New materials require development of advanced tools for study
- **Ex and in situ spectroelectrochemical studies**
- **Specialized Transfer Capsule for "Anoxic" Surface Analysis**

Raman is an excellent technique for characterizing energy storage materials, composites and surface chemistry
- **Enables assessment of phase purity & compositions**
- **Enables study of Li+ charge transfer reactivity at interfaces and elucidation of charge storage mechanisms**

Nano-sized architechures show promise as advanced energy storage materials
- **Yet are not thermodynamically stable and have reactive surface chemistry**
- **Can achieve high capacities with enhanced kinetics (rate capability)**

Interfacial layers form on both cathodes and anodes due to both spontaneous and electrochemically driven decomposition processes
- **V and Mn based cathodes are reactive to solvent and HF and form dynamic SEI layers**
- **SEI composition on Si influenced by potential, surface chemistry and environmental exposure**
  - **SEI library needed to understand parameter space**

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