The Role of Surface Chemistry on the Cycling and Rate Capability of Lithium Positive Electrode Materials

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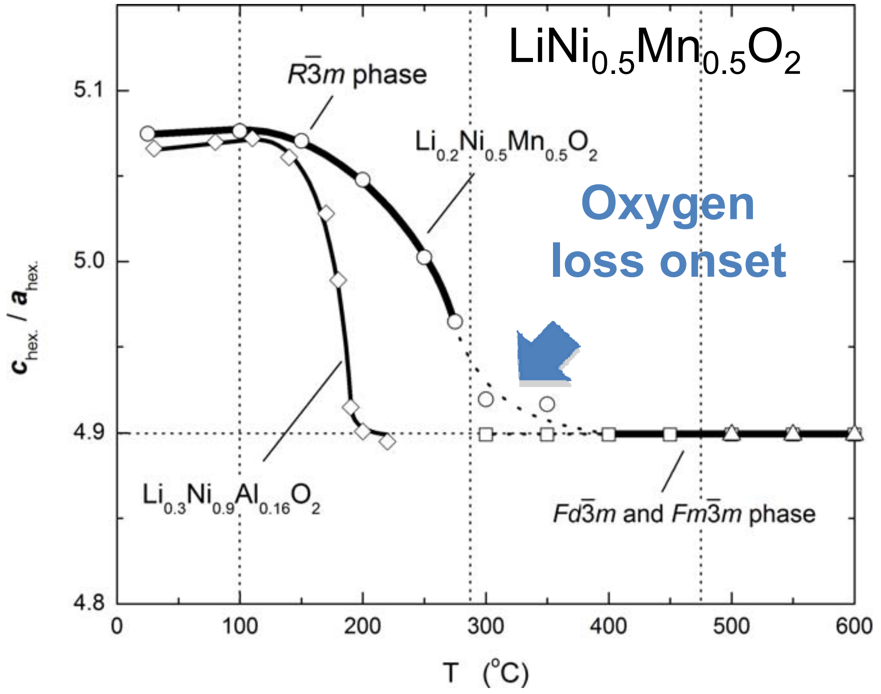
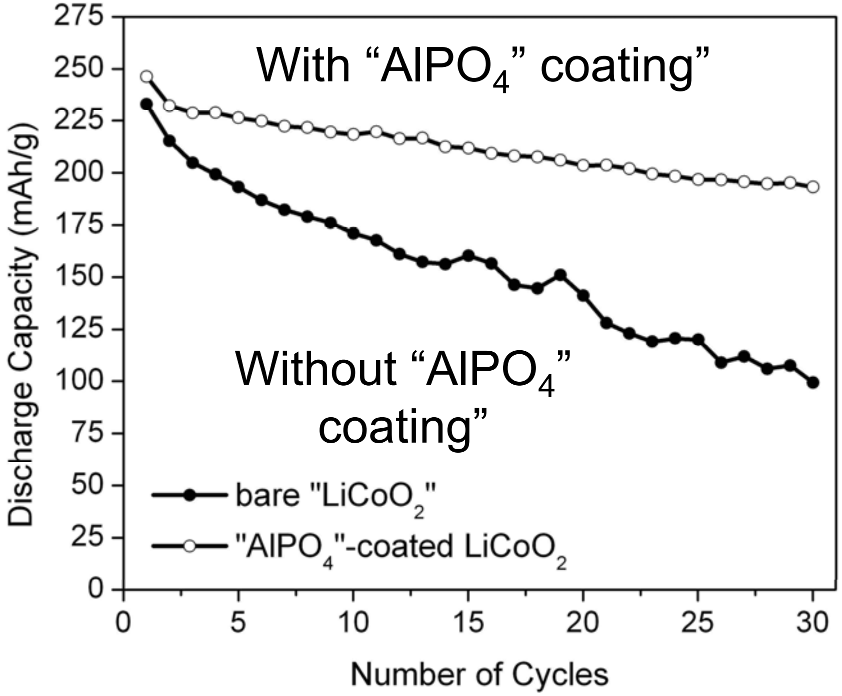
Project ID #
es_21_Shao-Horn

Barriers: low cycle life, abuse tolerance and limited operating temperatures



Oxygen loss onset

Yabuuchi and Shao-Horn et al. JES and Chemistry of Materials 2007 and 2008



Appapillai and Shao-Horn et al., Chem Mater, 2007

Our previous studies have shown oxygen loss from active materials (left) and the surface of active materials (right) can greatly influence cycle life and rate capability.

⬇

The processes associated with the interfacial instability between active materials and electrolyte are not understood

Research Objectives:

- To develop fundamental understanding of processes associated with the interfacial instability between active materials and electrolyte

- To design positive electrodes with stable electrode-electrolyte interface with improved cycling performance and rate capability in wider operating temperatures

Research Approaches:

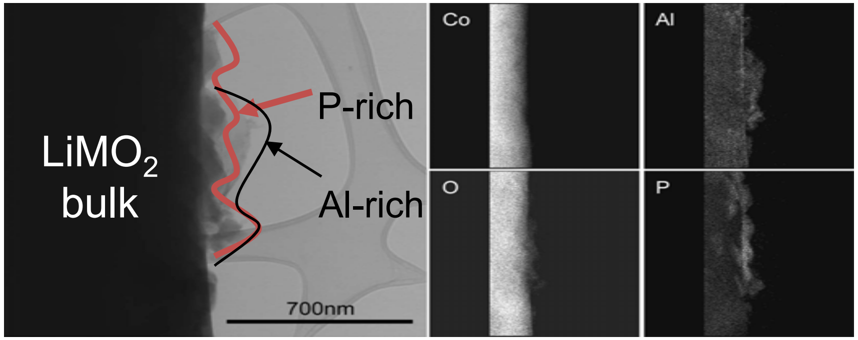
- Probing the ***surface chemistry*** of positive electrode materials before and after cycling using surface-sensitive electron microscopy, X-ray photoelectron spectroscopy and electron-yield X-ray adsorption spectroscopy.

- Studying the ***bulk structure*** of positive electrode materials before and after cycling using synchrotron X-ray diffraction and transmission X-ray absorption spectroscopy.

- Correlating surface chemistry and bulk structure information with ***electrochemical performance characteristics*** such as capacity retention and rate capability to determine the origin of surface instability.

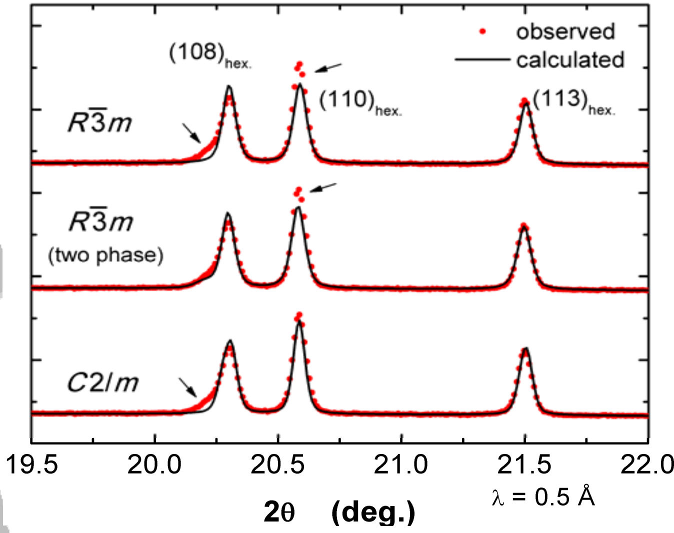
Research Approaches:

Surface Chemistry: **Electron microscopy**



Bulk Structure: **Synchrotron X-ray diffraction**

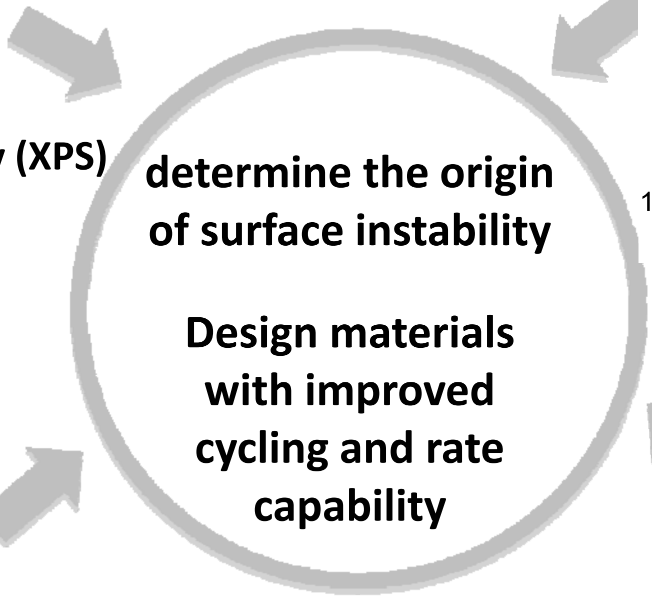
Bare LiCoO$_2$ after 20 cycles



Surface Chemistry:

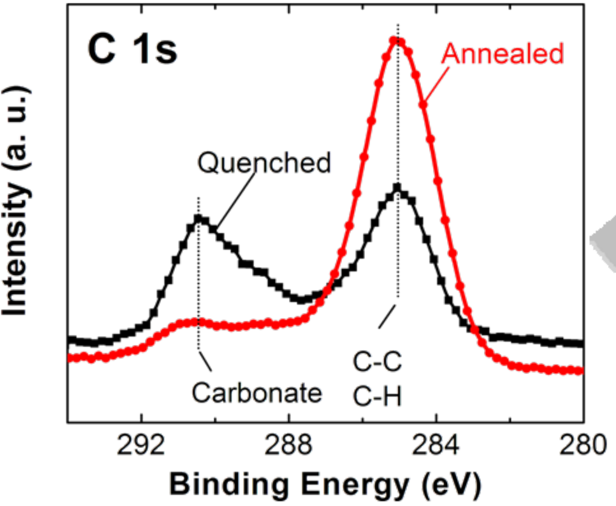
X-ray photoelectron spectroscopy (XPS)

X-ray absorption spectroscopy

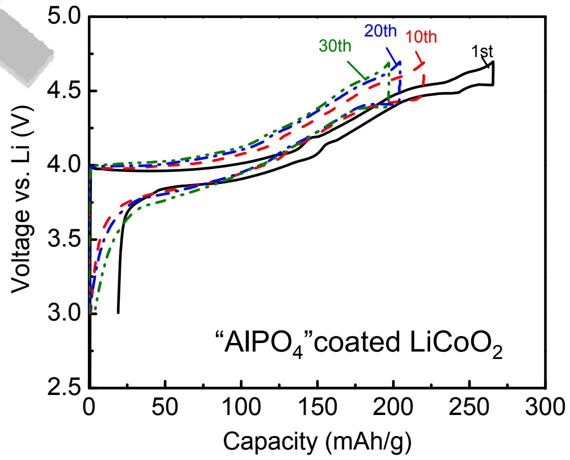


determine the origin of surface instability

Design materials with improved cycling and rate capability

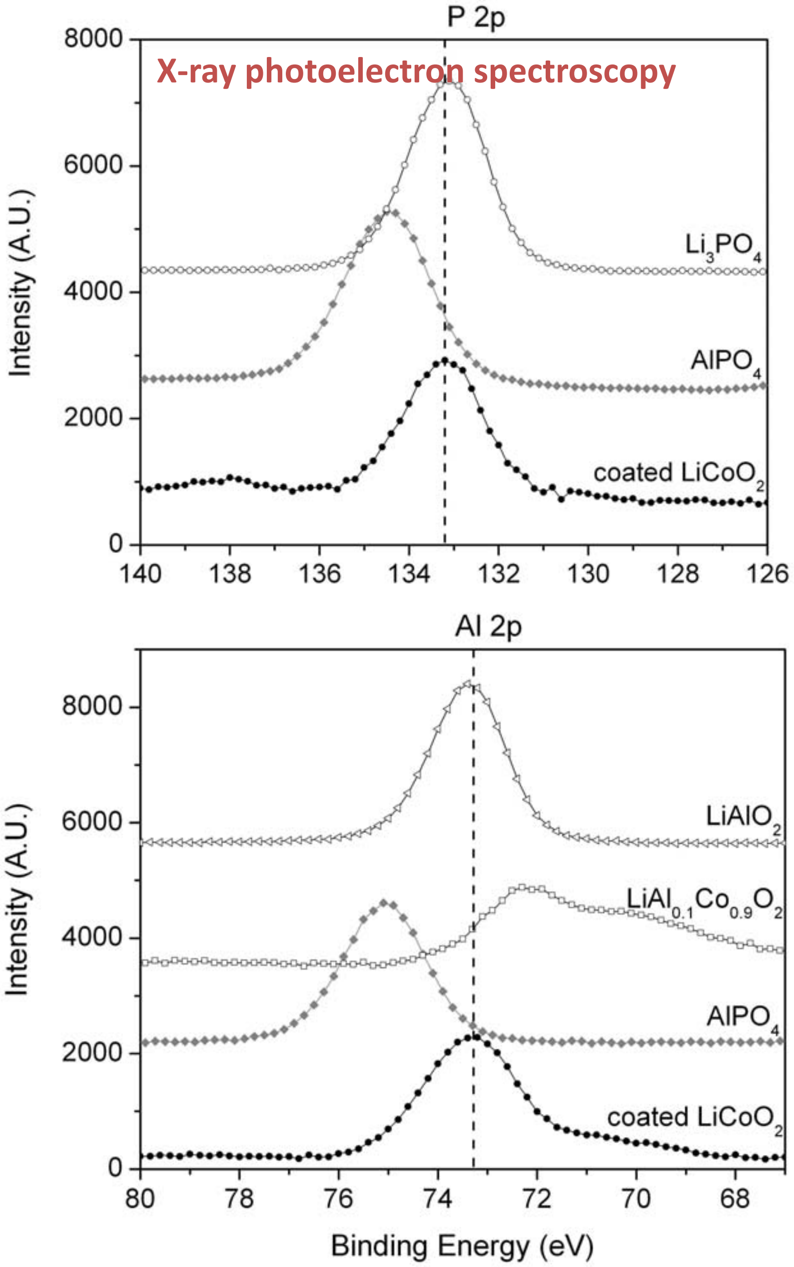


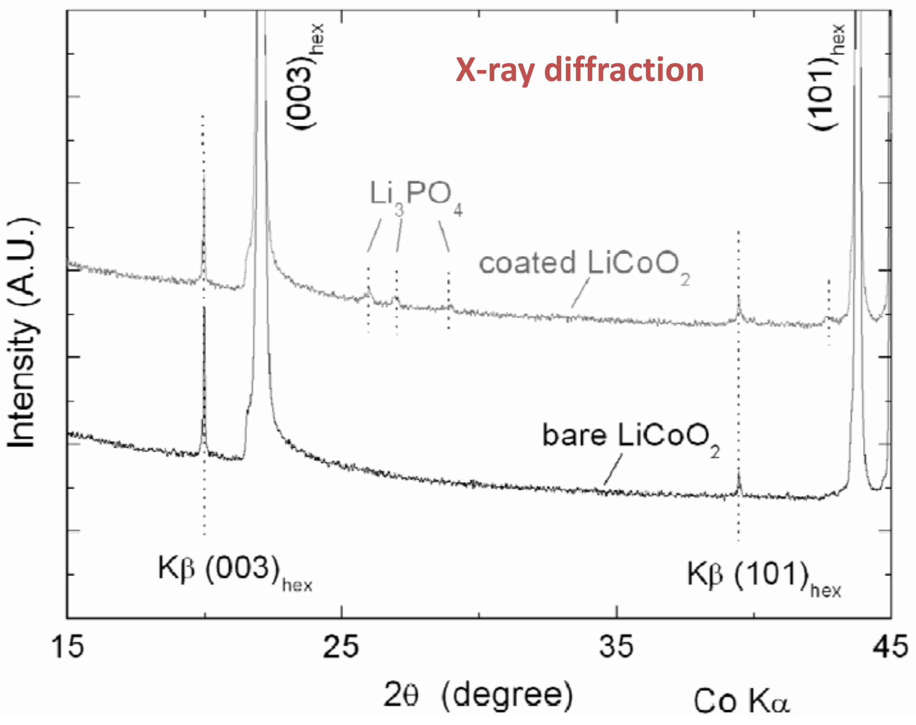
Electrochemical Reactivity:



In collaboration with Azzam Mansour

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - I





Previous findings:

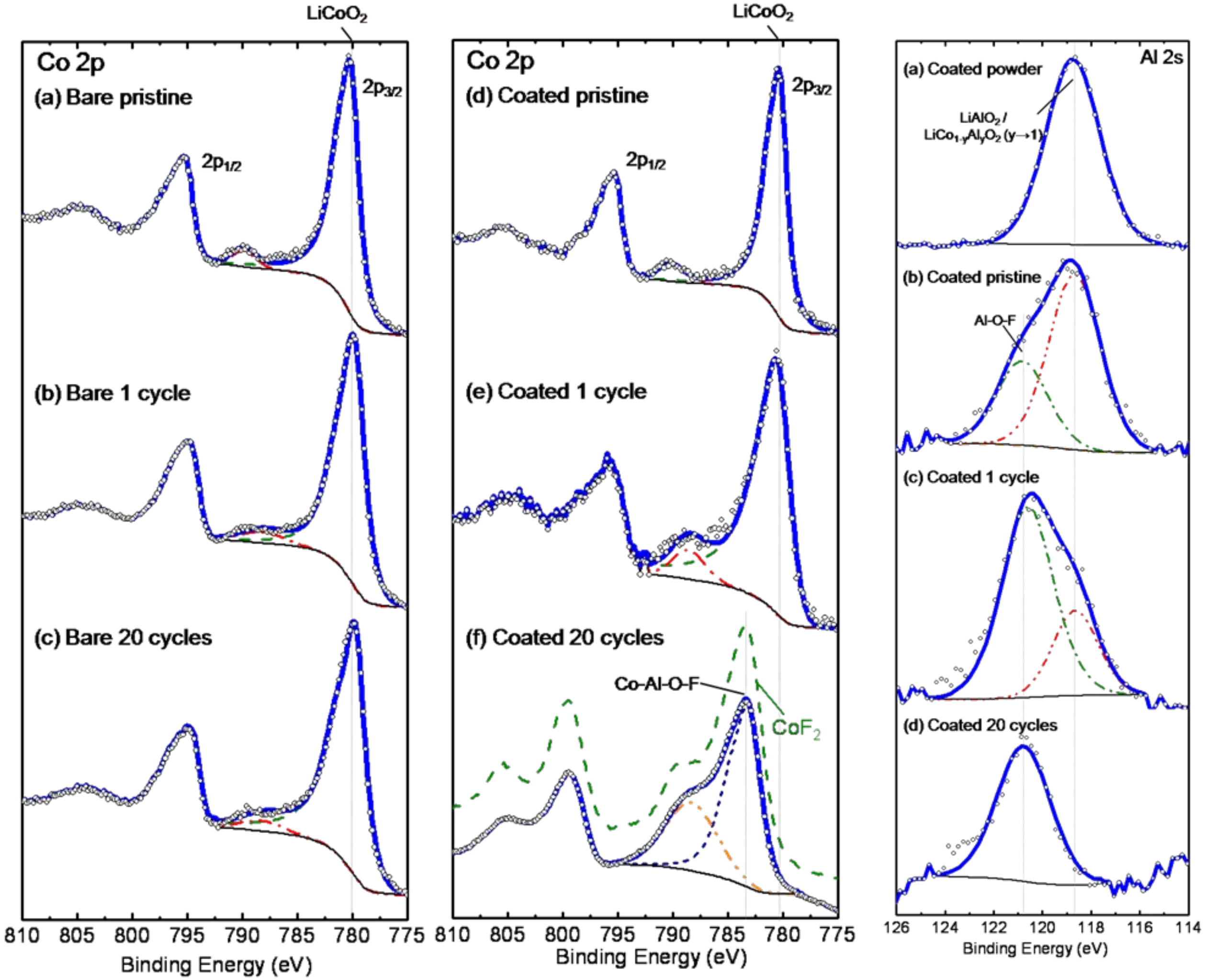
identified phases present in the "$AlPO_4$" coating

- **Al-rich surface regions: $LiAlO_2$**
- **P-rich surface regions: Li_3PO_4**

Appapillai and Shao-Horn et al, Chemistry of Materials, 2007

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with “$AlPO_4$” surface modification - II

XPS-I: the changes in the surface metal chemistry of bare and “$AlPO_4$”-coated electrodes during cycling



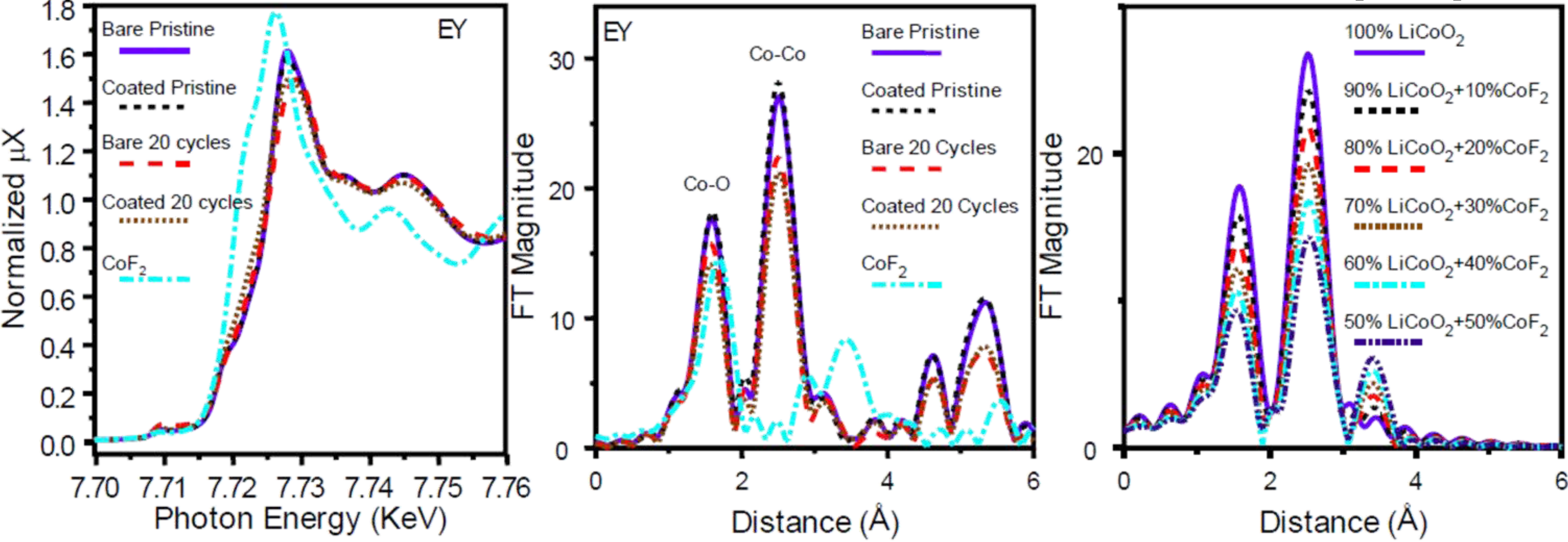
Lu and Shao-Horn et al,
Chemistry of materials,
submitted 2009

Bare: No apparent changes for Co chemistry

Coated: Surface coating promote Co-containing and Al-containing fluorides and/or oxyfluorides formation

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - IIIa

Electron-Yield XAS-I: the changes in the surface metal chemistry of bare and "$AlPO_4$"-coated electrodes during cycling



Simulation for $CoF_2+LiCoO_2$

- XANES:
  - Bare: a small change after cycling.
  - Coated: a significant change in after cycling, which is consistent with the formation of surface CoF_2 and/or oxyfluorides.
- EXAFS:
  - Bare: reduction in the amplitude of Co-Co contribution after cycling
    - the origin: surface structural damage
  - Coated: reduction in the amplitude of Co-Co contribution after cycling
    - the origin: the formation of CoF_2 and/or oxyfluorides as suggested by theoretical simulation of a mixture of $LiCoO_2$ and CoF_2.

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - IIIb

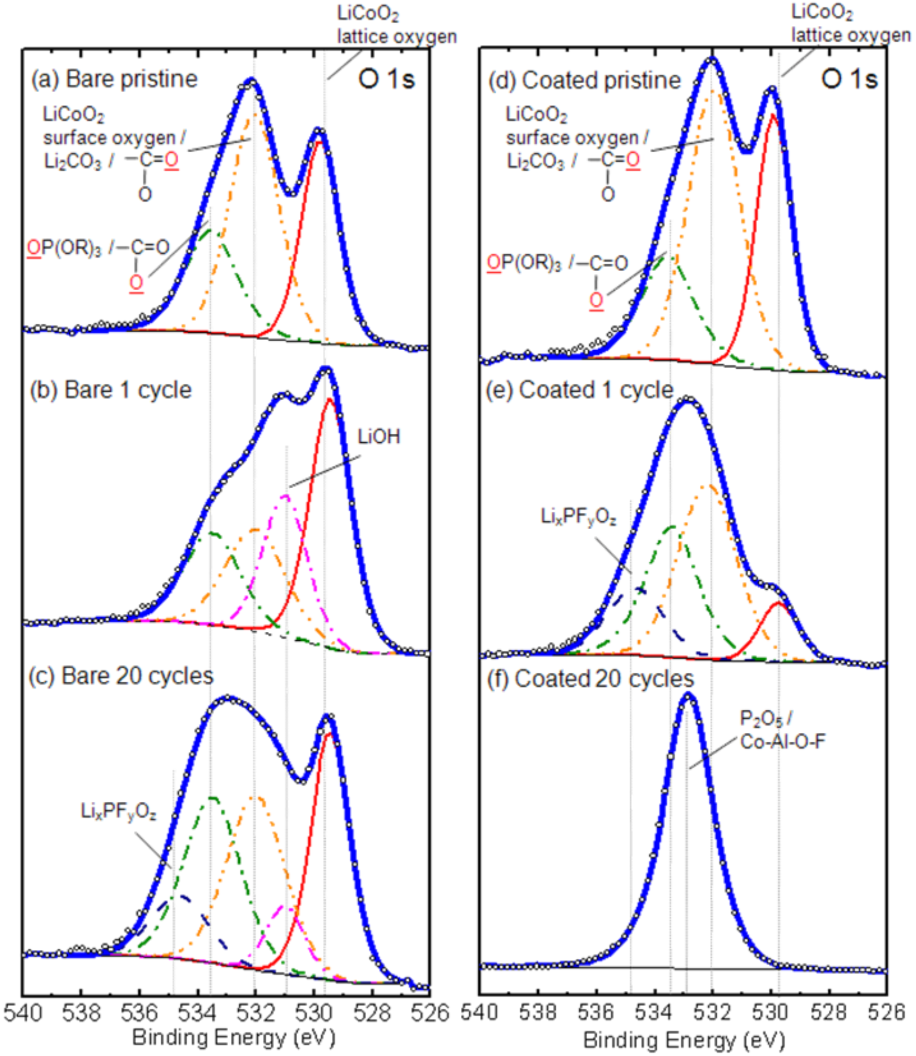
Transmission and Electron-Yield XAS-I: the changes in the bulk and surface metal chemistry of bare and "$AlPO_4$"-coated electrodes during cycling

Sample	Mode	$N_{Co\text{-}O}$	$R_{Co\text{-}O}$ (Å)	$\sigma^2_{Co\text{-}Co}$ (10^{-3}Å^2)	$N_{Co\text{-}Co}$	$R_{Co\text{-}Co}$ (Å)	$\sigma^2_{Co\text{-}Co}$ (10^{-3}Å^2)
Bare pristine	Bulk	6.1±0.3	1.922	3.7±0.5	5.9±0.3	2.820	2.5±0.3
Bare 20 cycles	Bulk	5.8±0.3	1.914	4.0±0.6	6.2±0.3	2.826	4.1±0.4
Coated pristine	Bulk	6.0±0.3	1.927	3.6±0.5	6.1±0.3	2.818	2.5±0.3
Coated 20 cycles	Bulk	6.0±0.3	1.926	4.2±0.5	5.8±0.3	2.823	2.9±0.3
Bare pristine	Surface	6.1±0.3	1.929	4.5±0.5	5.9±0.3	2.821	3.2±0.3
Bare 20 cycles	Surface	5.5±0.3	1.916	4.6±0.6	5.2±0.3	2.823	3.7±0.4
Coated pristine	Surface	5.8±0.3	1.928	3.8±0.5	5.7±0.3	2.818	2.8±0.3
Coated 20 cycles	Surface	5.3±0.2	1.924	4.9±0.5	4.8±0.2	2.826	3.5±0.3
XRD ($LiCoO_2$)	N/A	6 Co-O	1.918		6 Co-Co	2.811	
XRD (CoF_2)	N/A	2 Co-F 4 Co-F	2.032 2.046		2 Co-Co	3.180	

- **Bare after 20 cycles:** bulk structure has higher degree of disorder relative to pristine.
- **Coated after 20 cycles:** bulk structure retained same degree of disorder as pristine.
- **Coated after 20 cycles:** reduction in Co-Co coordination is consistent with the formation of CoF_2-like species

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - IV

XPS-II: the changes in the surface oxygen chemistry of bare and "$AlPO_4$"-coated electrodes during cycling

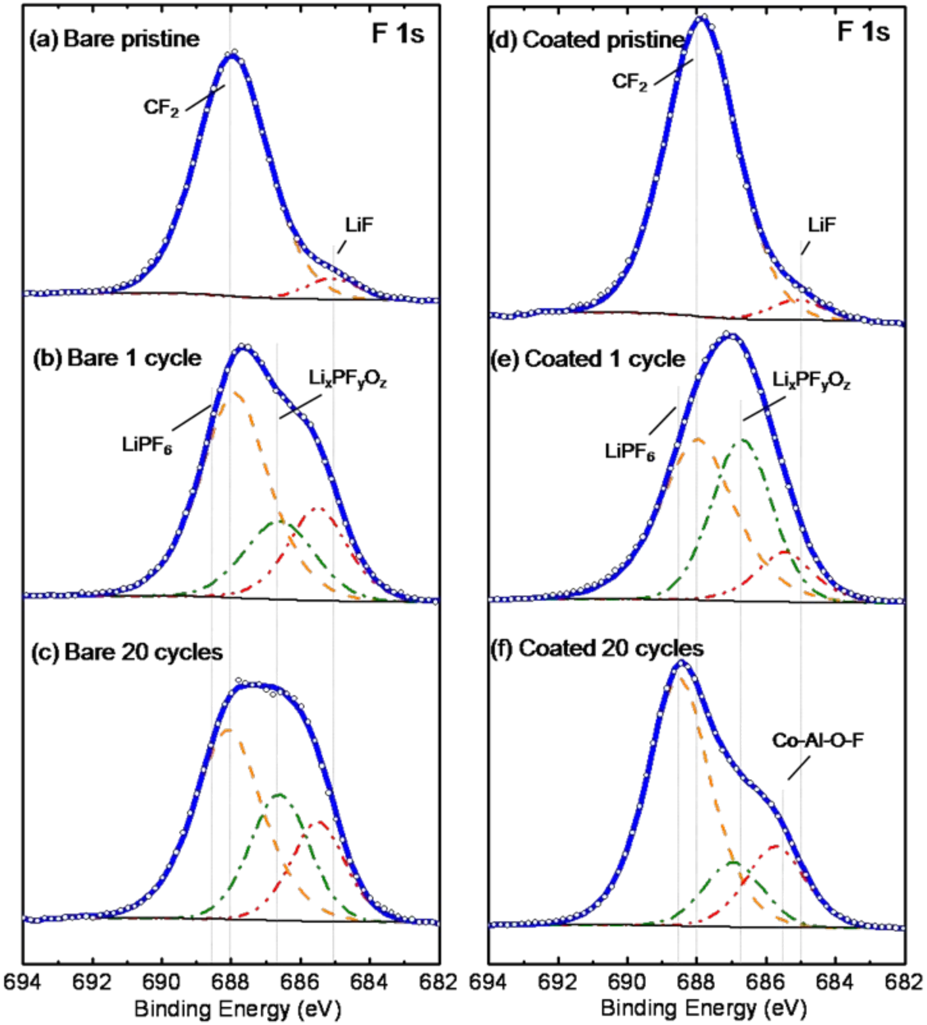


Bare: surface O environments dominated by those of resistant organic species such as $OP(OR)_3$ and $ROCO_2Li$ with high oxygen binding energies

Coated: surface O environments dominated by P_2O_5 and those of oxyfluoride species

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - V

XPS-III: the changes in the surface fluorine chemistry of bare and "$AlPO_4$"-coated electrodes during cycling



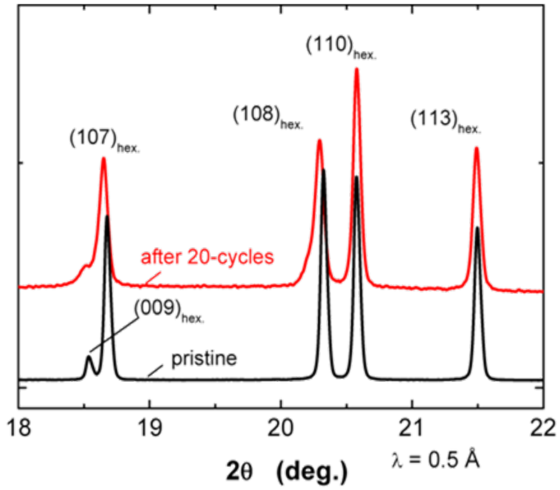
Bare: surface F environments dominated by LiF

Coated: surface F environments dominated by Co- and Al-containing oxyfluorides and less LiF

Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - VI

XRD-I: the changes in the bulk structure of bare and "$AlPO_4$"-coated electrodes during cycling

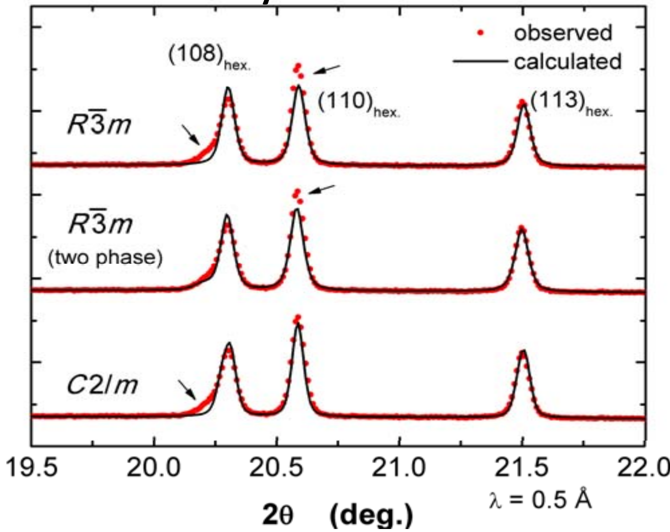
Bare



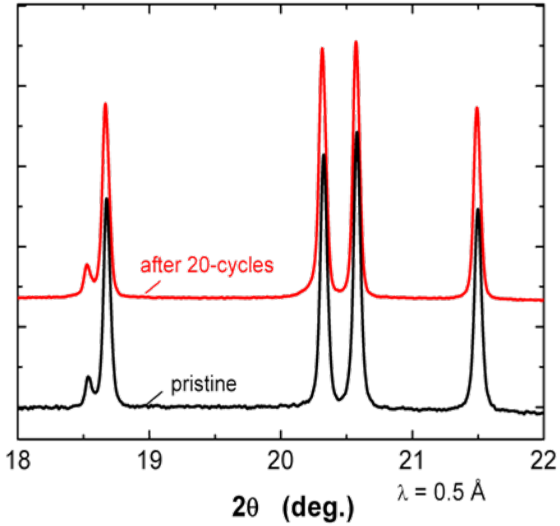
$(10l)_{hex}$ peaks was broadened selectively toward lower angles after cycling →

- cannot be explained by monoclinic distortion
- cannot be explained by two Rhombohedral phases

Bare after 20 cycles



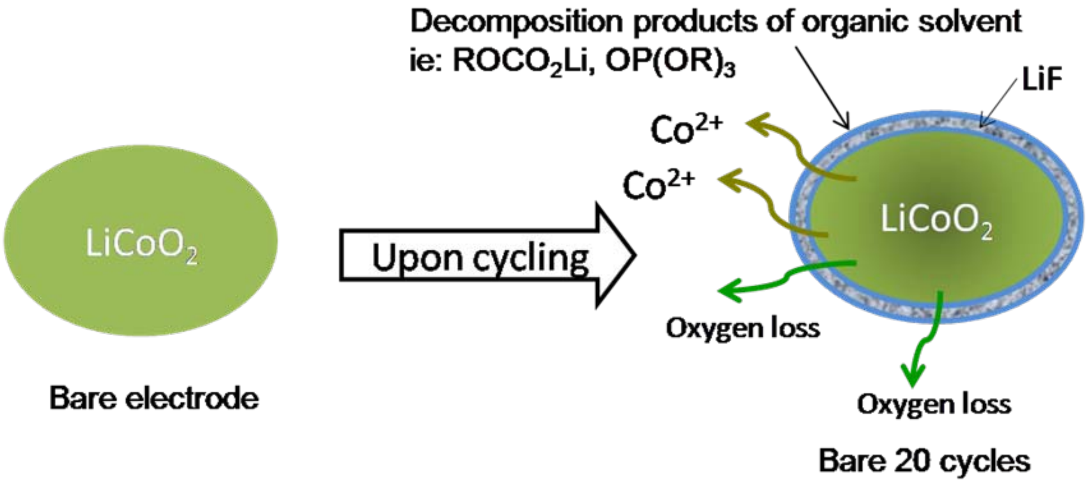
"$AlPO_4$" -coated



Bare: bulk structure damage ➔ oxygen loss
Coated: bulk structure intact

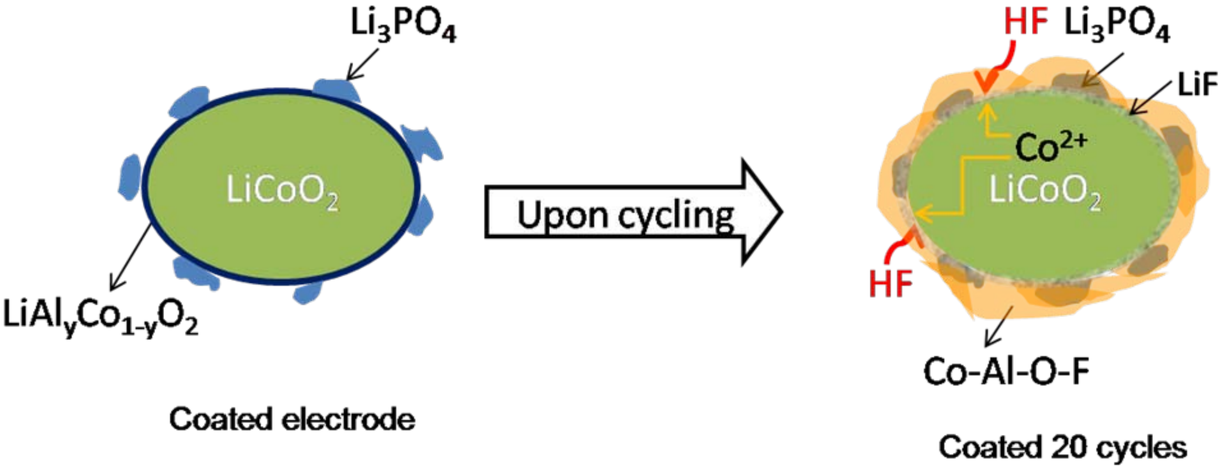
Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification - VII

Hypothesis: the origin of enhanced stability of "$AlPO_4$"-coated electrodes during cycling



Bare:

- ➢Forms highly resistant organic species on the surface, significantly increase the polarization.
- ➢ Co dissolution and oxygen loss lead to structural instability.

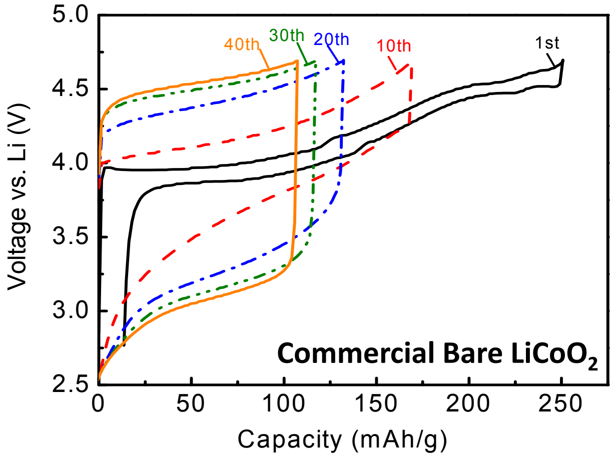


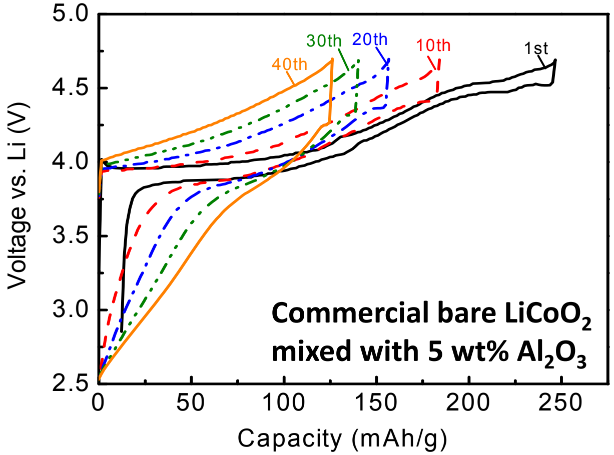
"$AlPO_4$"-Coated:

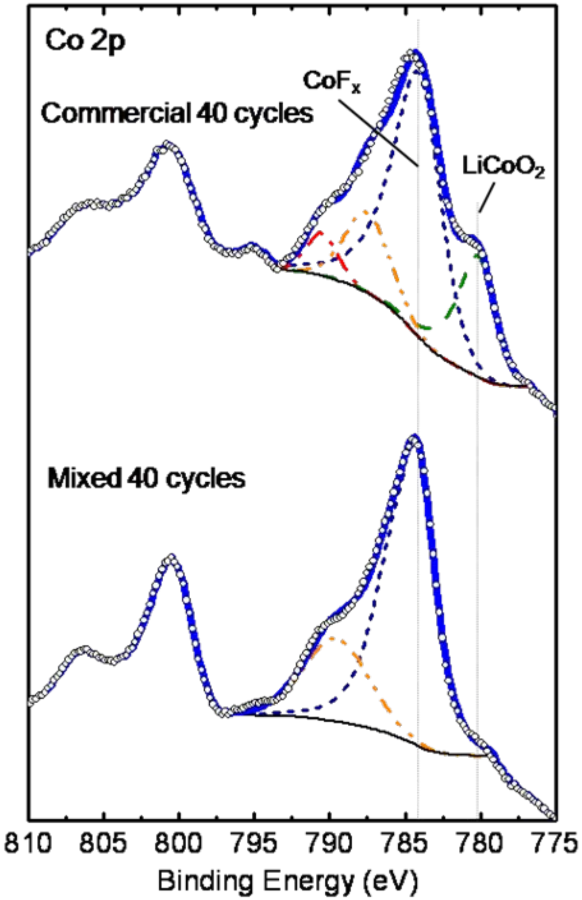
- ➢ Forms surface Co-Al-O-F oxyfluorides by reacting with HF.
- ➢ surface Co-Al-O-F oxyfluorides reduces the amount of resistant surface organic species and LiF, and reduces further Co dissolution and bulk oxygen loss.

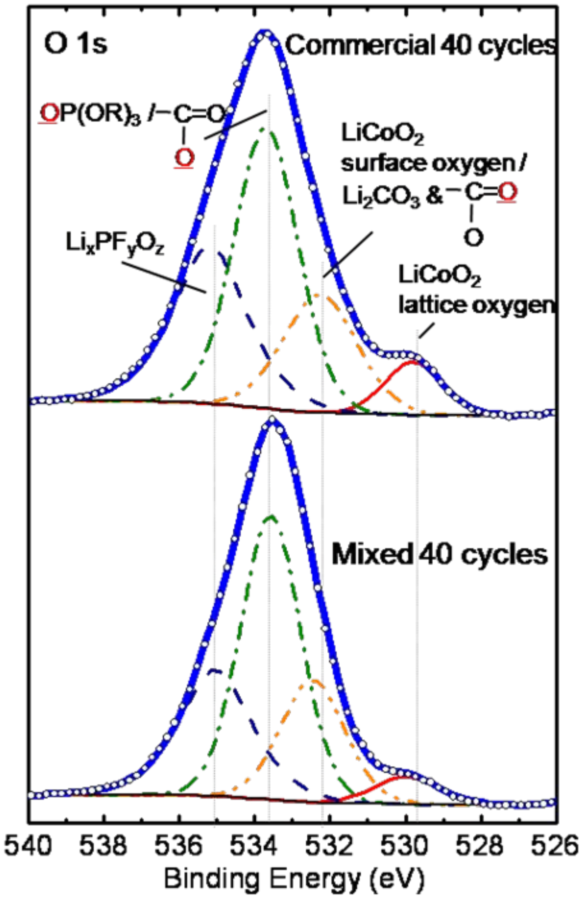
Results: Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with “$AlPO_4$” surface modification - VIII

Test of Hypothesis: mixing “Al_2O_3” in the positive electrode should lead to enhanced stability during cycling









mixing “Al_2O_3” in the positive electrode ➔ *enhanced capacity retention and reduced polarization*

mixing “Al_2O_3” in the positive electrode ➔ *leads to higher coverage of surface Co-Al-containing fluorides and or oxyfluorides, which supports the proposed hypothesis.*

Results: Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability - I

Synthesis conditions of $LiNi_{0.5}Mn_{0.5}O_2$ and phase identification by XRD

1.0 M TM metal ($NiNO_3$: $MnNO_3$ = 1 : 1) 50 ml

1.2 M TMAH
(tetramethyl ammonium hydroxide)
with NH_4OH sol.
100 ml

at 20 °C (N_2)

$Ni_{0.5}Mn_{0.5}(OH)_2$

at 680 °C for 12 h (Air)

$NiMnO_3$

Li_2CO_3
($NiMnO_3$: Li_2CO_3 = 1.00 : 1.03)

mixing with mortar
and pestle and
then pelletizing

1000 °C for 30min
Quenched @ 1000 °C

Quenched $LiNi_{0.5}Mn_{0.5}O_2$

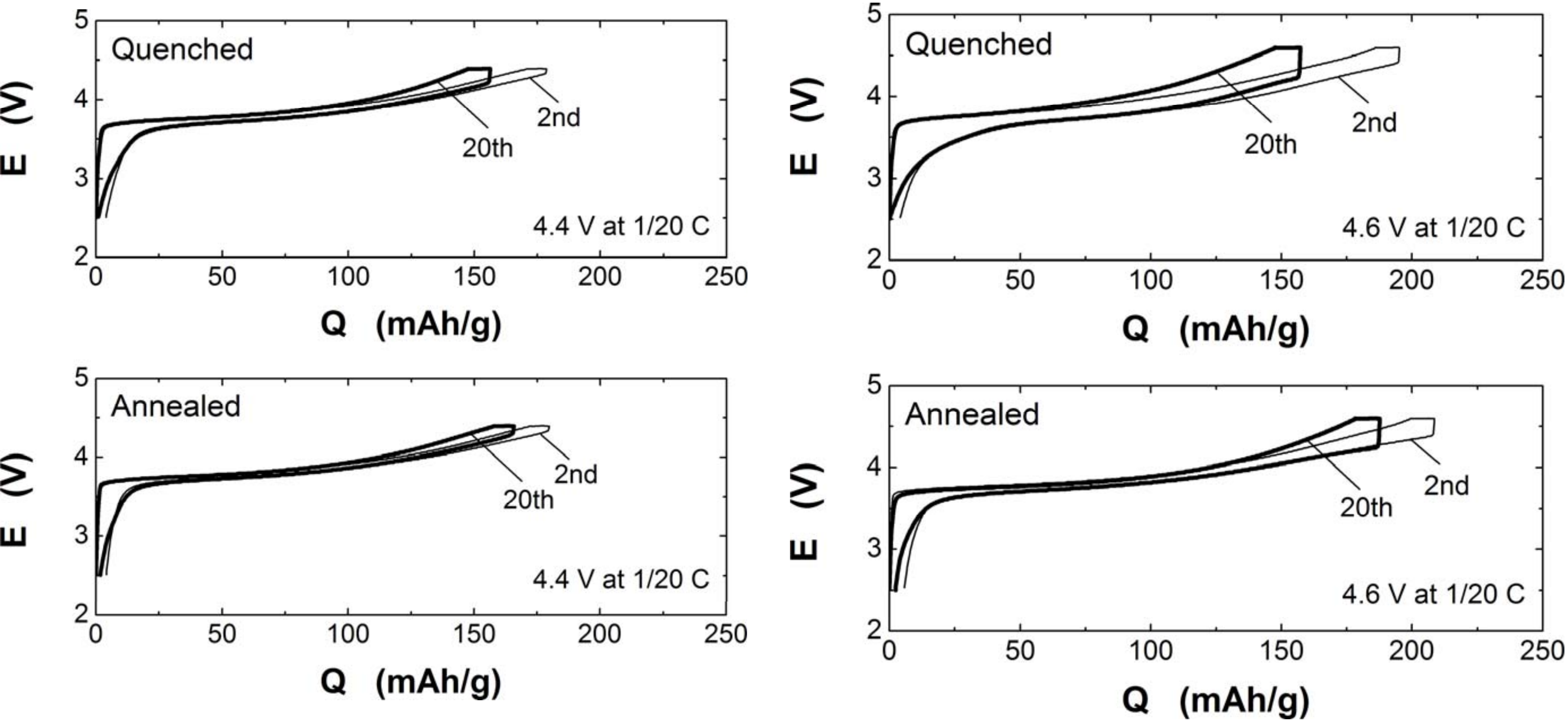
Annealing @ 700 °C
for 12hr

Annealed $LiNi_{0.5}Mn_{0.5}O_2$

Yabuuchi and Shao-Horn et al,
Electrochemistry Communications,
submitted

Results: Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability - II

Electrochemical testing-I: Capacity retention during cycling

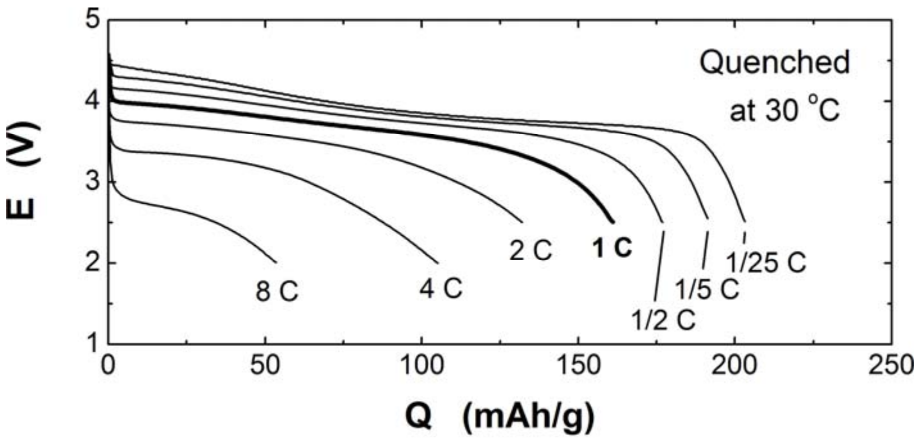


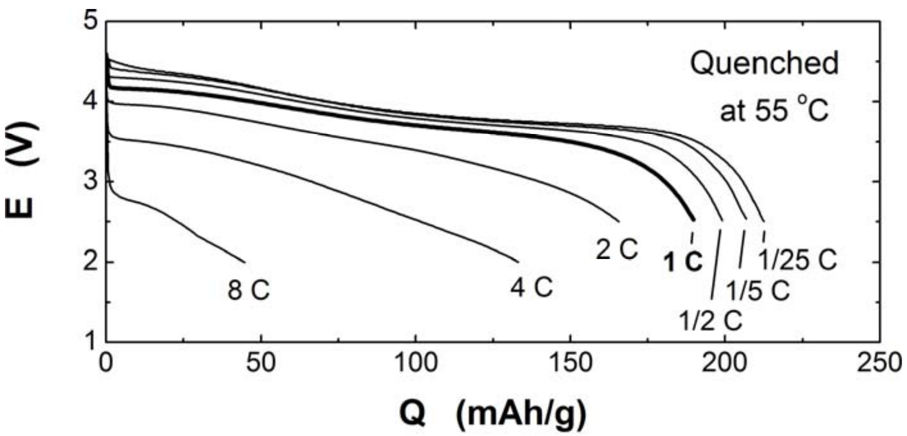
The annealed $LiNi_{0.5}Mn_{0.5}O_2$ has better capacity retention during cycling to 4.4 and 4.6 V vs. Li in comparison to quenched $LiNi_{0.5}Mn_{0.5}O_2$

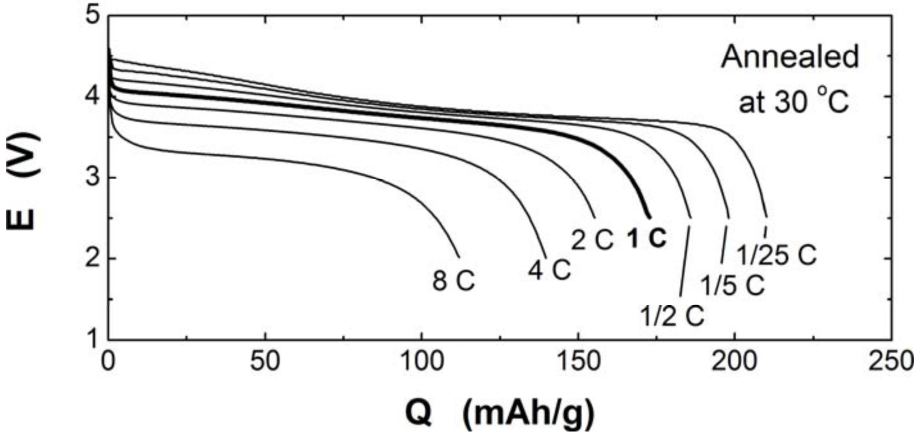
Yabuuchi and Shao-Horn et al, Electrochemistry Communications, submitted

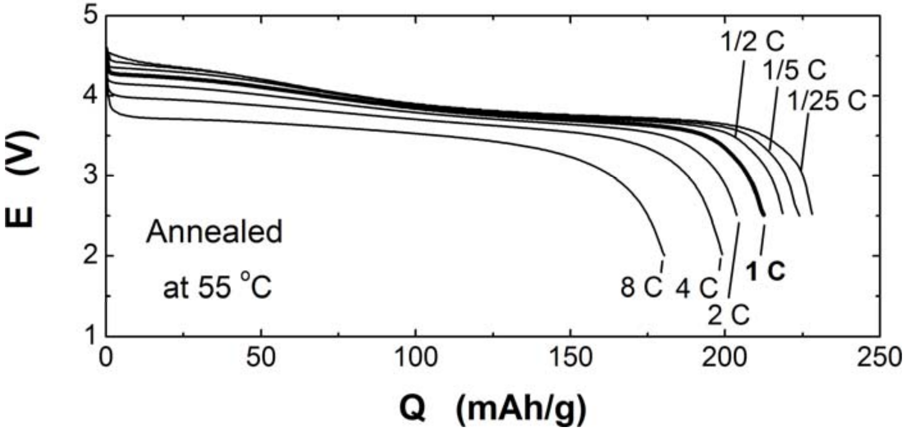
Results: Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability - III

Electrochemical testing-II: Rate capability at 30 °C and 55 °C







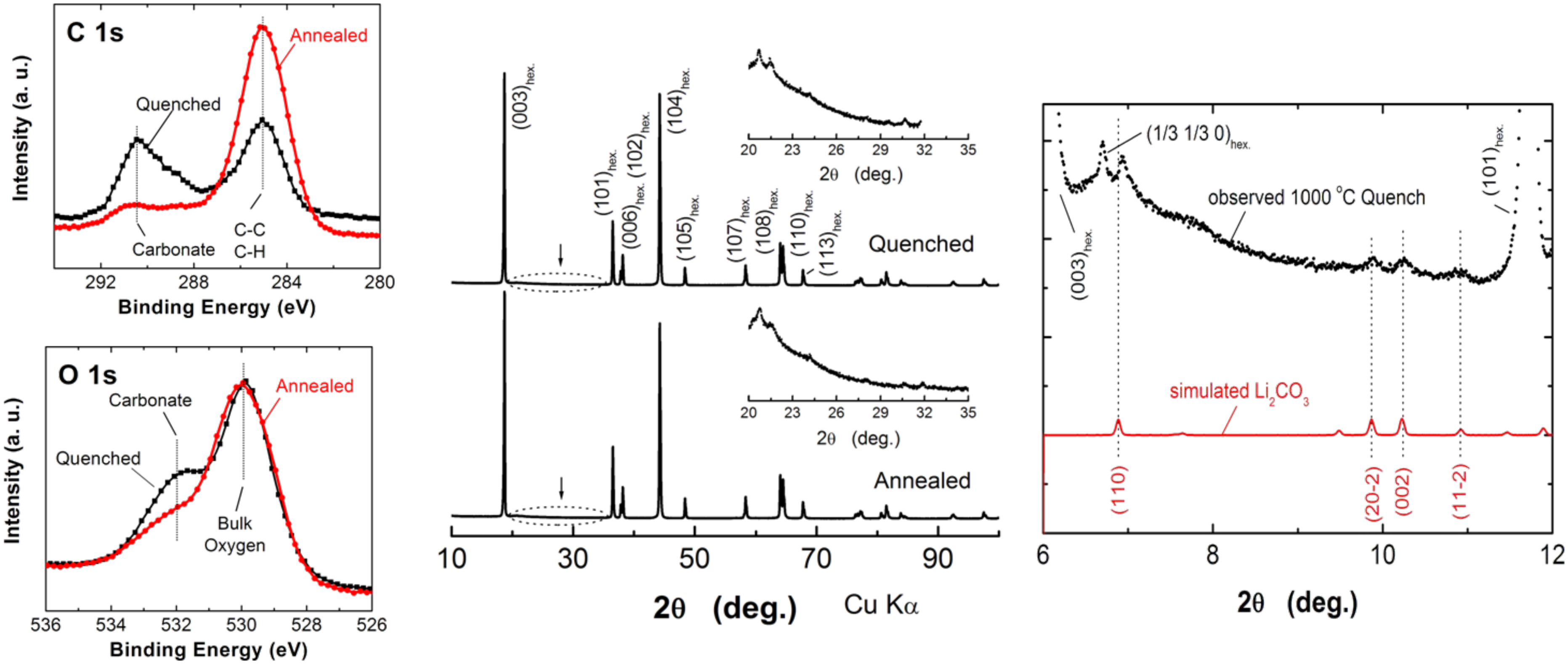


Annealed $LiNi_{0.5}Mn_{0.5}O_2$ has much better rate capability at 30 °C and 55 °C in comparison to quenched $LiNi_{0.5}Mn_{0.5}O_2$
Annealed $LiNi_{0.5}Mn_{0.5}O_2$ exhibits >110 mAh/g at a rate of 8 C.

Yabuuchi and Shao-Horn et al, Electrochemistry Communications, submitted

Results: Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability - IV

XPS-I and XRD-I: Surface carbon and oxygen chemistry of quenched and annealed $LiNi_{0.5}Mn_{0.5}O_2$



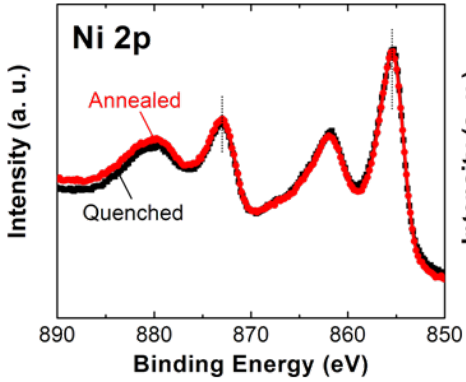
Annealed $LiNi_{0.5}Mn_{0.5}O_2$ has less surface Li_2CO_3 in comparison to quenched $LiNi_{0.5}Mn_{0.5}O_2$
Annealing reduces surface Li_2CO_3.

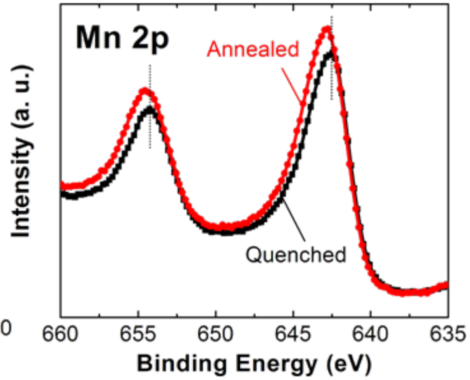
Yabuuchi and Shao-Horn et al, Electrochemistry Communications, submitted

Results: Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability - V

XPS-II: Surface metal chemistry of quenched and annealed $LiNi_{0.5}Mn_{0.5}O_2$

Hypothesis: the origin in the difference of surface chemistry of quenched and annealed $LiNi_{0.5}Mn_{0.5}O_2$





<u>Hypothesis:</u>

At 1000 °C, partial decomposition of $LiNi_{0.5}Mn_{0.5}O_2$ near the surface

$\rightarrow$ $\mathbf{xLi_2O}$ + $Li_{1-x/2}Ni_{0.5}^{2+}Mn^{4+}_{0.5-2/x}\mathbf{Mn^{3+}}_{2/x}O_2$

- Formation of the Li-poor phase (or metal-rich phase)
  - Some Mn ions are reduced to 3+.
- Li_2O changes into Li_2CO_3 during quenching

- **Increased binding energy of Mn upon annealing**
  - **due to oxidation of Mn^{3+} to Mn^{4+}**
- **Ni-rich surface with Ni/Mn ratio greater than 1**
- **The extent of Ni-enrichment on the surface is reduced during annealing**

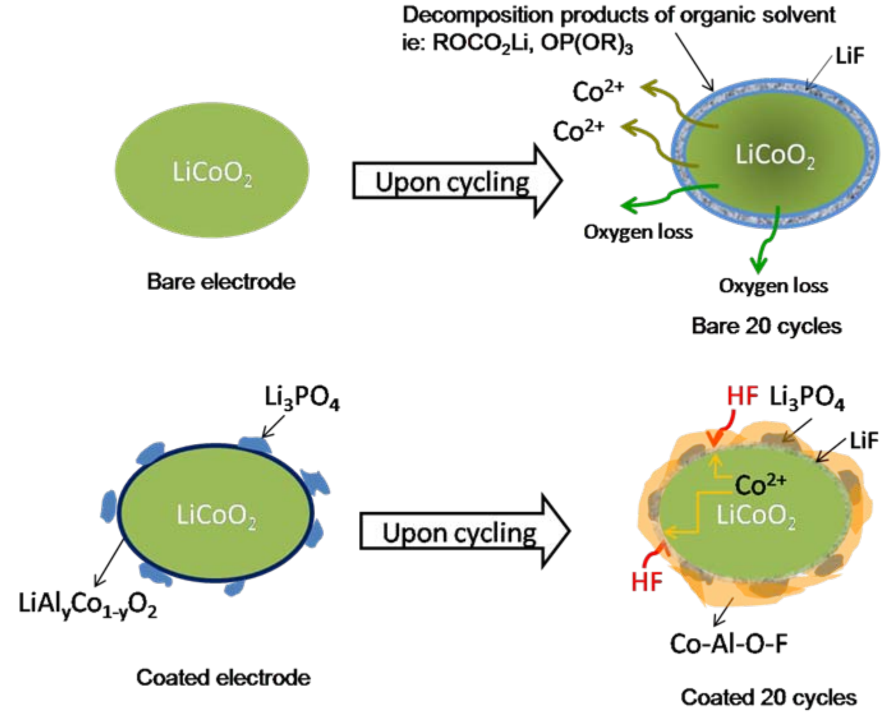
Annealing process at 700 °C; Li_2CO_3 near the surface reacts with Li poor phase

- Formation of a nearly stoichiometric phase –
  - $Li^{+}_{0.9}Ni^{2+}_{0.1})_{3b}(Li^{+}_{0.1}Ni^{2+}_{0.4}Mn^{4+}_{0.5})_{3a}O_2$
  - Less lithium carbonate
  - oxidized Mn into 4+
- Reduced Ni occupation in the Li layer from XRD (~2%)

Yabuuchi and Shao-Horn et al, Electrochemistry Communications, submitted

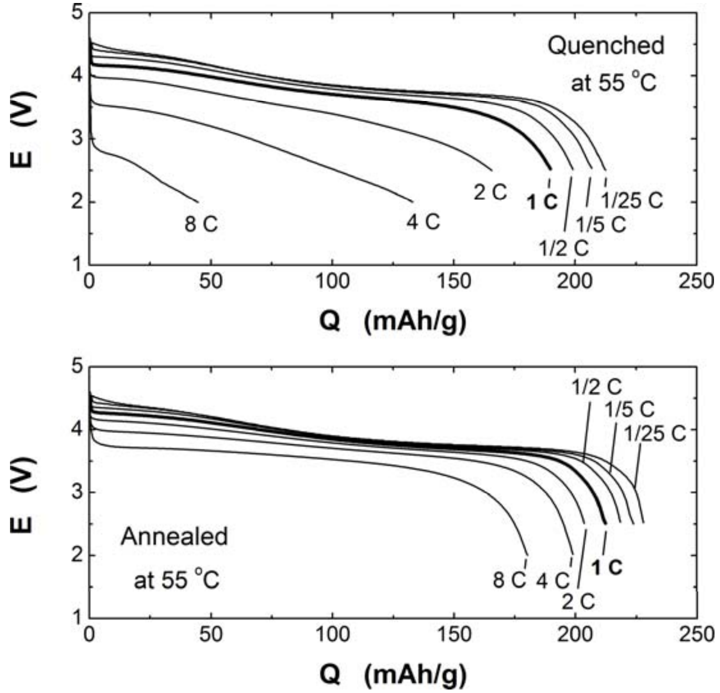
Summary

Probing the origin of surface instability of Li_xCoO_2 and the enhanced stability associated with "$AlPO_4$" surface modification



- ➢ Coating promotes the formation of surface Co-Al-O-F oxyfluorides.
- ➢ Surface Co-Al-O-F oxyfluorides reduces the amount of resistant surface organic species and LiF, and reduces further Co dissolution and bulk oxygen loss ➔ enhanced capacity retention during cycling to high voltages

Probing the effects of synthesis conditions and surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ on the cycling performance and rate capability



- ➢ Annealed $LiNi_{0.5}Mn_{0.5}O_2$ has much improved capacity retention and rate capability relative to quenched $LiNi_{0.5}Mn_{0.5}O_2$
- ➢ The presence of surface Mn^{3+} species on the quenched can lead to high-resistance surface films, which reduces capacity retention and rate capability during cycling.

Ongoing and Planned Activities

- Further probing the formation mechanism of metal oxyfluoride-like species on lithium storage oxide surfaces during electrochemical cycling and test the hypothesis that the presence of surface metal fluorites protects the surface and suppress the growth of resistive, high-impedance layer during cycling.

- Investigating the role of the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ obtained from different processing conditions on the rate capability, reversible capacity and cycling stability of $LiNi_{0.5}Mn_{0.5}O_2$ electrodes.

- Studying functionalized carbon nanotube based positive electrodes for high-power applications. We have recently assembled functionalized multiwall carbon nanotube (MWNTs) thin film electrodes, where the thickness from the nanometer to micrometer scale can be controlled. Such electrodes have exhibited high specific and volumetric capacitance in aqueous environment (Lee and Shao-Horn et al., JACS 2009).

- XPS and synchrotron X-ray absorption data of oxide-based and carbon nanotube-based electrode materials will be collected in collaboration with Dr. A. Mansour at NSWC of the Carderock Division under the BATT program.