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

Yang Shao-Horn
Materials Science and Engineering and Mechanical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139
May 12, 2011

Project ID ES084

Overview

Timeline

- Start date: April 2010
- End date: May 2011 - renewing
- Percent complete:

  - project on-going

Barriers

- High cost
- Low energy density
- Poor cycle and calendar life
- Abuse tolerance limitations

Budget

- Total Project Funding: $945K
- FY10 funding: $315K
- FY09 funding: $315K
- FY08funding: $315K

Partners

- Lead PI: Yang Shao-Horn
- Co-PI: Azzam Mansour (NSWC)
- Collaborators: Michael M. Thackeray (ANL)

Research Objectives:

➢ To develop fundamental understanding of surface chemistry and bulk cation distributions on cycling performance and rate capability

➢ To design positive electrodes with stable electrode-electrolyte interface with improved cycling performance and rate capability

Research Approaches:

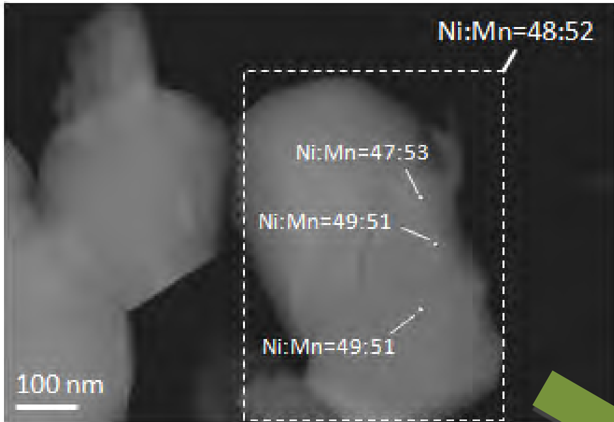
➢ Probing the ***surface chemistry*** of positive electrode materials before and after cycling using surface-sensitive electron microscopy, X-ray photoelectron spectroscopy and electron-yield X-ray adsorption spectroscopy.

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

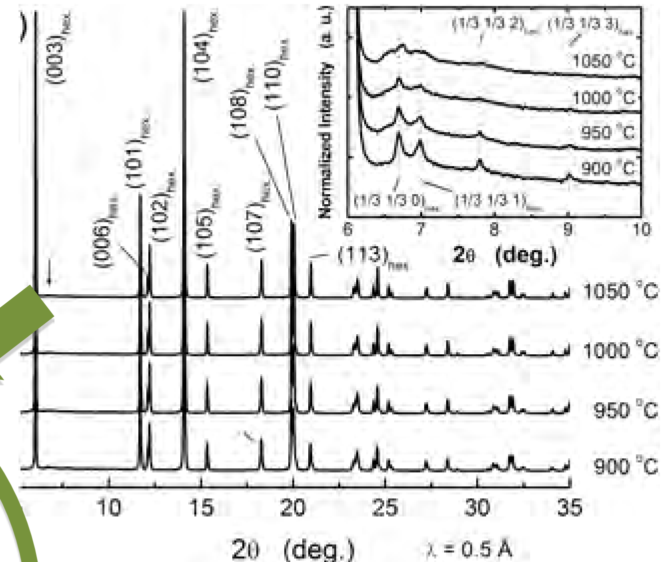
➢ Correlating surface chemistry and bulk structure information with ***electrochemical performance characteristics*** such as capacity retention and rate capability to determine the origin of surface instability.

Research Approach Overview

Surface and Bulk Chemistry: **Electron microscopy**



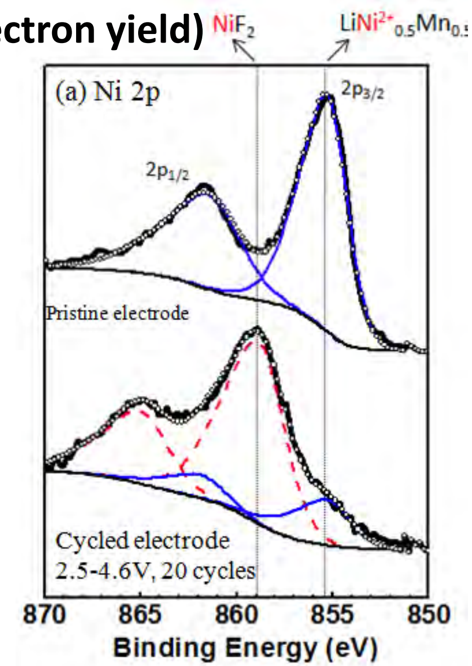
Bulk Structure: **Synchrotron X-ray diffraction & X-ray absorption spectroscopy (transmission)**



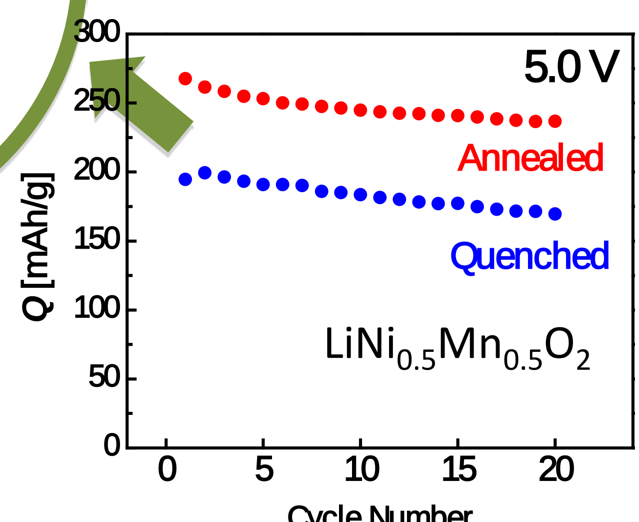
Determine the origin of surface instability & bulk degradation

Design materials with improved cycling and rate capability

Surface Chemistry:
X-ray photoelectron spectroscopy (XPS)
X-ray absorption spectroscopy (electron yield)



Electrochemical Reactivity:



Milestones FY10

Develop fundamental understanding in the relationship between the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ (ref. $LiCoO_2$) and rate/cycle characteristics - completed

Apply the fundamental understanding to design and develop stable surfaces of cycled high-energy cathodes - completed

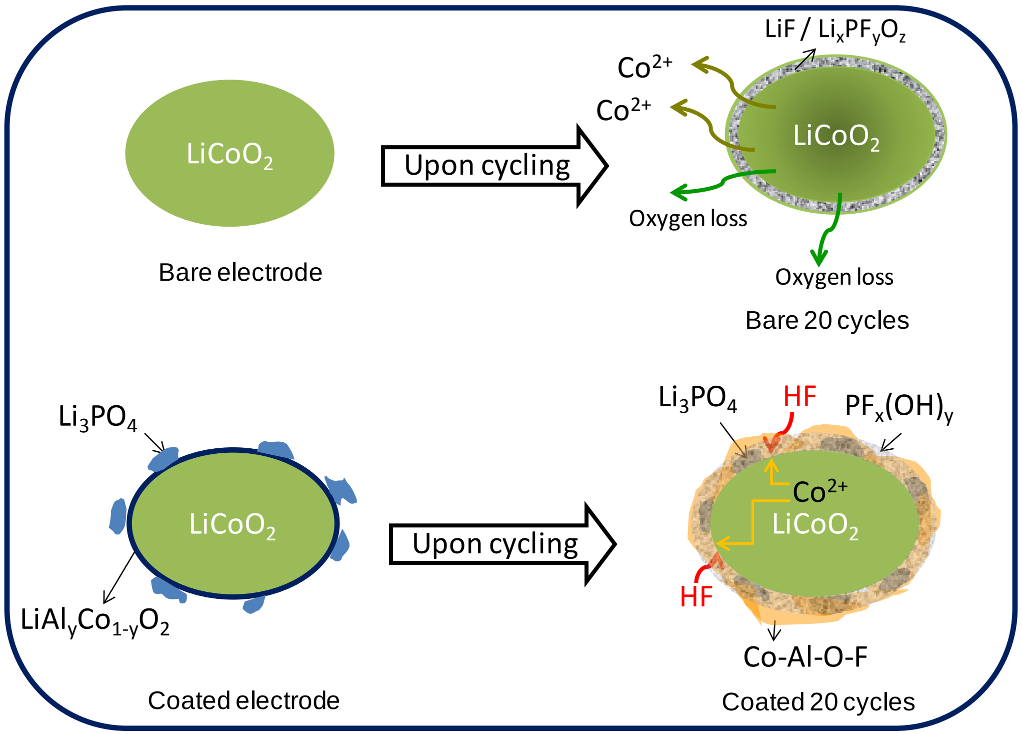
Develop angle resolved X-ray photoelectron spectroscopy (ARXPS) to study the surface chemistry of $LiNi_{0.5}Mn_{0.5}O_2$ and $LiCoO_2$ as a function of depth from surface - completed

Survey, synthesize and test select Li-rich $(Li_2O)_x(MO_2)_y$ (where M = Mn, Co, Ni, etc.) layered compounds – ongoing

Collect and analyze XPS and TEM data to study the surface chemistry changes of select Li rich $(Li_2O)_x(MO_2)_y$ during charge and discharge – to be performed

Identify the working principle of surface coatings on cathode

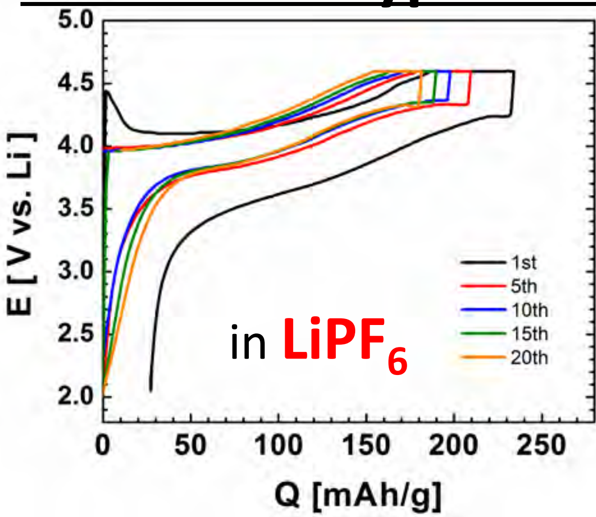
Proposed Mechanism



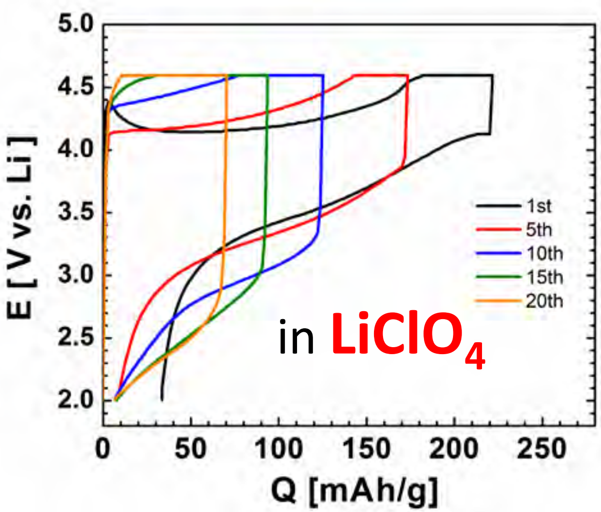
Shao-Horn et al, CM 2009

- **Formation of metal fluorides/oxyfluorides at the interface is key to achieve long cycle life and high efficiency**
- **Coating does not enhance capacity retention in $LiClO_4$-based electrolyte**

Test of the hypothesis

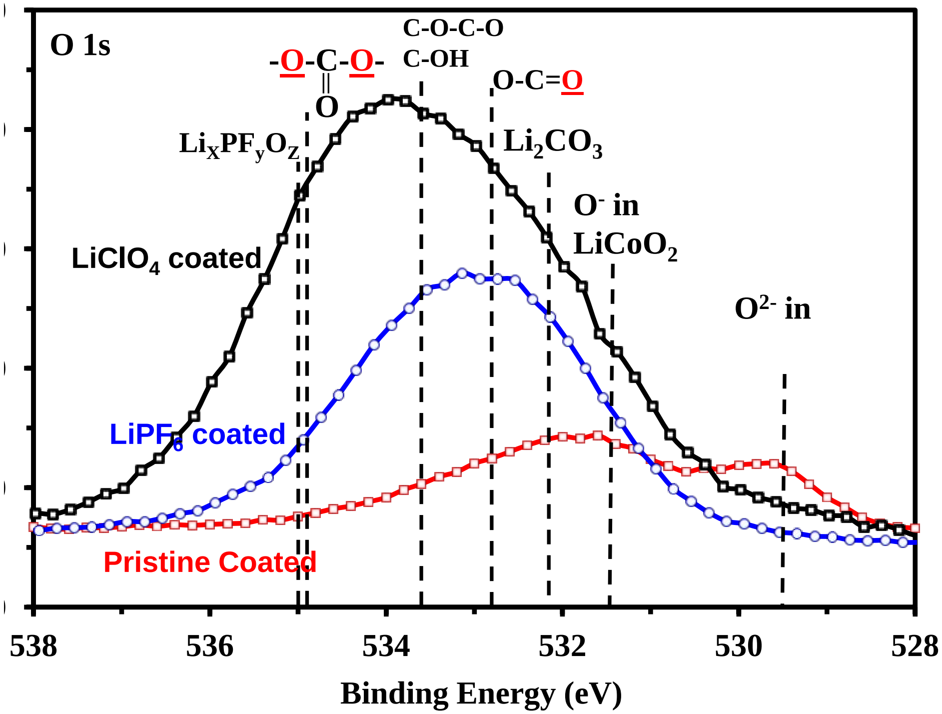


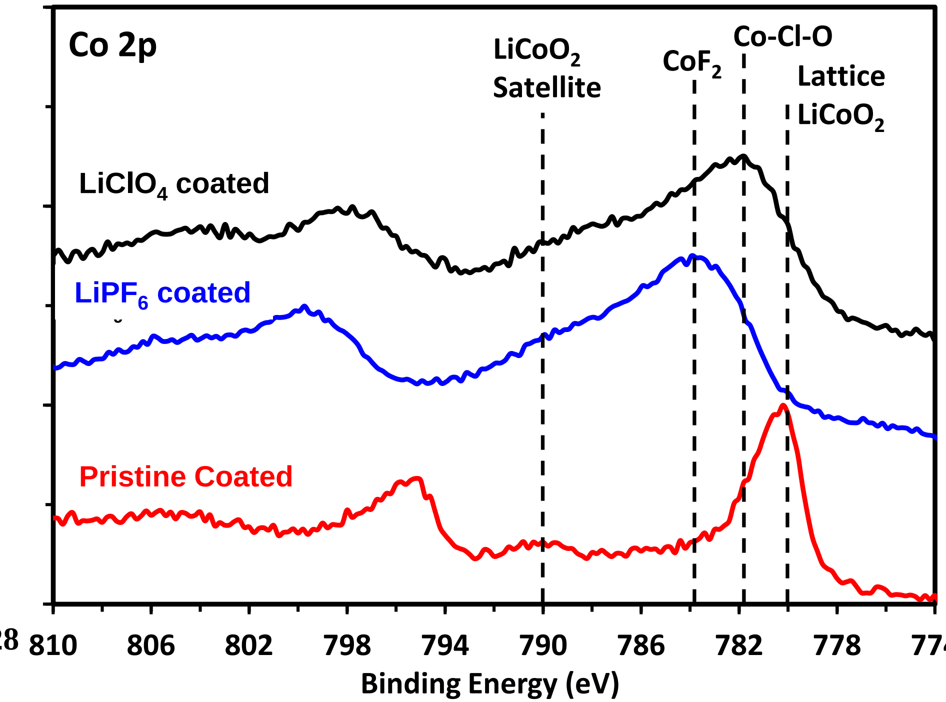
"$AlPO_4$"coated $LiCoO_2$
2.5-4.6V, 1/5C, 4.6V hold for 4hrs



Why doesn't "$AlPO_4$" coating enhance capacity retention in $LiClO_4$-based electrolyte?

X-ray photoelectron spectroscopy



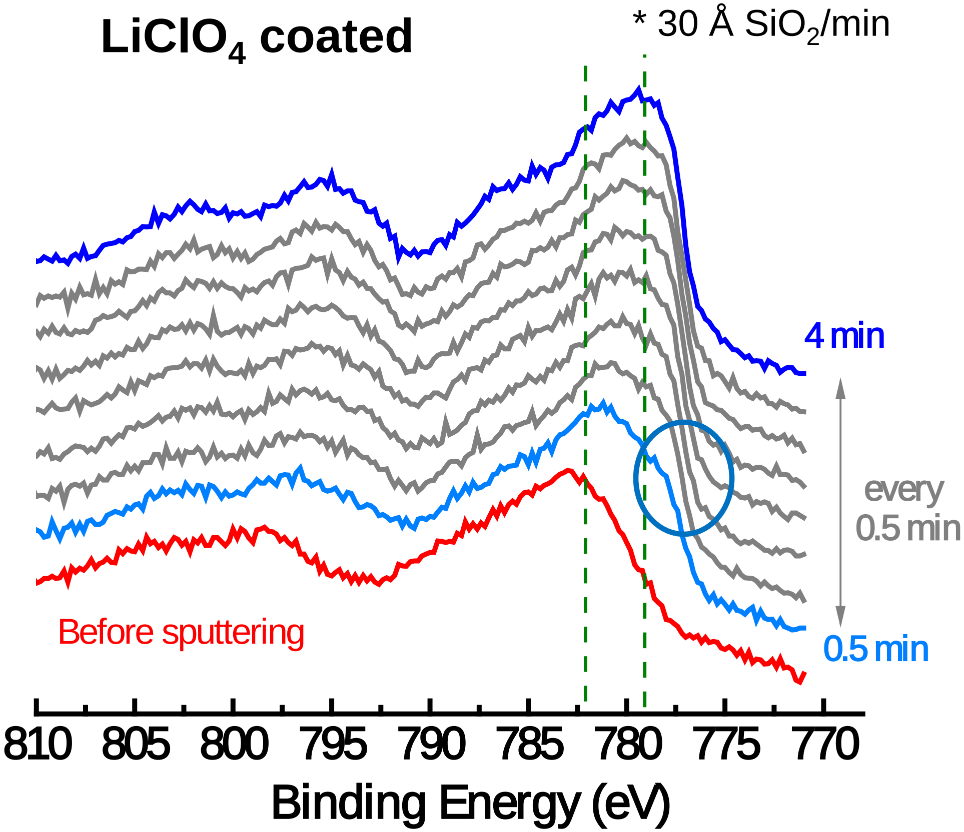


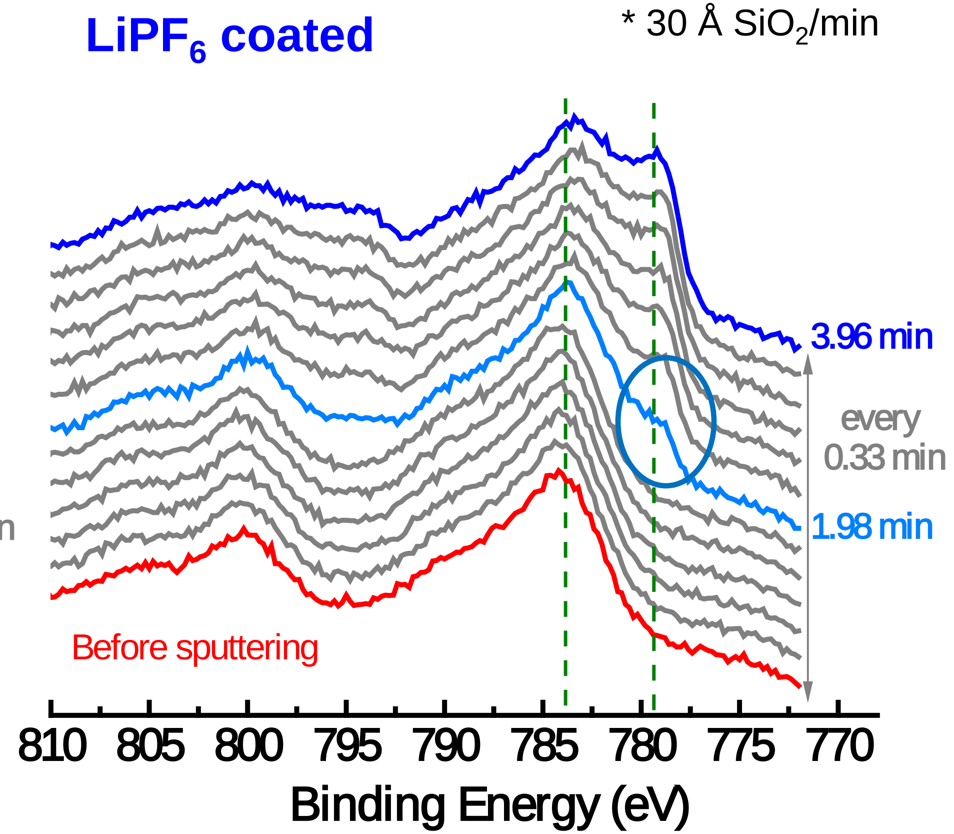
$LiPF_6$ → less organic decomposition
$LiClO_4$ → more organic decomposition

$LiPF_6$ → formation of CoF_2
$LiClO_4$ → no CoF_2

Formation of metal fluorides/oxyfluorides is key to enhance the cycle life.

X-ray photoelectron spectroscopy – depth profile



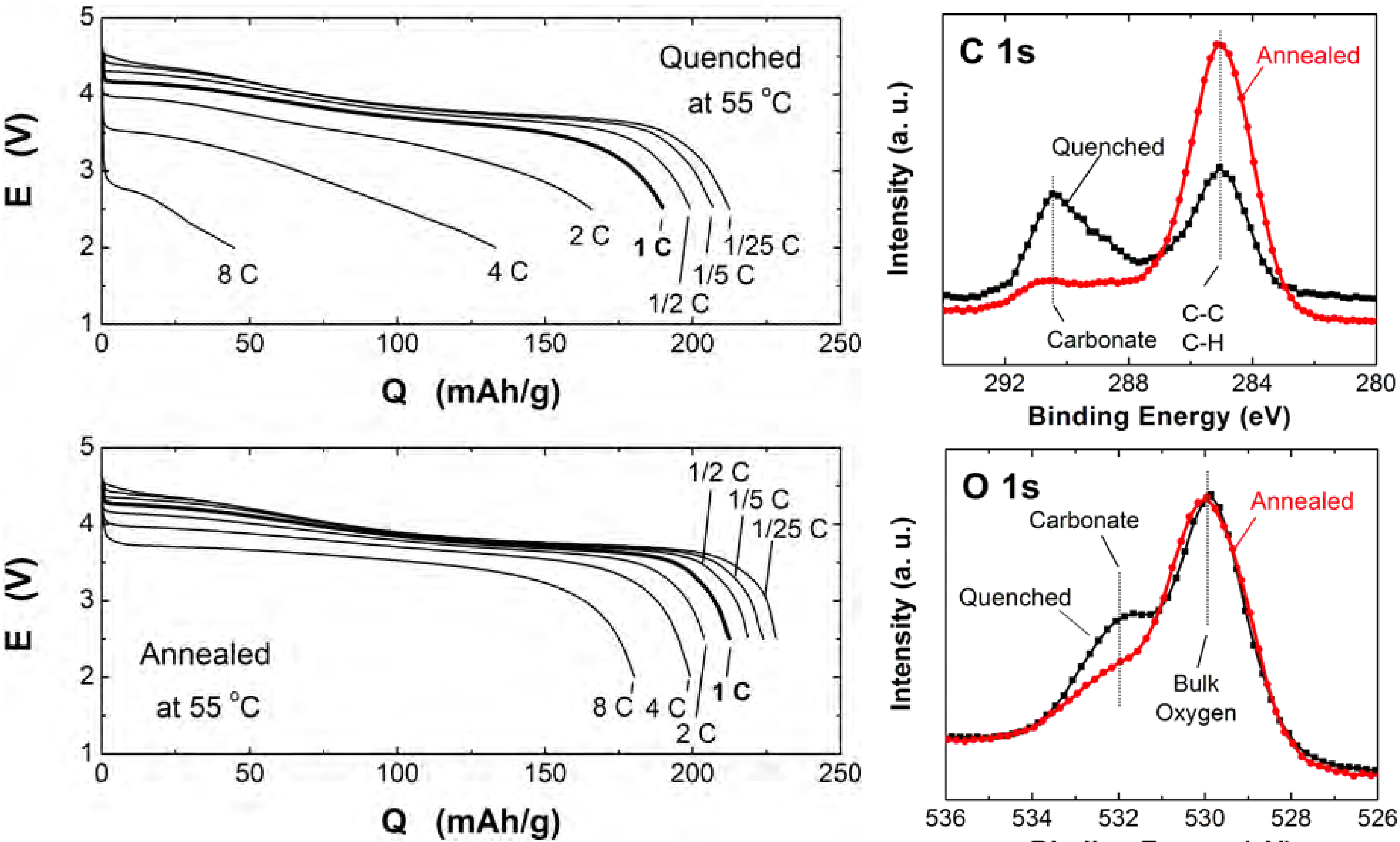


Bulk signal revealed after 0.5 min of sputtering

Bulk signal revealed after 2 min of sputtering

Right thickness (~5-6 nm) is key for a stable solid-electrolyte interface

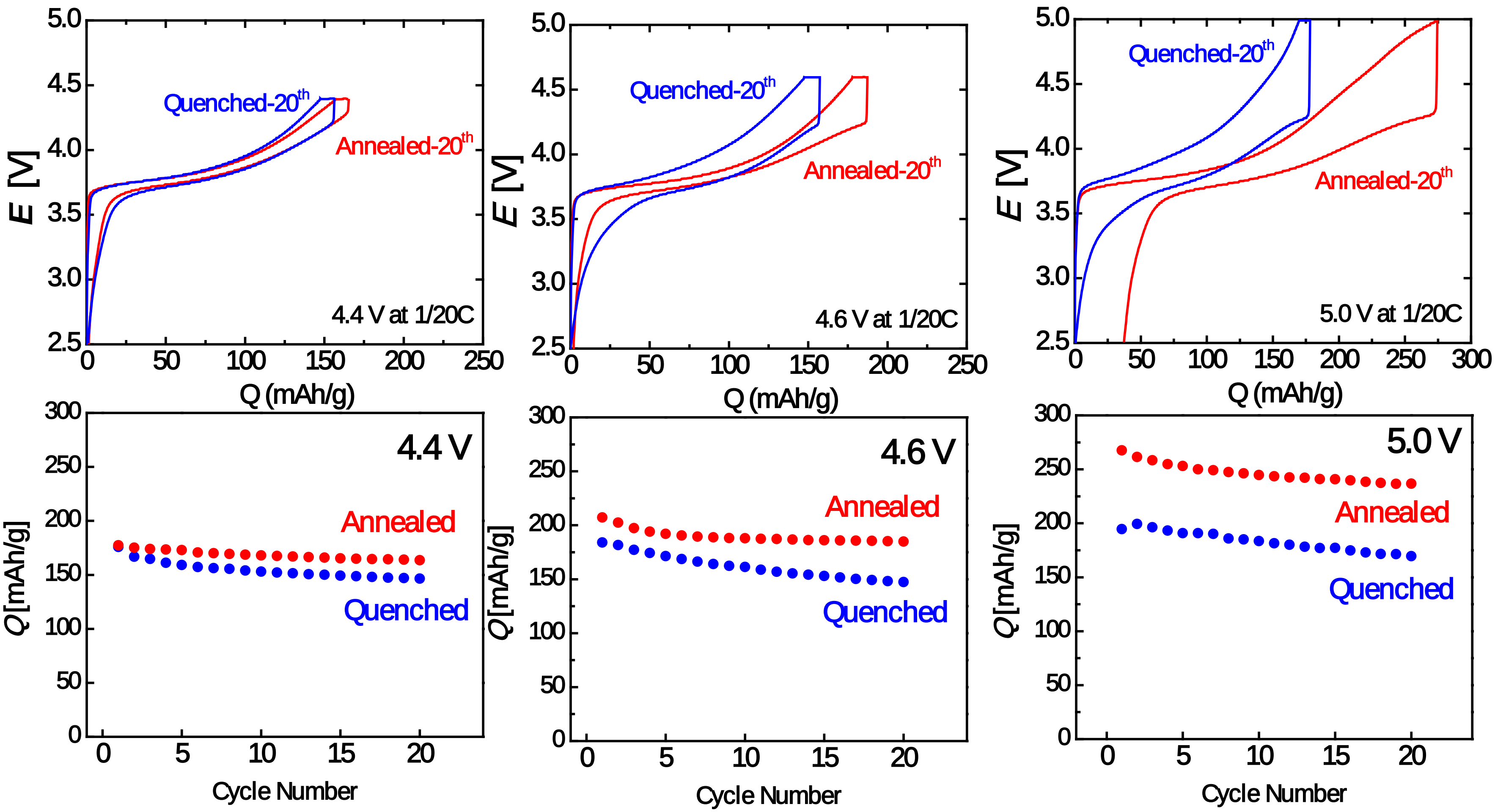
Technical Accomplishment (2010) – $LiNi_{0.5}Mn_{0.5}O_2$
Reduction of surface carbonates improves rate capability



N. Yabuuchi, Y.C. Lu, A.N. Mansour, T. Kawaguchi, and Y. Shao-Horn, Electrochem. Solid-State Lett., 13 , A158-A161 (2010)

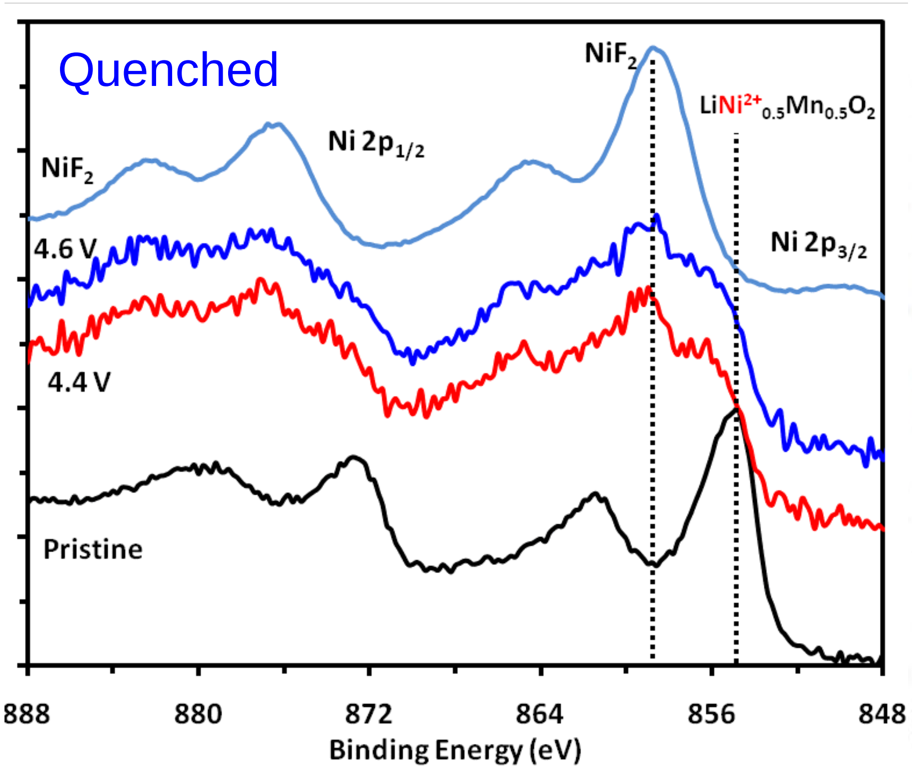
N. Yabuuchi, Y.C. Lu, A.N. Mansour, S. Chen, and Y. Shao-Horn, J. Electrochem. Soc., 2 , A192-A200 (2011)

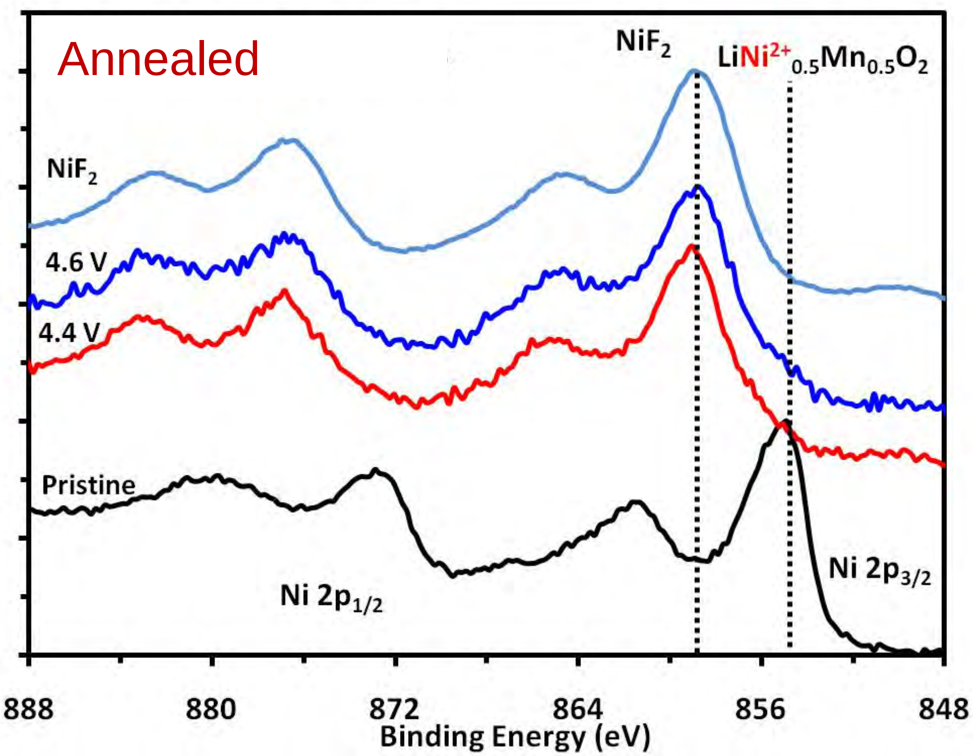
Annealed $LiNi_{0.5}Mn_{0.5}O_2$ shows better cycling than quenched to high voltages



NiF_2 found on cycled quenched & annealed $LiNi_{0.5}Mn_{0.5}O_2$

X-ray photoelectron spectroscopy – Ni 2p

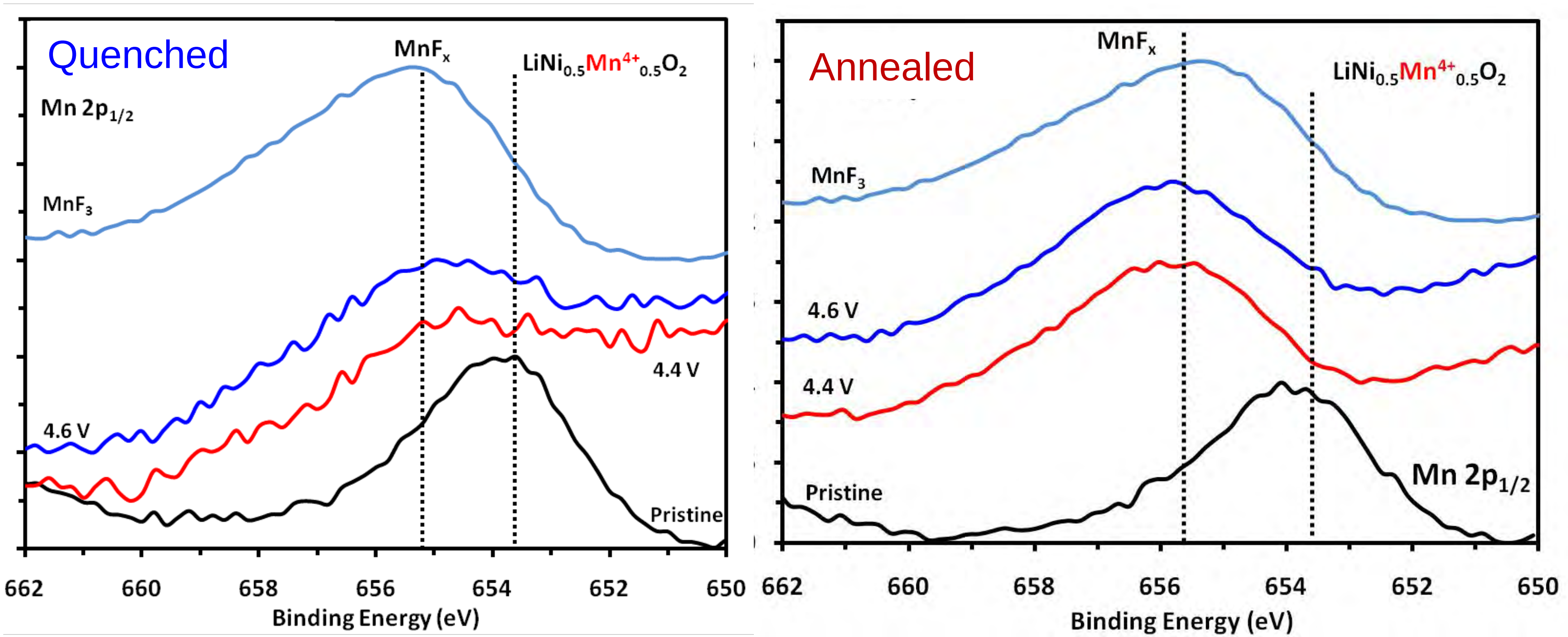




Thicker (Ni, Mn)F_x films formed on annealed electrodes

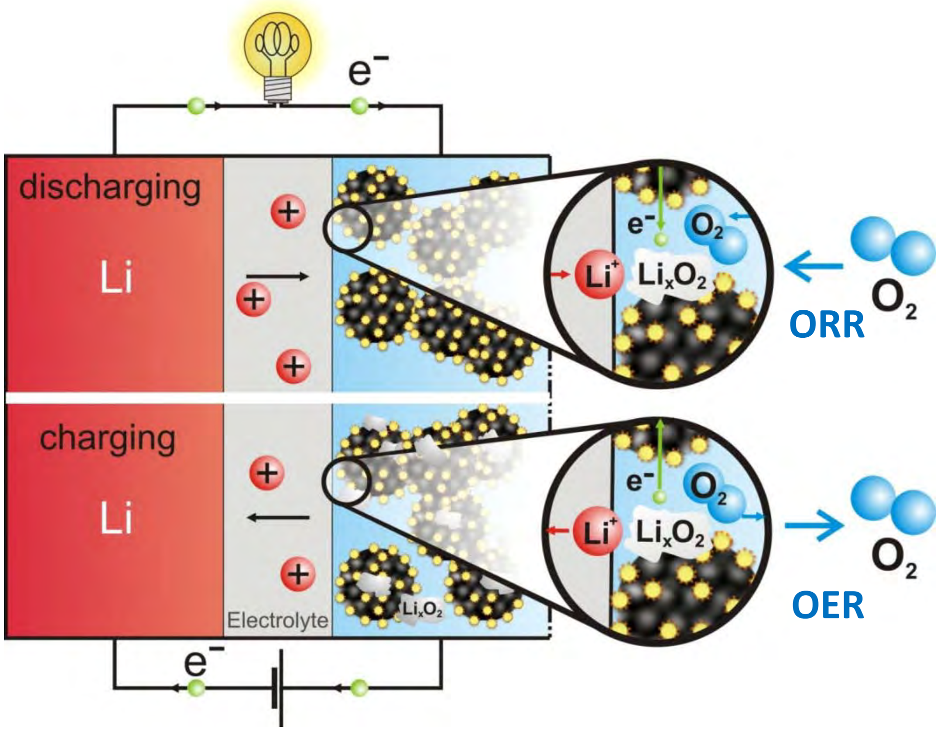
MnF_x was found on cycled quenched & annealed $LiNi_{0.5}Mn_{0.5}O_2$ but thicker films formed on annealed electrodes

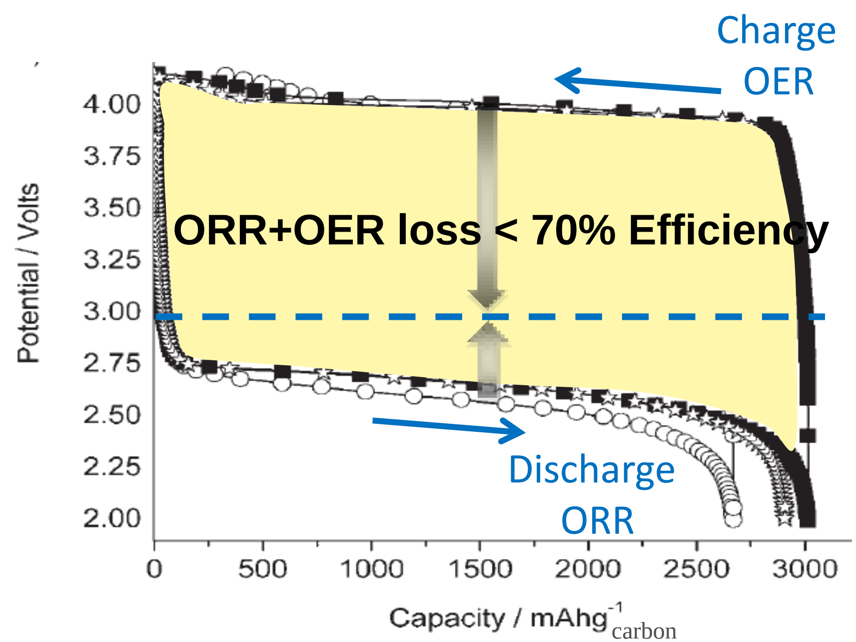
X-ray photoelectron spectroscopy – Mn $2p_{1/2}$



Thicker (Ni, Mn)F_x films formed on annealed electrodes

Promoting the kinetics of lithium oxide electrodes with catalysts

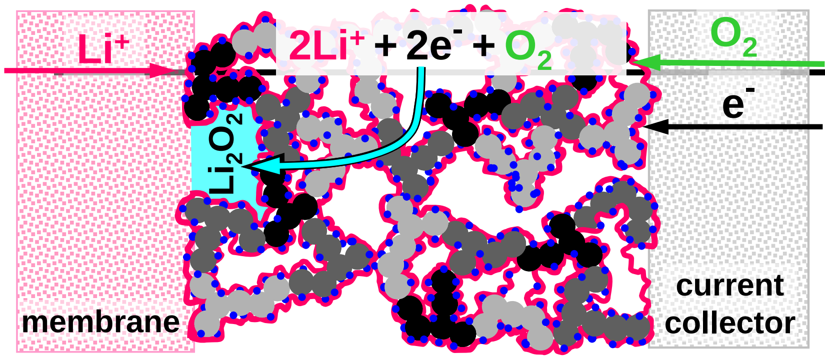




A. Débart et al, *Angew. Chem. Int. Ed. 47* (2008) 4521

Large polarization observed in decomposing lithium oxides

3-5-fold in gravimetric energy of Li_2O_x vs. Li-Ion batteries



assumptions:
$0.36 g_{carbon}/cm^{3*)}$, 15% ε_{carbon}, 25% $\varepsilon_{electrolyte}$, 60% ε_{Li2Ox}

	Li_2O_2	Li_2O	$LiCoO_2$
Q_s wrt. C [mAh/g_{carbon}]	4600	6000	
Q_s wrt. C+Li_2O_x [$mAh/g_{(C+Li2Ox)}$]	**900**	**1350**	**160**
average discharge voltage [V]	2.75	2.75	3.9
E_s wrt. C+Li_2O_x [$Wh/kg_{(C+Li2Ox)}$]	**2450**	**3700**	**620**

*) W. Gu, D.R. Baker, Y. Liu, H.A. Gasteiger; in: *Handbook of Fuel Cells* (eds.: W. Vielstich et al.); Wiley (2009): *vol. 6*, p 631

Li-Air

Estimated gravimetric energy
~ 3000 $Wh/kg_{Li2Ox\text{-}cathode}$

Projecting on the cell level – 1/3
~ 1000 $Wh/kg_{Li\text{-}air\ cell}$

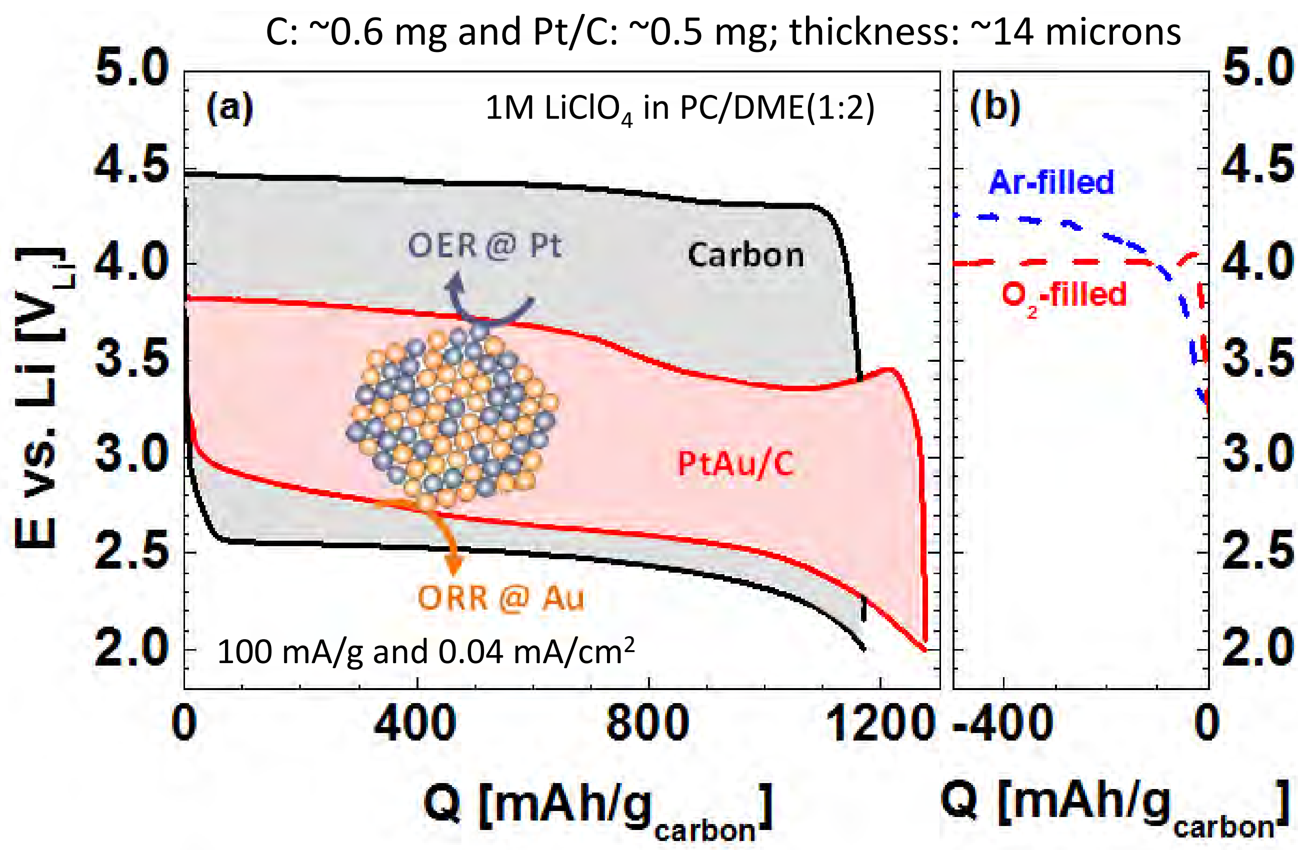
Li-Ion ($LiCoO_2$)

Estimated gravimetric energy
~ 620 $Wh/kg_{LiCoO2\text{-}cathode}$

Projecting on the cell level – 1/3
~ 210 $Wh/kg_{LiCoO2\ cell}$

Lu et al, ESSL 2010

PtAu/C exhibits record round-trip efficiency to date

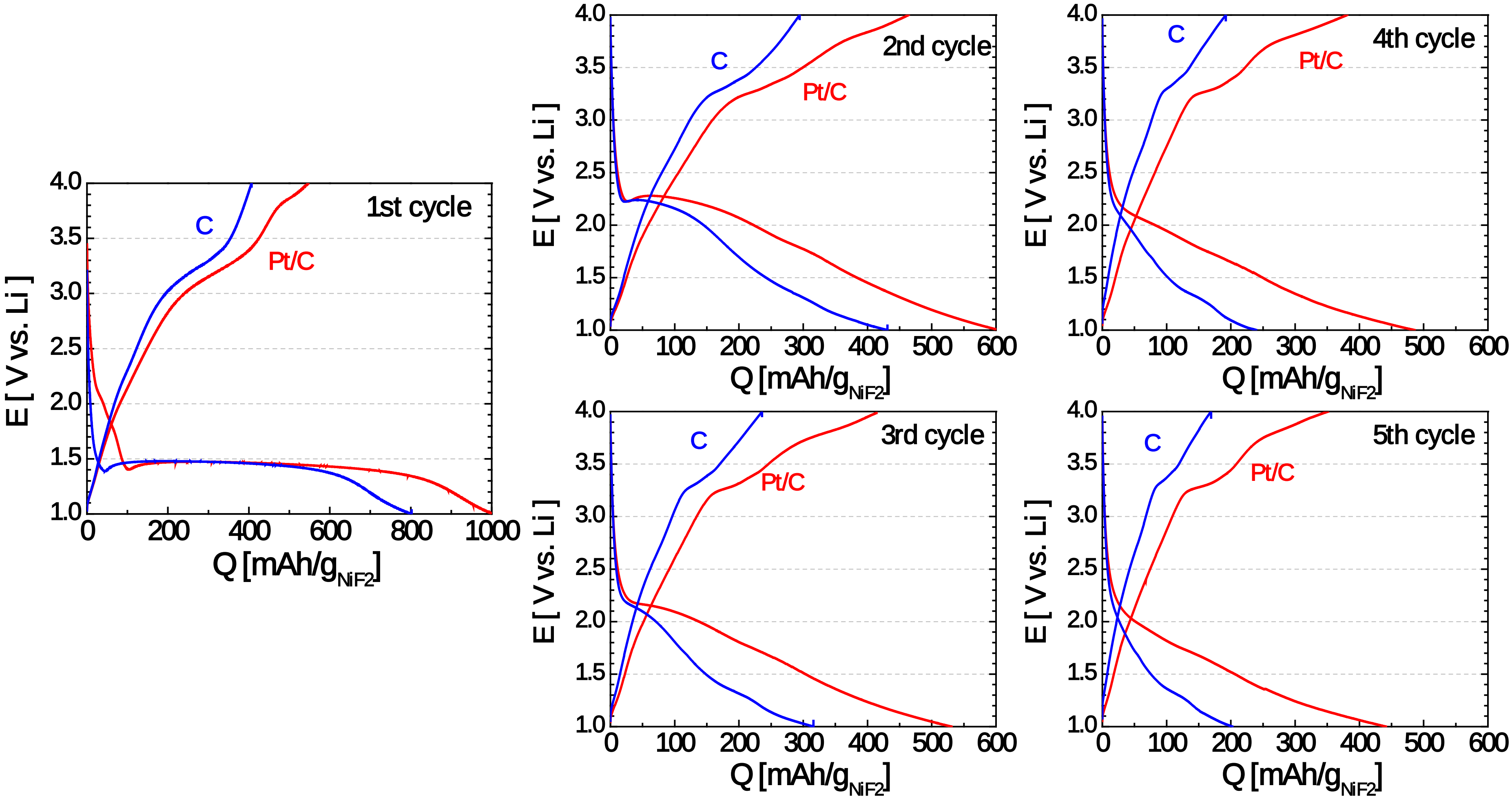


Achieved Round-trip efficiency: 75%

What is the origin for the high bifunctional activity?

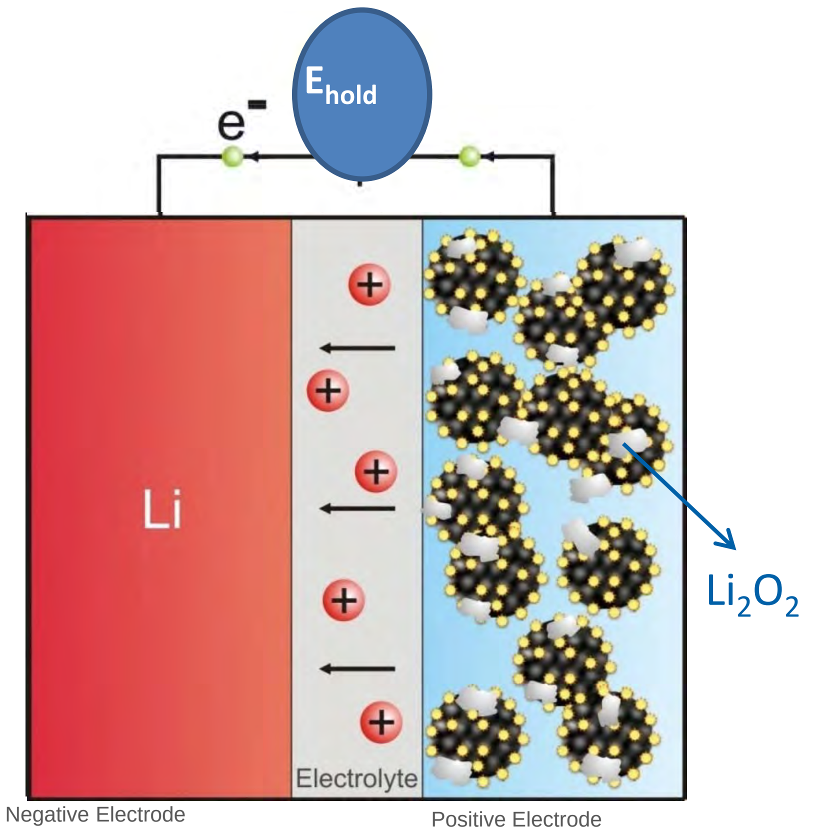
Yi-Chun Lu, Zhichuan Xu, Hubert Gasteiger, Shuo Chen, Kimberly Hamad-Schifferli, and Yang Shao-Horn, *JACS,* **132** 12170 (2010)

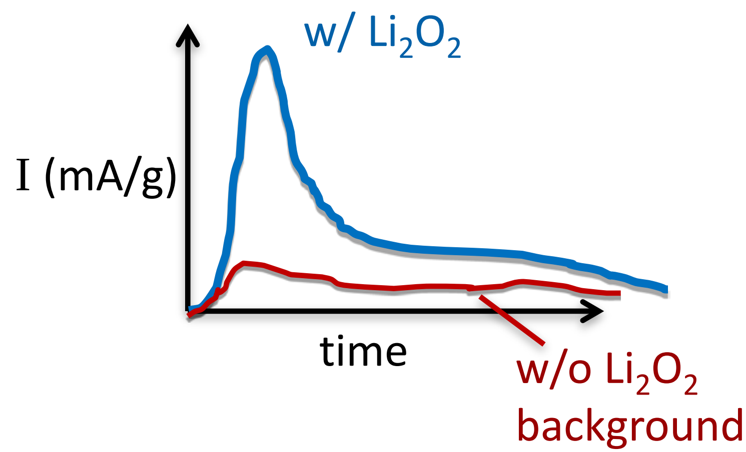
Catalyst effects on lithium metal-fluoride batteries

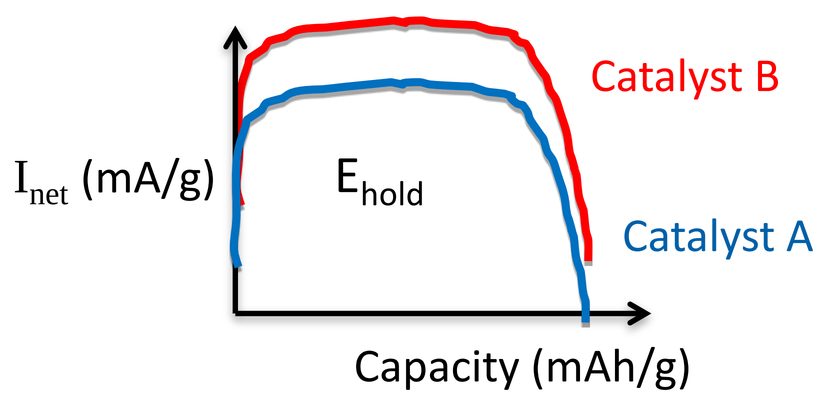


Catalyst effects present upon cycling

Li_2O_x-filled composite electrodes to quantify the oxygen evolution reaction (OER) activity



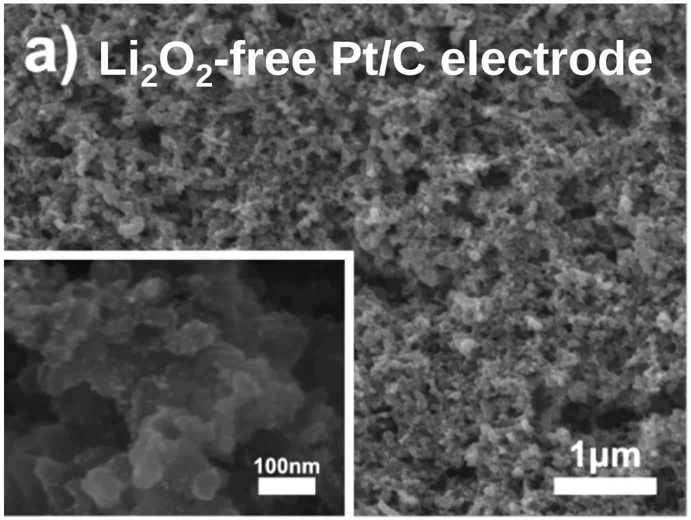


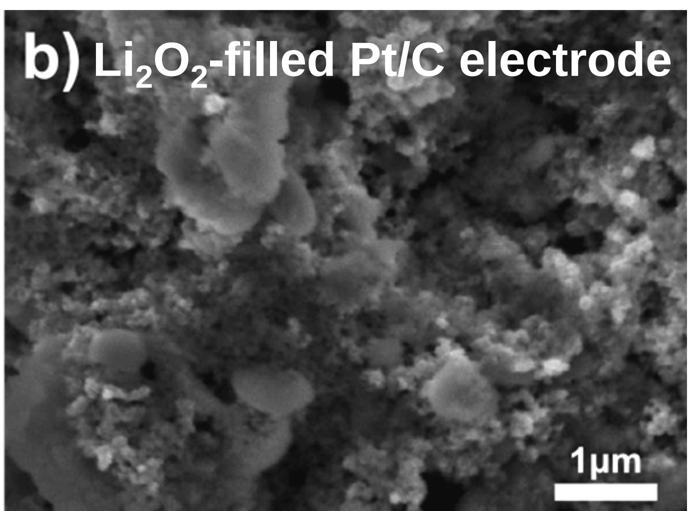


Yi-Chun Lu, Hubert A. Gasteiger, Michael C. Parent, Vazrik Chiloyan, and Yang Shao-Horn, *Electrochem. Solid State Lett.* 13(6), A69-A72 (2010)

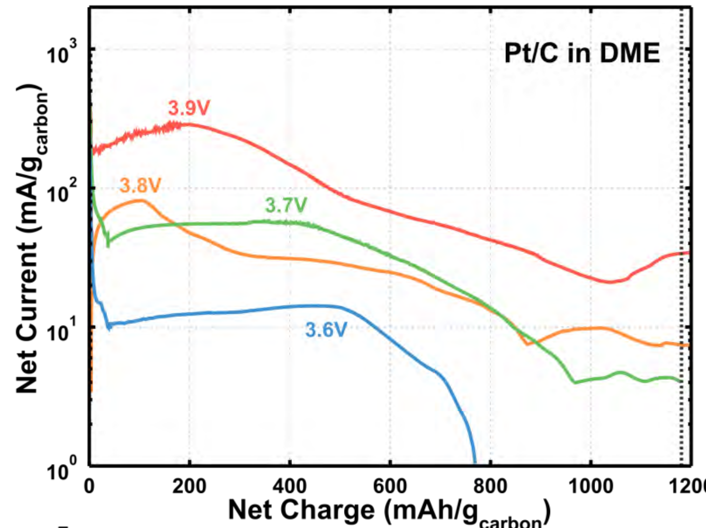
OER activity of Pt nanoparticles was examined by Li_2O_2-filled composite electrode

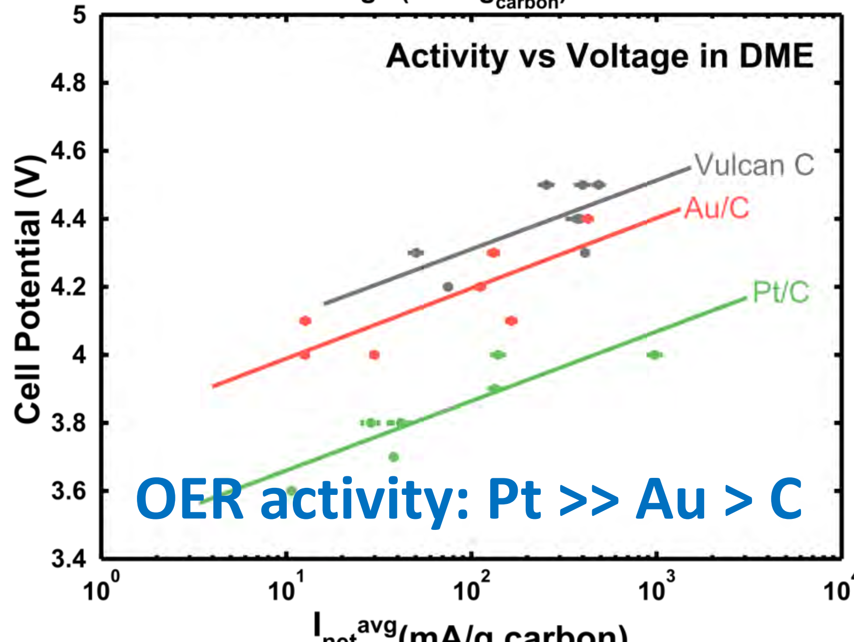
Scanning electron microscopy





Potentiostatic test of Li_2O_2-filled Pt/C electrode

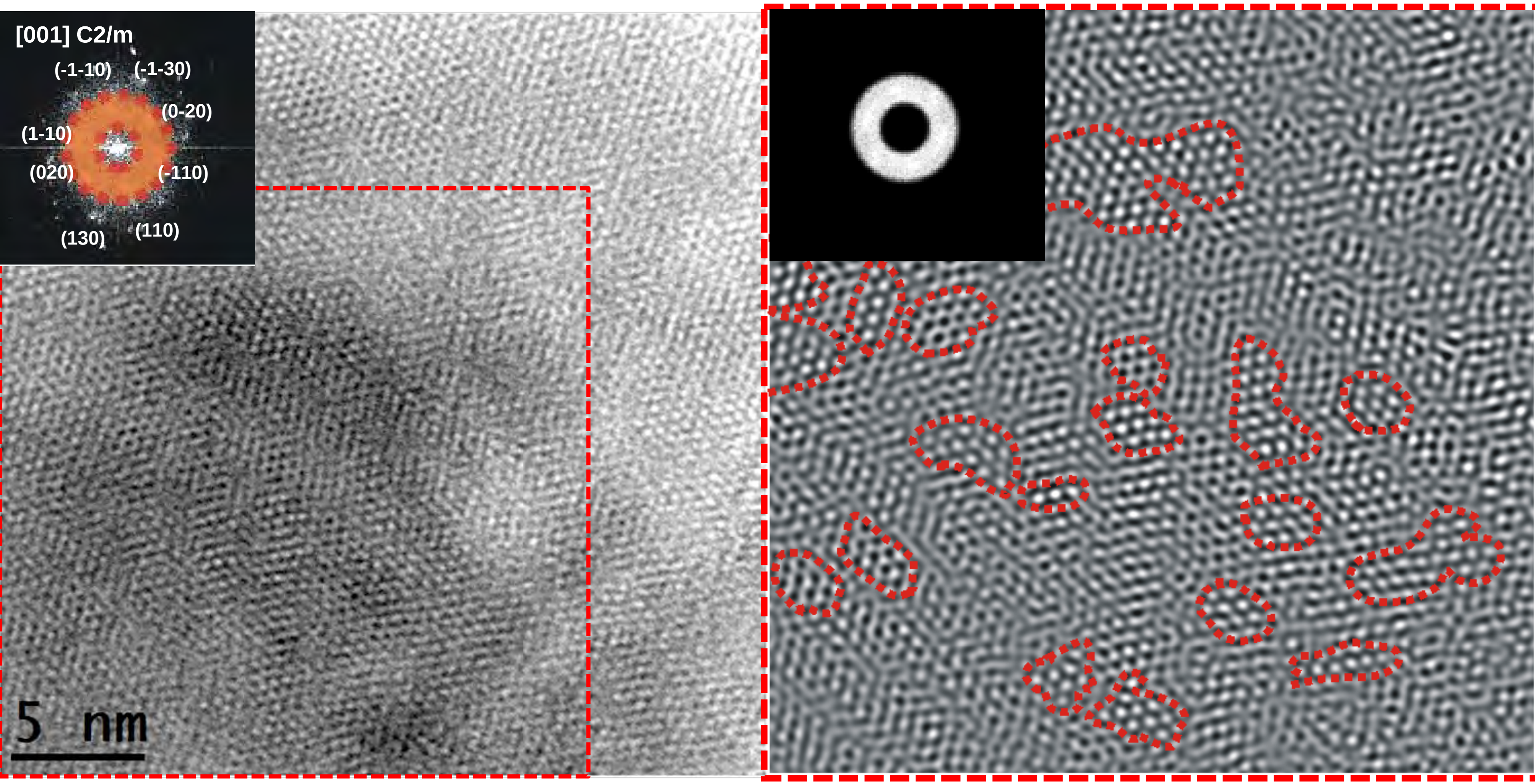




Harding and Shao-Horn et al., Manuscript in preparation (2011)

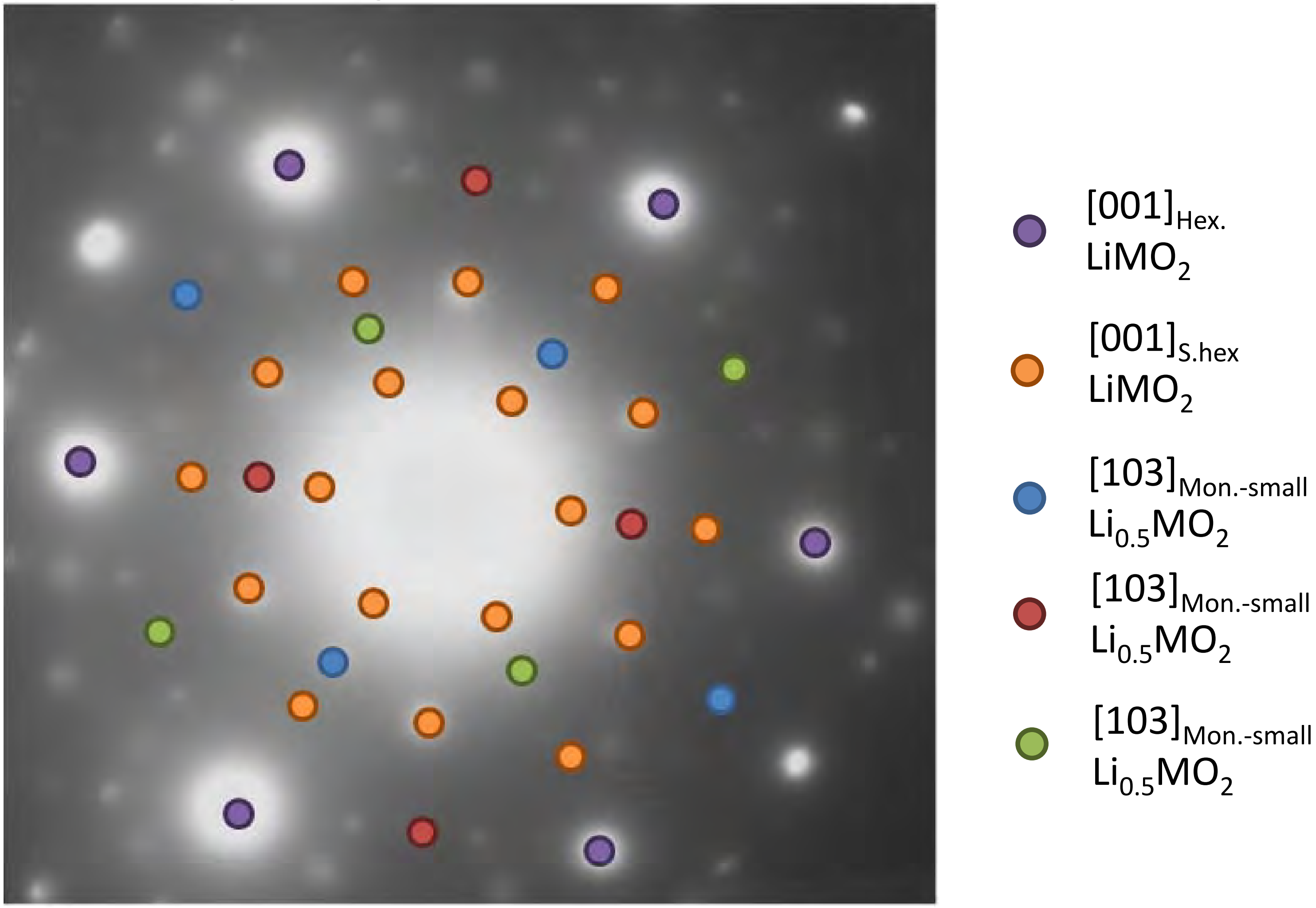
Collaboration with S.H. Kang and M.M. Thackeray

Fourier filtering of pristine $0.5Li_2MnO_3+0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ layered-layered composite cathode revealed evidence of monoclinic Li_2MnO_3 nanodomains



Collaboration with S.H. Kang and M.M. Thackeray

Diffraction patterns of cycled $0.5Li_2MnO_3 + 0.5LiNi_{0.44}Co_{0.25}Mn_{0.31}O_2$ layered-layered composite cathode reveal integration between several different crystal symmetries and orientations



The electron diffraction pattern reveals integration between hexagonal $LiMO_2$, super-lattice ordered hexagonal $LiMO_2$ and 3-different orientations of monoclinic $Li_{0.5}MnO_2$

Ongoing and Planned Activities

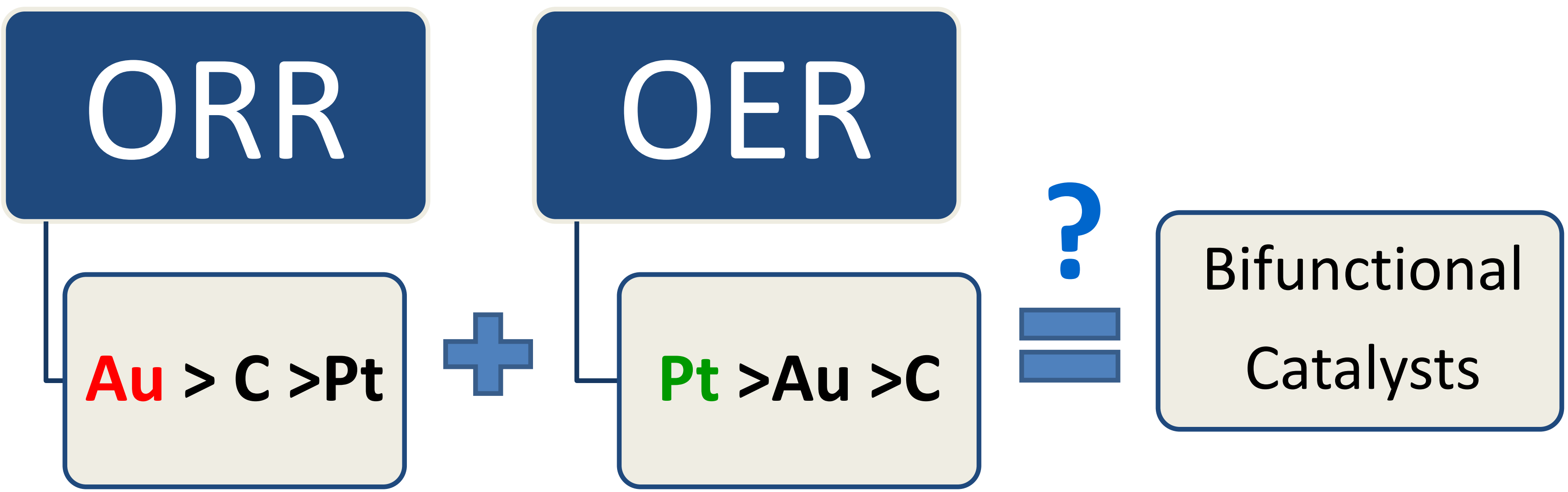
- Continue to examine the role of surface chemistry on cycle life and rate capability of low cost and high energy positive electrode materials such as $LiNi_{0.5}Mn_{0.5}O_2$ using angle-resolved XPS and electron yield XAS:
  - Examine variations in the surface chemistry of cycled $LiNi_{0.5}Mn_{0.5}O_2$ electrodes. In this case, the electrodes will be transferred from an Ar filled glove box to the analysis chamber of the XPS system without exposure to ambient conditions.

- Continue to develop high-energy electrode materials $Li_2O_x(MO_y)_z$ electrodes (M = nonnoble metal transition metals) and examine the reaction mechanisms
  - Examine the catalyst effects on the decomposition rate of Li_2O_2 and Li_2O in composite electrodes of $Li_2O_x(MO_y)_z$ by systematic potentiostatic tests, SEM, XPS, Raman, FT-IR and XRD characterization.

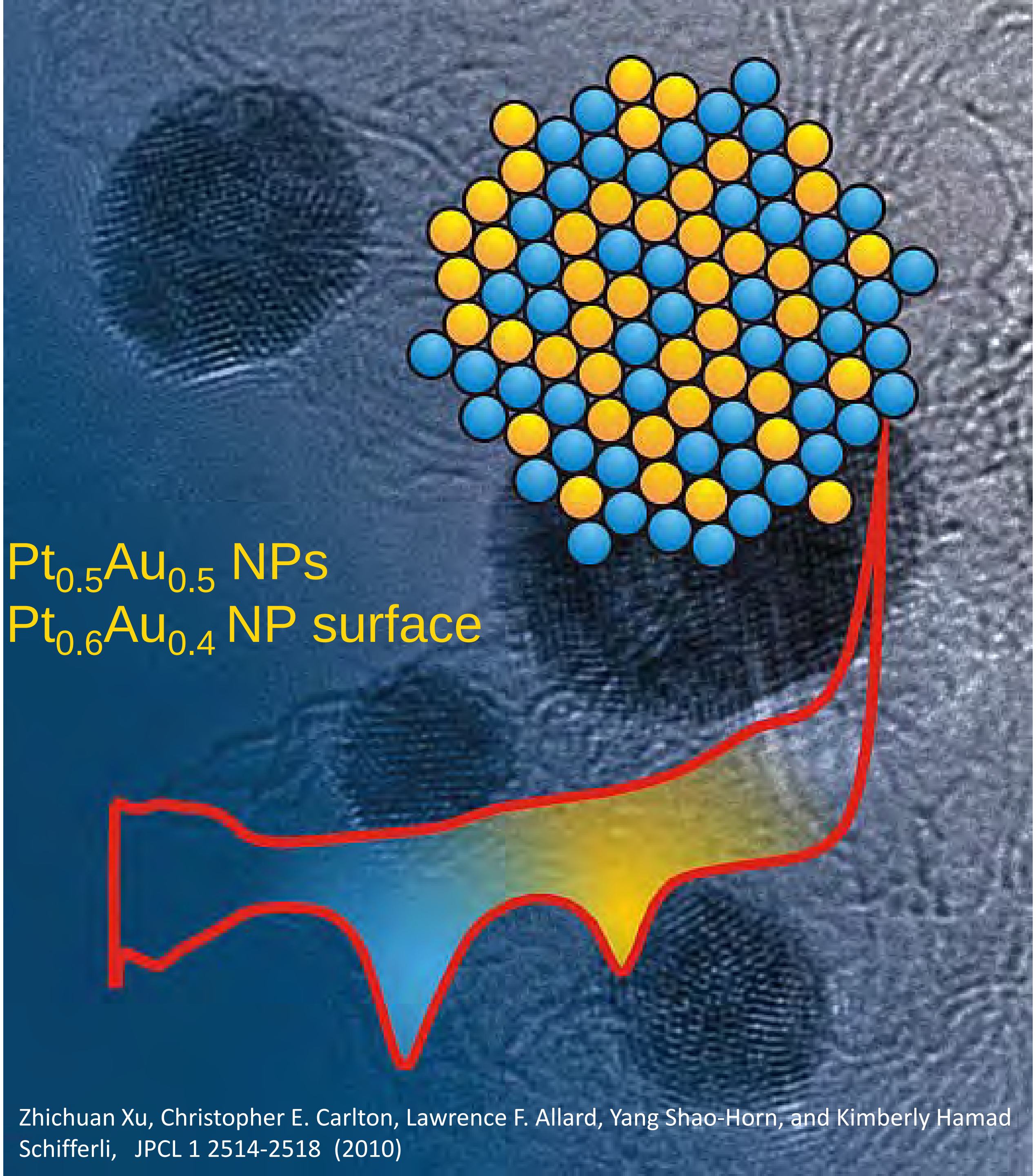
Contact information

Yang Shao-Horn at 617 253-2259
shaohorn@mit.edu

Au is the most active for ORR and Pt is the most active for OER among Au, Pt, C



Yi-Chun Lu, Hubert A Gasteiger, Ethan Crumlin, Robert McGuire, and Yang Shao-Horn, , *J. Electrochem. Soc. 157(9) A1016* (2010)
Yi-Chun Lu, Hubert A. Gasteiger, Michael C. Parent, Vazrik Chiloyan, and Yang Shao-Horn,, *Electrochem. Solid State Lett.* 13(6), A69-A72 (2010)
Harding and Shao-Horn et al., Manuscript in preparation (2011)



Zhichuan Xu, Christopher E. Carlton, Lawrence F. Allard, Yang Shao-Horn, and Kimberly Hamad Schifferli, JPCL 1 2514-2518 (2010)

Examine the effects of sample washing on XPS analysis

Typical XPS analysis procedure for cycled electrodes

- Sample is **washed** with solvent prior to XPS analysis

Our XPS analysis procedure for cycled electrodes

- ***No*** wash step or any pretreatment prior to XPS analysis

Search for ideal surface chemistries for long cycle life under high voltage operation

Quenched

$LiNi_{0.5}Mn_{0.5}O_2$

- 1000 C quenched
- **2.5 – 4.4 ,4.6 and 5.0 V**
- 3 hour hold at high voltage

Annealed

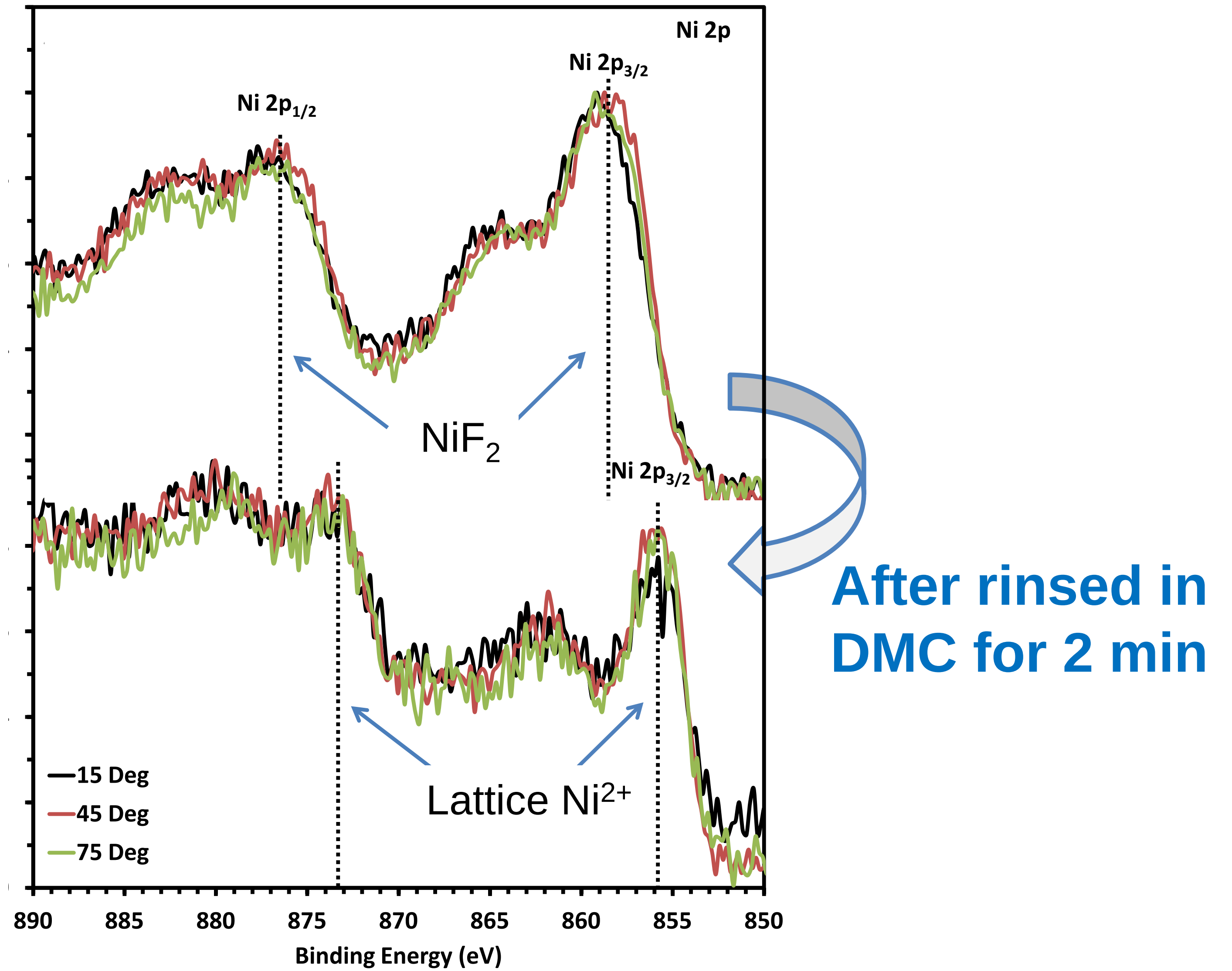
$LiNi_{0.5}Mn_{0.5}O_2$

- 1000 C quenched - 700 C annealed for 12 hours
- **2.5 – 4.4 ,4.6 and 5.0 V**
- 3 hour hold at high voltage

Washing step removes the metal fluoride/oxyfluoride

Angel resolved X-ray photoelectron spectroscopy – Ni 2p

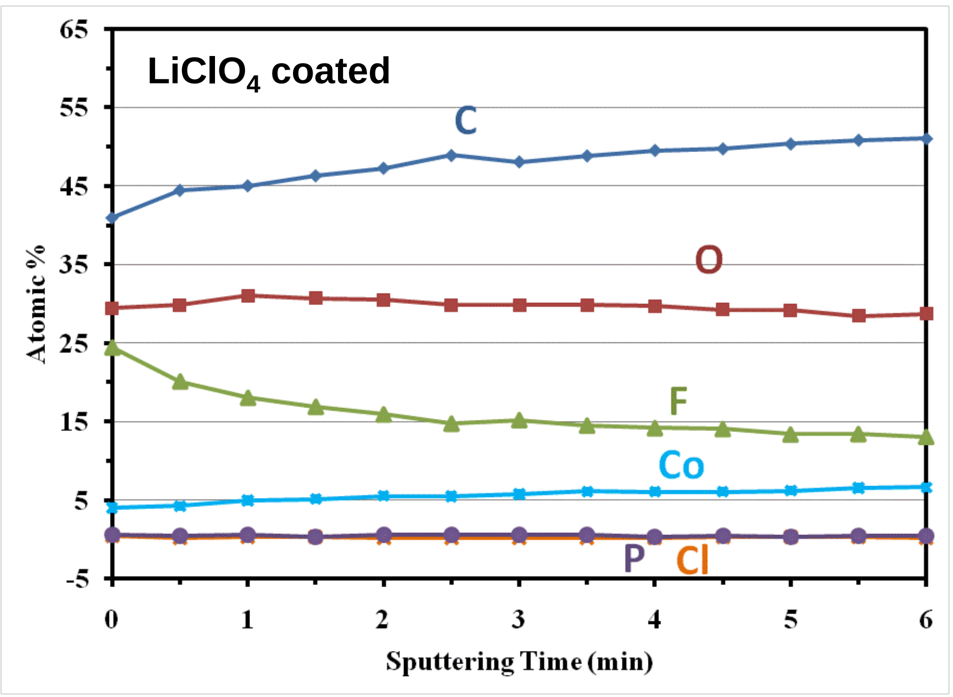
Annealed $LiNi_{0.5}Mn_{0.5}O_2$ cycled in $LiPF_6$

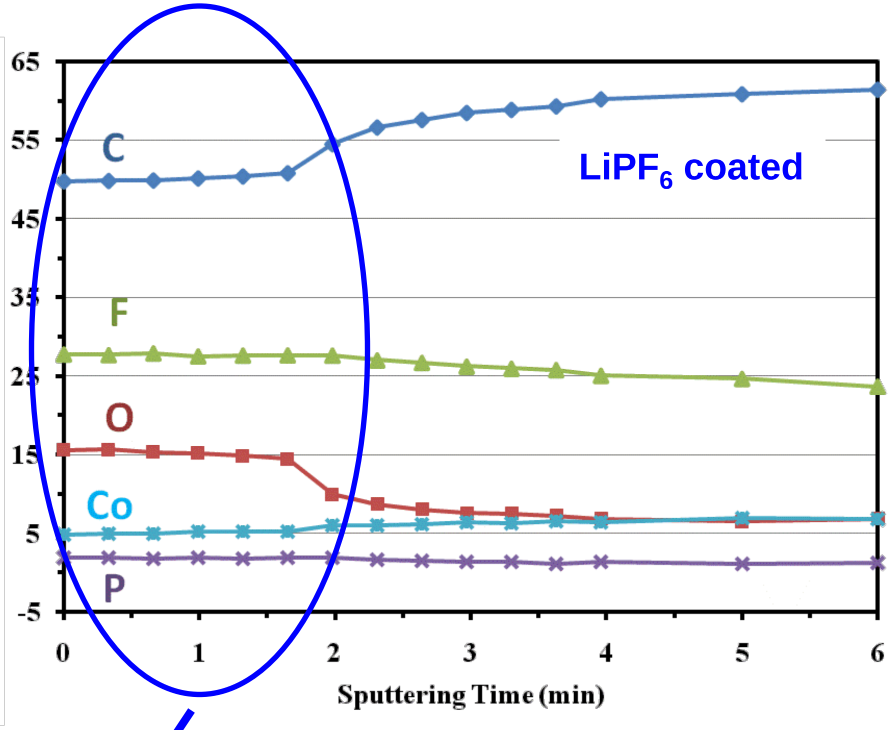


A desired solid-electrolyte interface consists of :

- **Right chemistry → metal fluoride / oxyfluoride**
- **Right thickness → ~ 5-6 nm**

X-ray photoelectron spectroscopy – sputtering profile

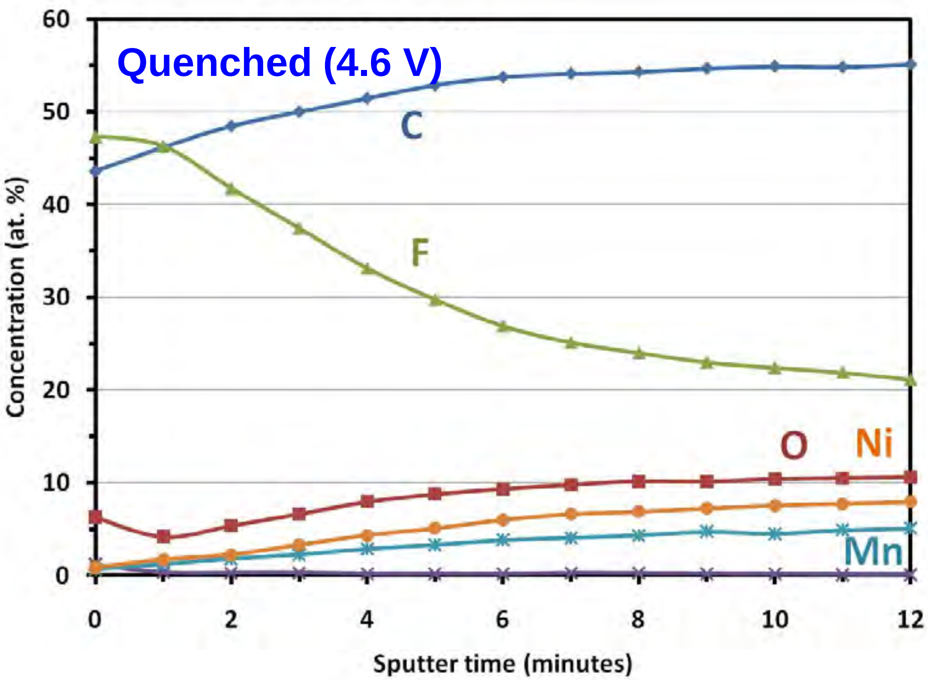


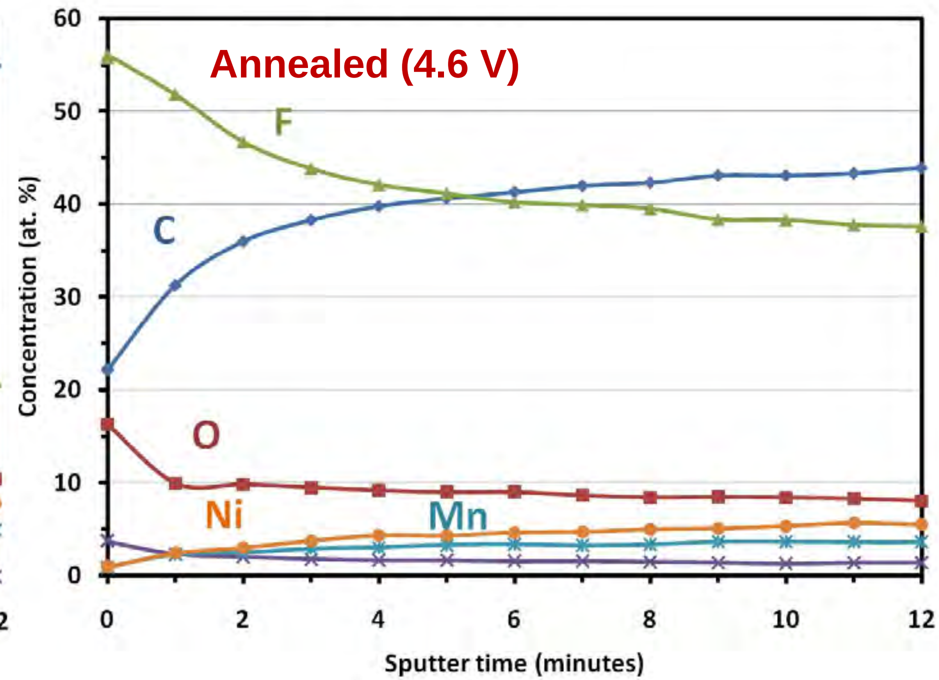


2 min of flat sputtering profile indicates
→ A stable film with a substantial thickness

Cycled annealed electrode is dominated by F-chemistry
Cycled quenched electrode is dominated by C & F-chemistry

X-ray photoelectron spectroscopy – sputtering profile



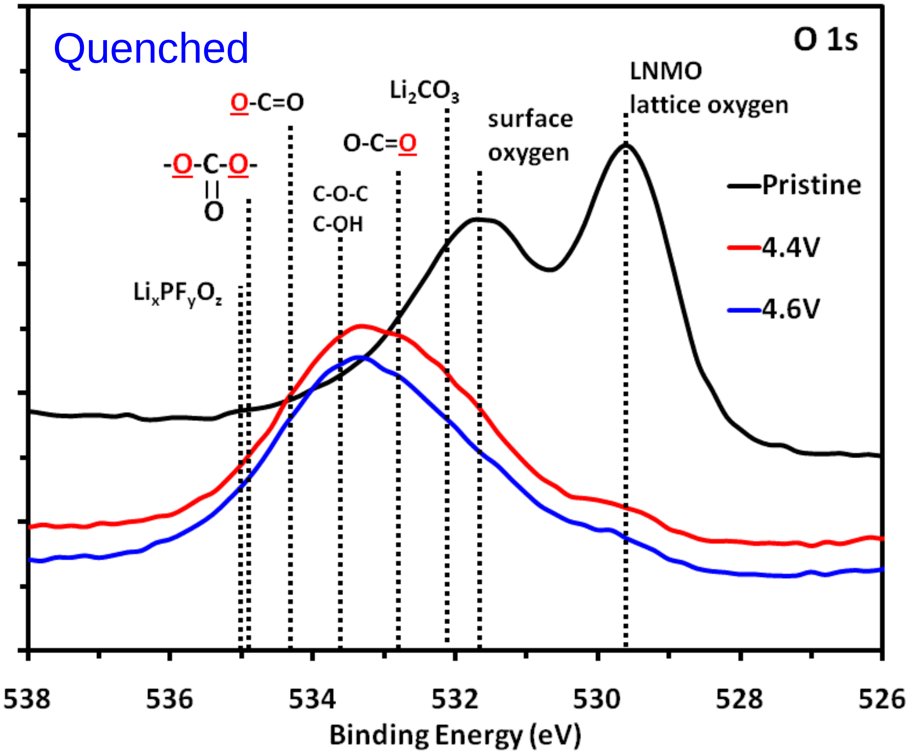


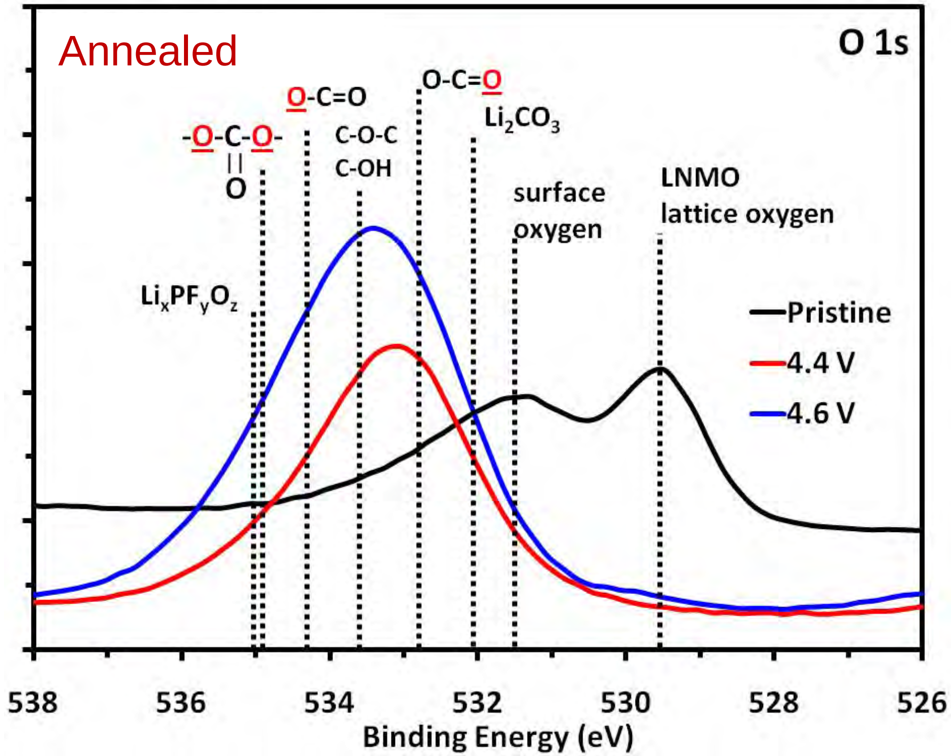
F/C ratio = 1.1

F/C ratio = 2.5

O 1s spectra confirm that thicker film is formed on cycled annealed electrode compared to cycled quenched electrode

X-ray photoelectron spectroscopy – O 1s



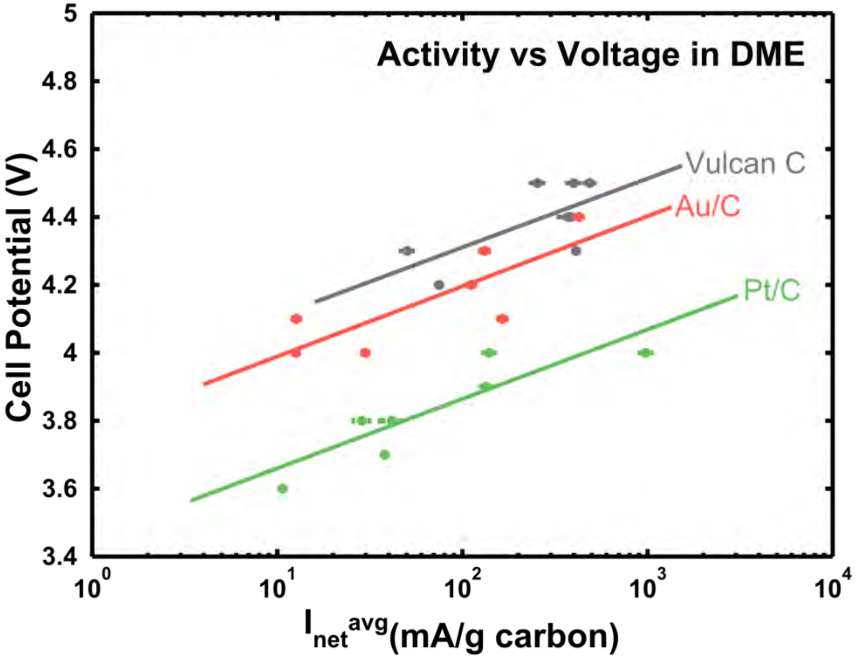


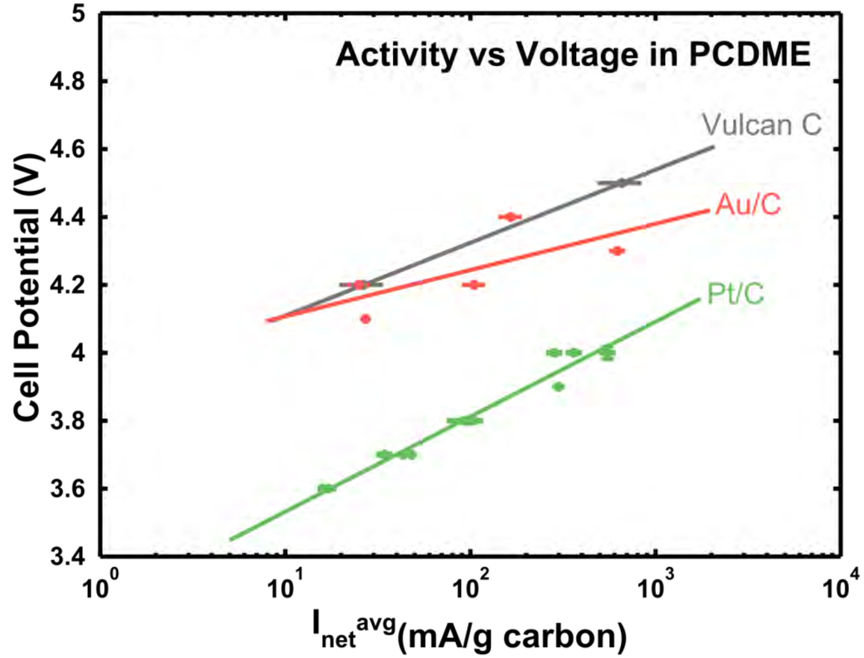
- Lattice oxygen signal is visible, suggesting thinner film formation

- Lattice oxygen signal is not visible, suggesting thicker film formation

Pt was shown to have the highest OER activity among Pt, Au and C

Activity vs cell potential





Harding and Shao-Horn et al., Manuscript in preparation (2011)