SAND2014-4025C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Nucleation and Electron Transfer Site Proximity in Peroxide Formation at Cathodes in the Lithium – Oxygen System

Katharine L. Harrison and Kevin R. Zavadil

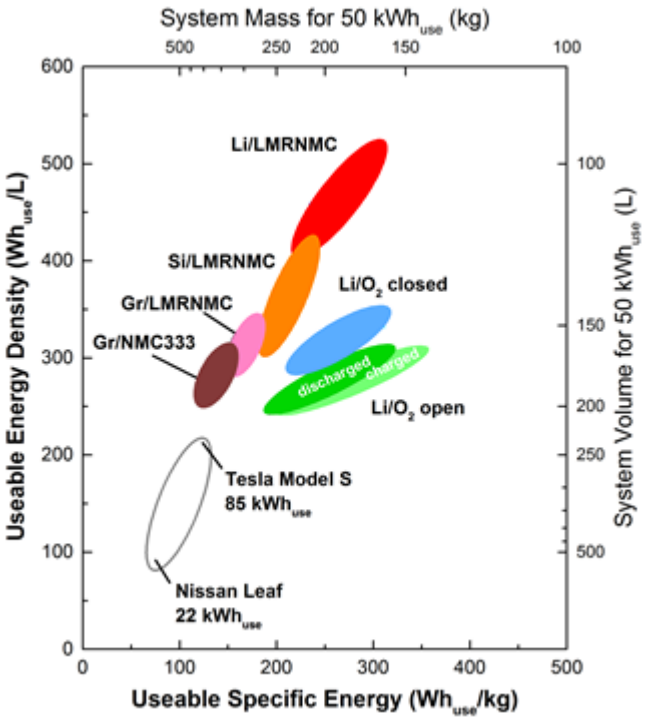
Sandia National Laboratories

2014 Spring ECS Meeting

Supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science. Sandia is a multiprogram laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Company, for the U.S. DOE's NNSA under contract DE-AC04-94AL85000.

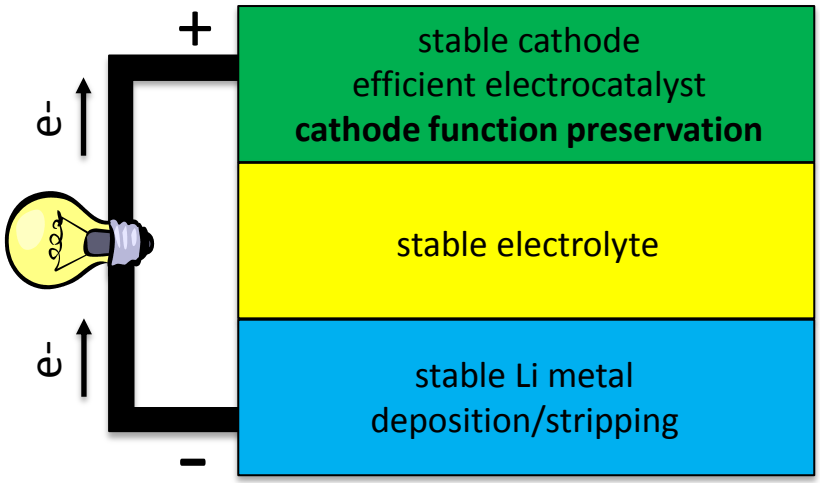
Li-O_2 Batteries Show Promise as Enhanced Energy Density Storage Systems

Full scale systems analysis



K.G. Gallagher et al. *Energy Environ. Sci.*
DOI: 10.1039/c3ee43870h

- Li-O_2 could delivery specific energy density gains 2-5X beyond state of art Li Ion
- To get there, many science challenges need to be overcome



Preserving Cathode Function: One Challenge to Achieving Efficient O_2 Electrochemistry for Li-O_2 Batteries

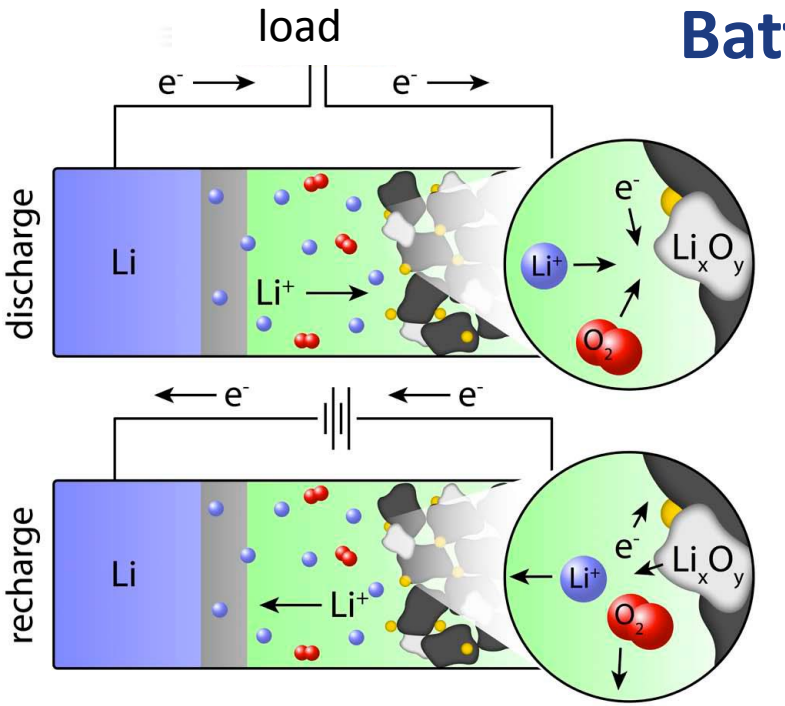


image courtesy of M. Radin and D. Siegel, U. Mich.

ORR Discharge

$O_2 + e^- + Li^+ \rightarrow LiO_2$

$LiO_2 + e^- + Li^+ \rightarrow Li_2O_2$

disproportionation

$2LiO_2 \rightarrow Li_2O_2 + O_2$

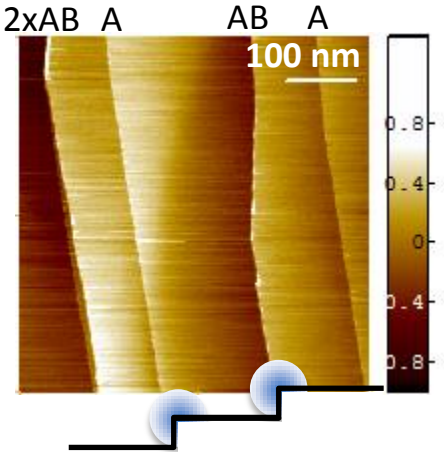
OER Charge

$Li_2O_2 \rightarrow O_2 + 2e^- + 2Li^+$

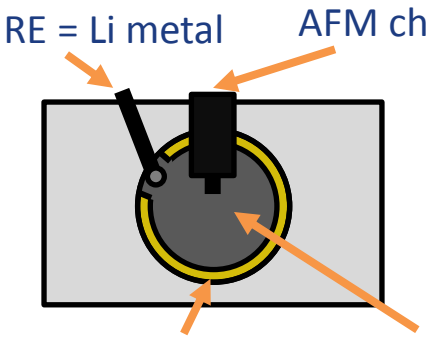
location matters!
electrocatalytic sites cannot be blocked
nucleation and growth sites must facilitate OER charge transfer

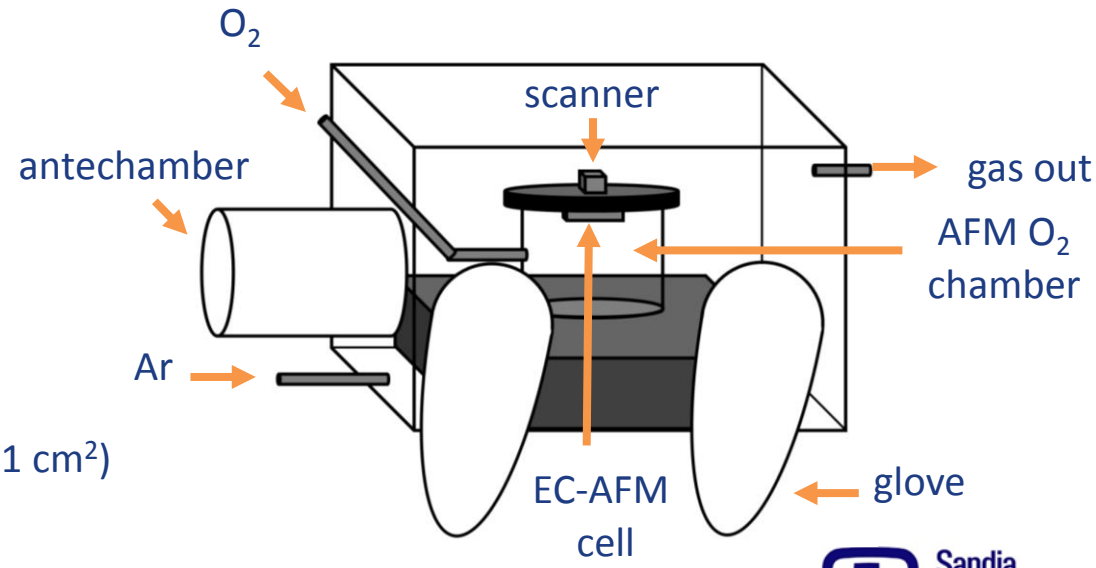
Motivation and Experimental Details

- Electrochemical AFM
  - 0.4 mL electrolyte volume
    - Distilled and dried TEGDME + 1 M dried LiTFSI
  - Galvanostatic & voltammetry electrochemistry
  - EC-AFM on HOPG and Au (Wen et al. *JACS* 2013; *ChemComm*, 2014)
- Goals
  - Understand effects of electrogeneration rate on product distribution (Adams et al. *Energy. Environ. Sci.* 2013)
  - Understand relationship between e- transfer sites (HOPG steps) and product distribution



nanoband electrode





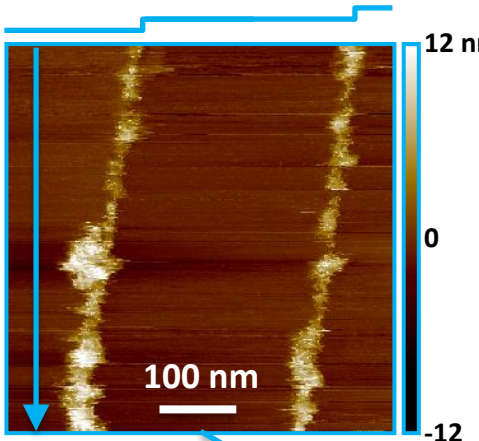
A Reproducible Product Growth Sequence is Observed

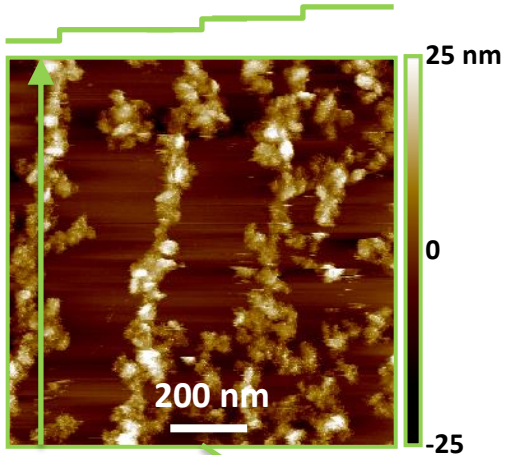
Initial growth on step edges after slight delay

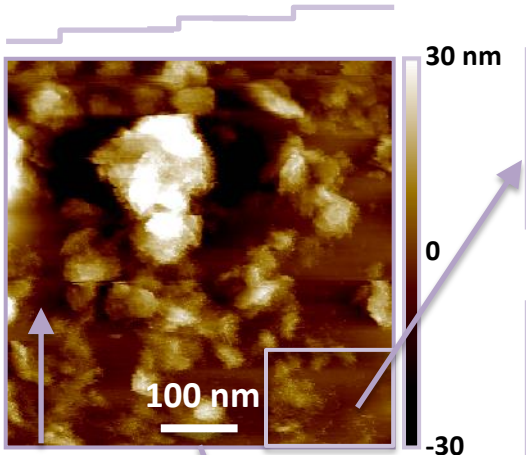
Continuous assembly growth - step preference

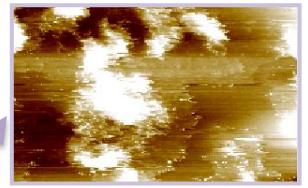
Compact film growth & passivation

Film infill at end of discharge

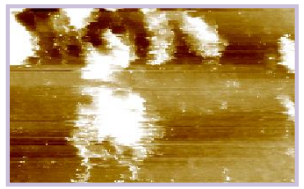


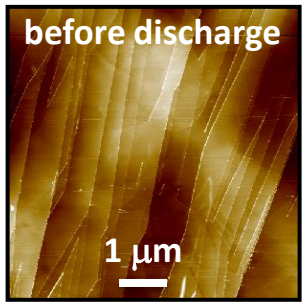


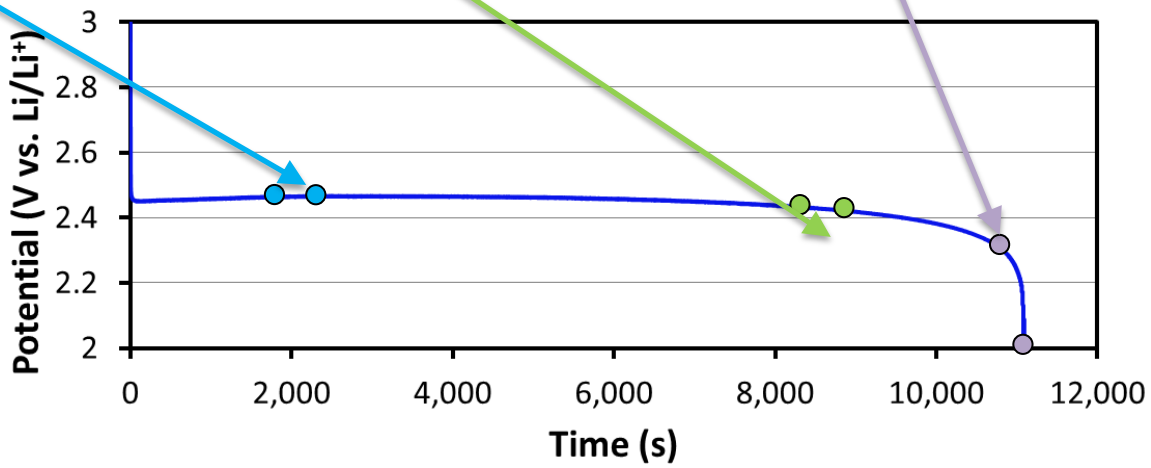


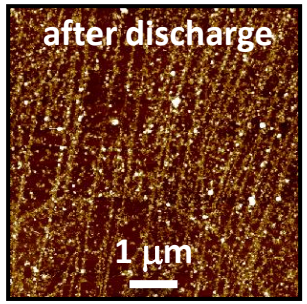


Next image

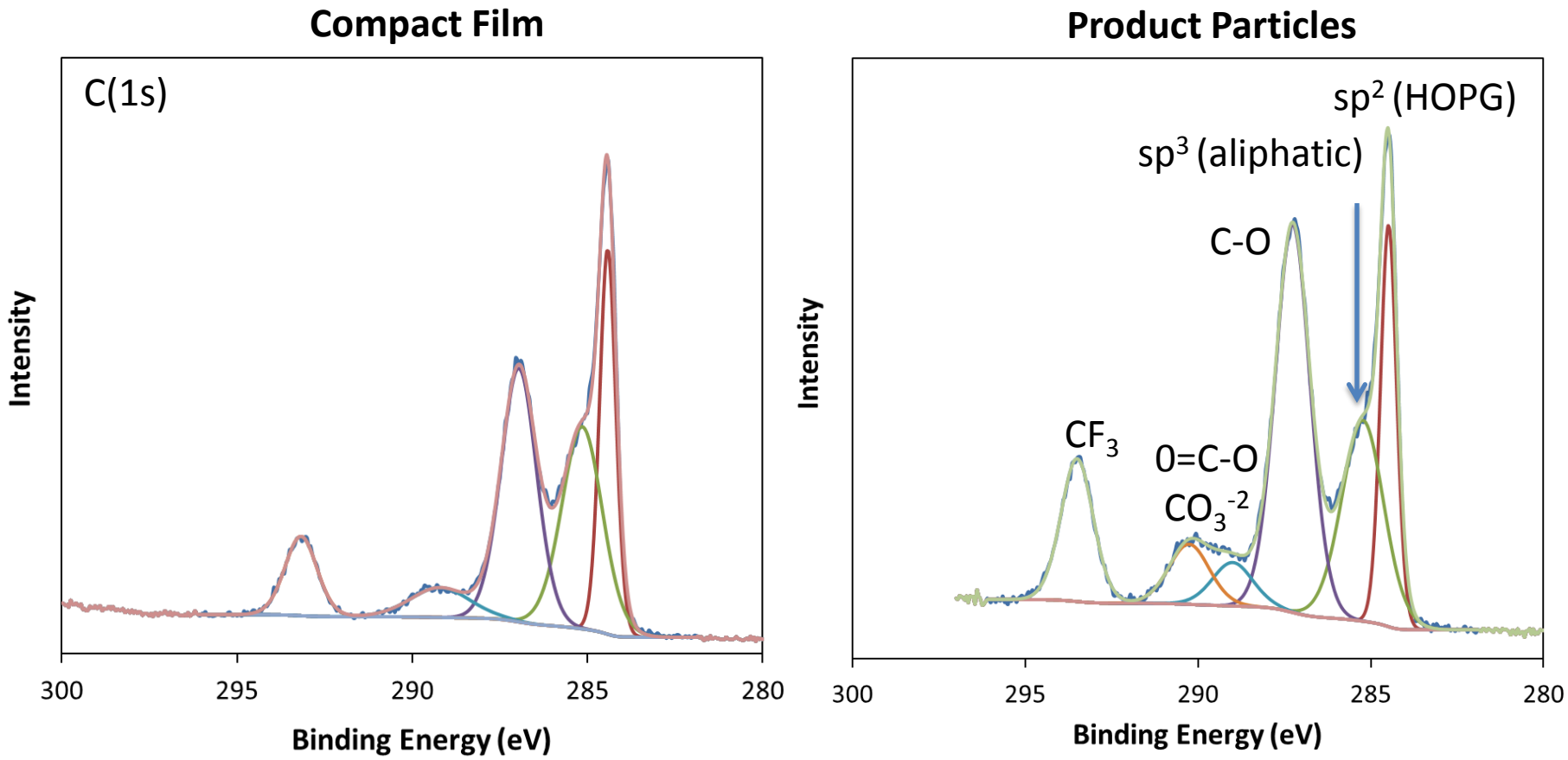








Nature of the Passivating Compact Film



Film composition = Li_xO_y w/ organic

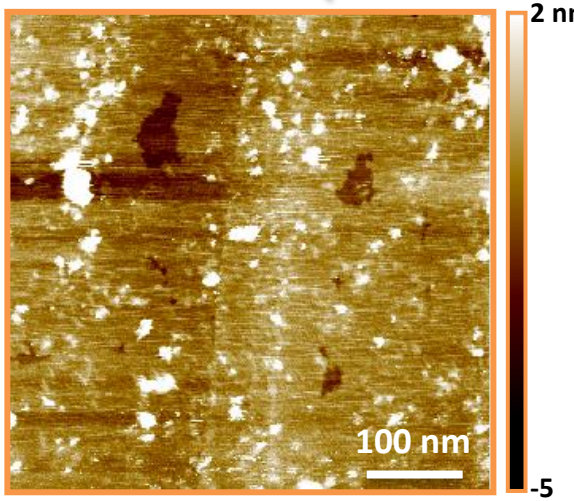
- ToF-SIMS - $Li_xO_y(H)^{\pm}$ & $LiCO_3^-$
- XPS – carbonate, high C-O content
- Residual (incorporated) TFSI

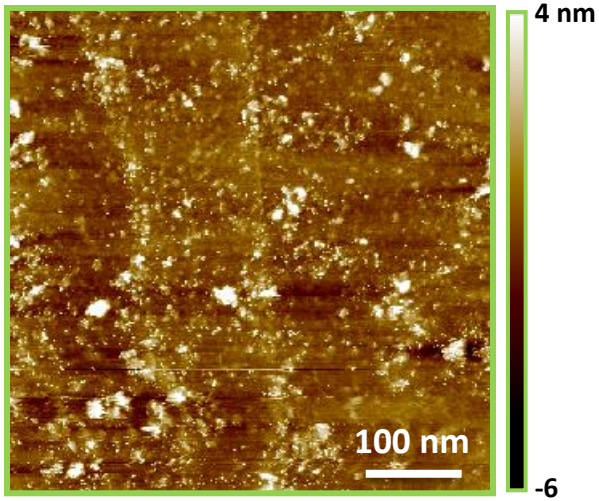
Increasing Rate Forces an Early Transition to Compact Film Formation and Passivation

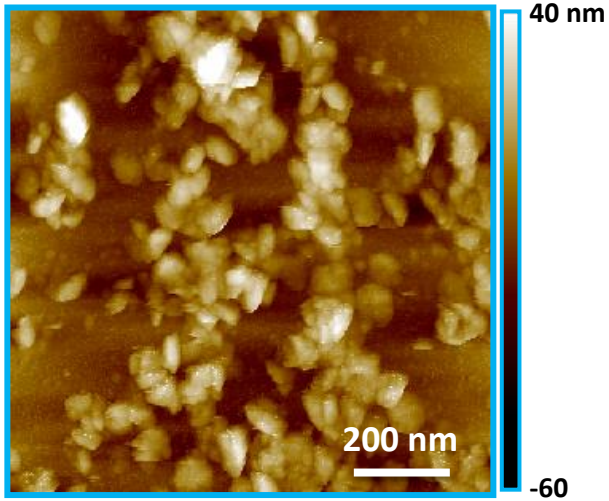
smaller peroxide particles

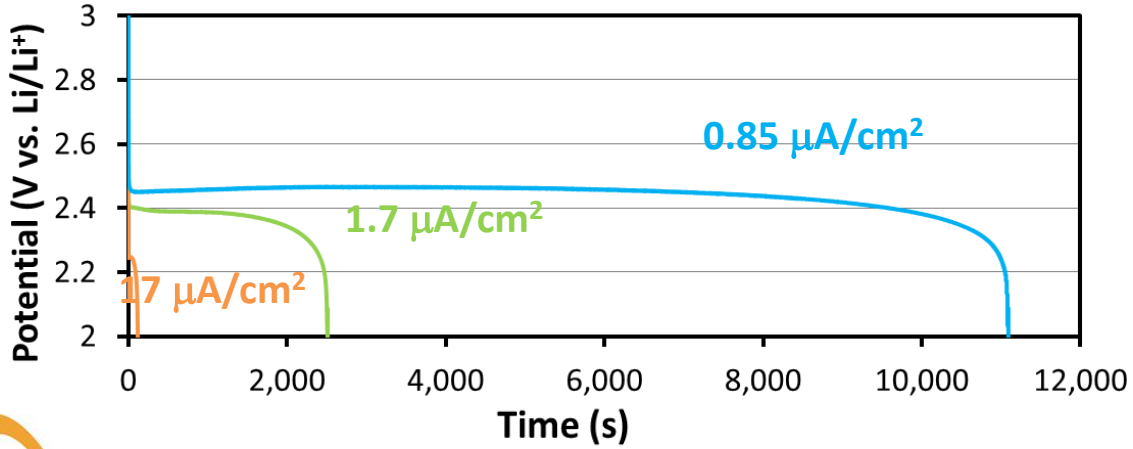
increasing rate

larger peroxide particles





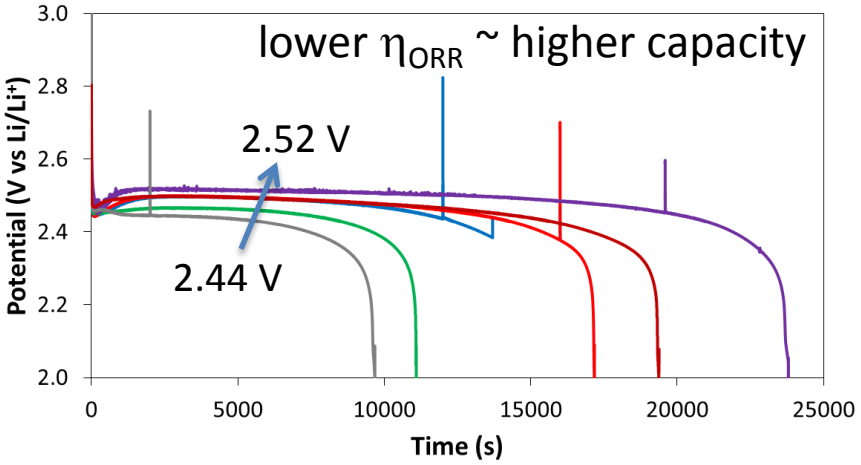


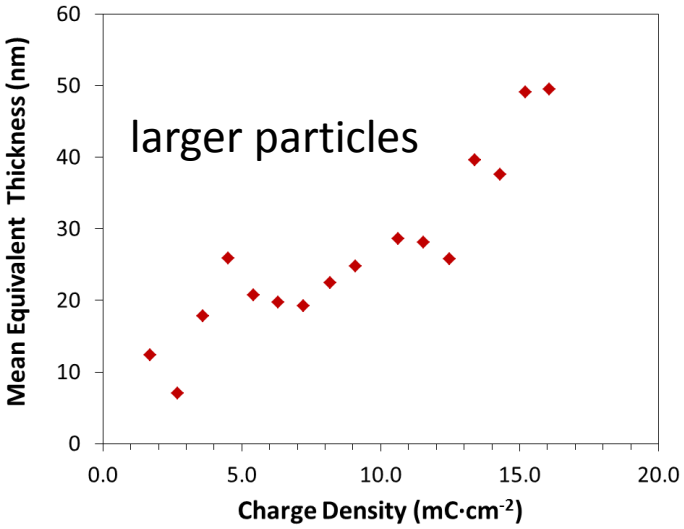


- Low rate leads to large step particles and a thin film between steps
- High rate leads to thin film formation

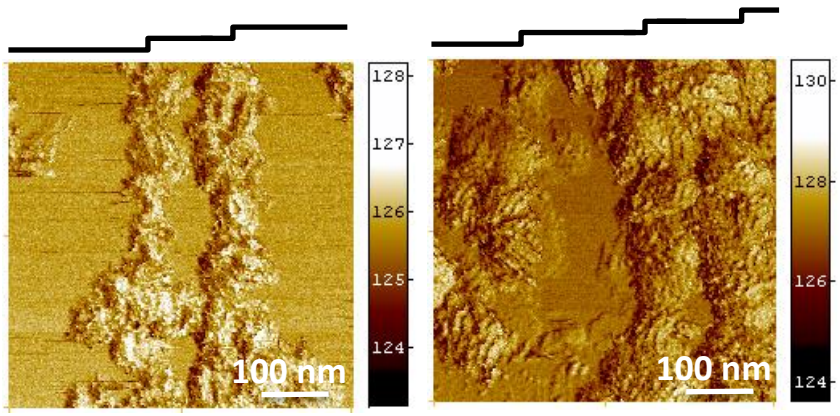
Product Quantity – Surface Capacity are Linked to Discharge Overpotential

- Surprising variance for a “defined and reproducible” HOPG electrode surface: WHY?



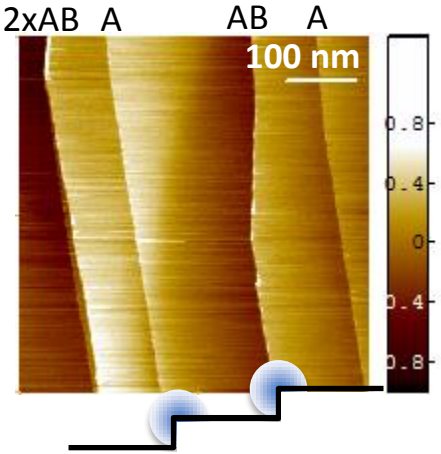


larger particles have the appearance of assembled structures

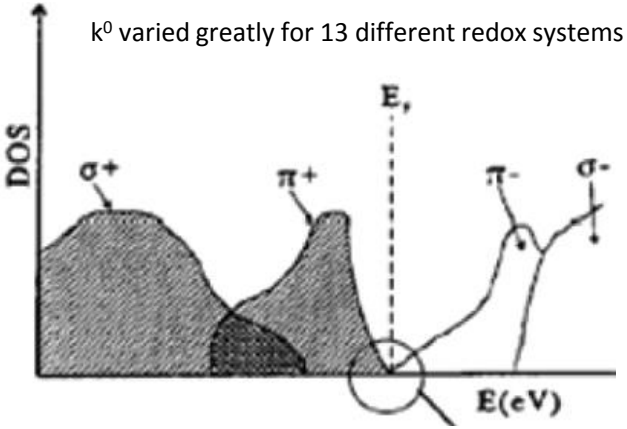


HOPG as a Constitutive Electrode

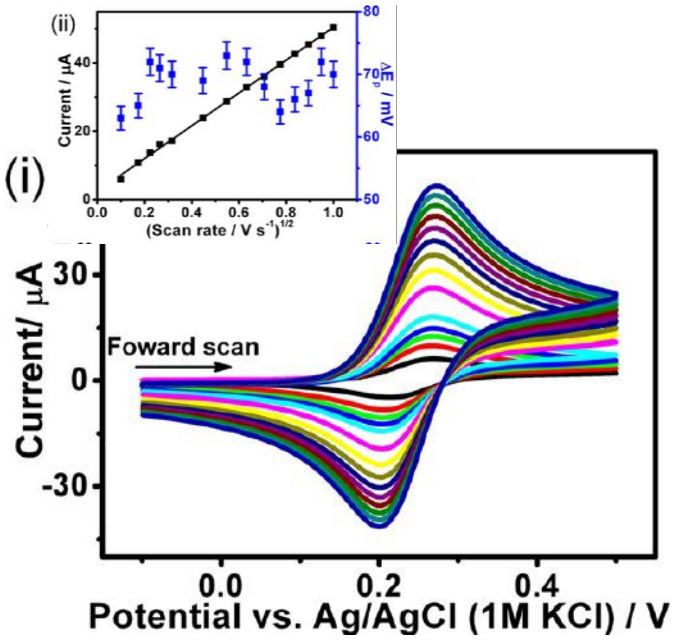
- HOPG chosen for readily identifiable e- transfer sites to correlate with product distribution
  - Conventional wisdom: $k^0_{step} >> k^0_{basal}$ (*e.g.* McCreery et al. *Anal Chem* 2012)
  - k^0 values for HOPG vary by 8 orders of magnitude!
  - Recent challenge: nearly reversible behavior and no differences in CV response with step density (Patel et al. *JACS* 2012)



nanoband electrode

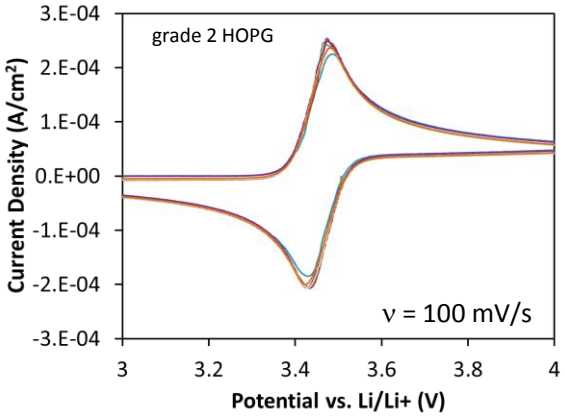


McCreery et al. *Anal Chem* 2012

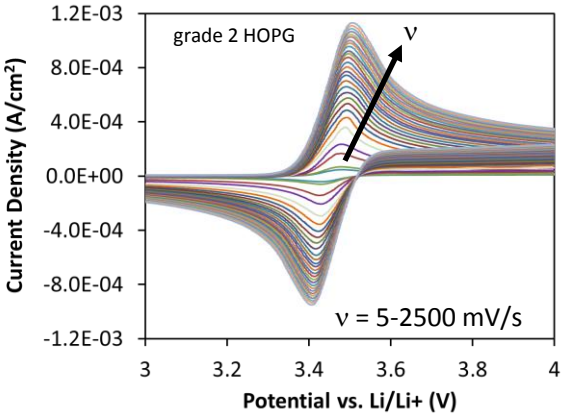


Patel et al. *JACS* 2012

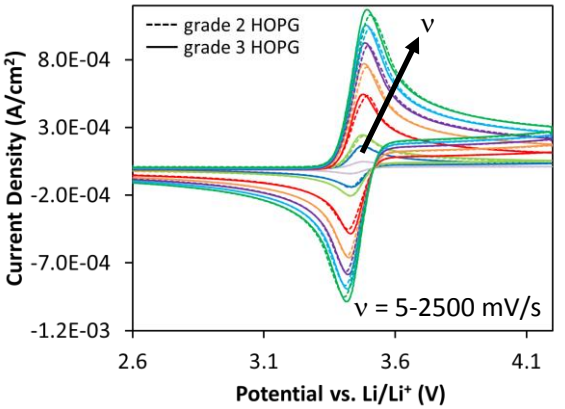
e- Transfer is Fast on HOPG Steps and Terraces



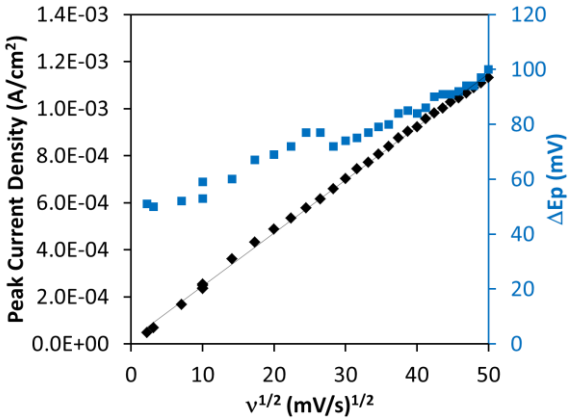
no change over several hours = no gradual surface passivation[1]



high scan rates result in little change in ΔE_p – near reversible behavior



little change with step edge density variation (can account for with changes in R_u)



$i_p \sim \nu^{1/2}$ as expected
ΔE_p shifts can be accounted for by R_u

- CV: 2 mM ferrocene + 1 M LiTFSI in TEGDME
- No change in CV from changes O-ring pressure[2]
- e- transfer is facile
- Step edges and terraces are both active to e- transfer
- Site specificity not being driven by e- transfer at steps
- Nucleation sites likely control product formation

Grade	Mosaic Angle	Grain Size
SPI-1	0.4+/-0.1°	~3 mm
SPI-2	0.8 +/-0.2°	~0.5 mm
SPI-3	3.5 +/-1.5°	<30-40 nm

1. Patel et al. *JACS* 2012 2. McCreery et al. *Anal Chem* 2012

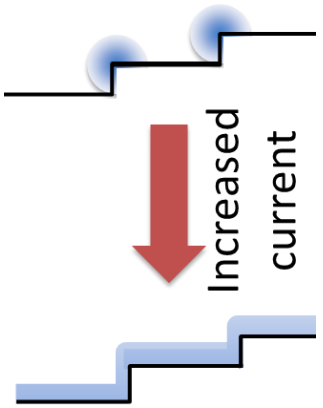
Step Edges as Favored Sites for Product Formation

- Steps are the favored nucleation sites
  - If steps are not the favored e- transfer sites, steps must be favored oxygen adsorption sites
  - Interfacial saturation due to mass transport

Observations consistent with:

$$O_2 + e^- + Li^+ \rightarrow LiO_2\,(soln)$$

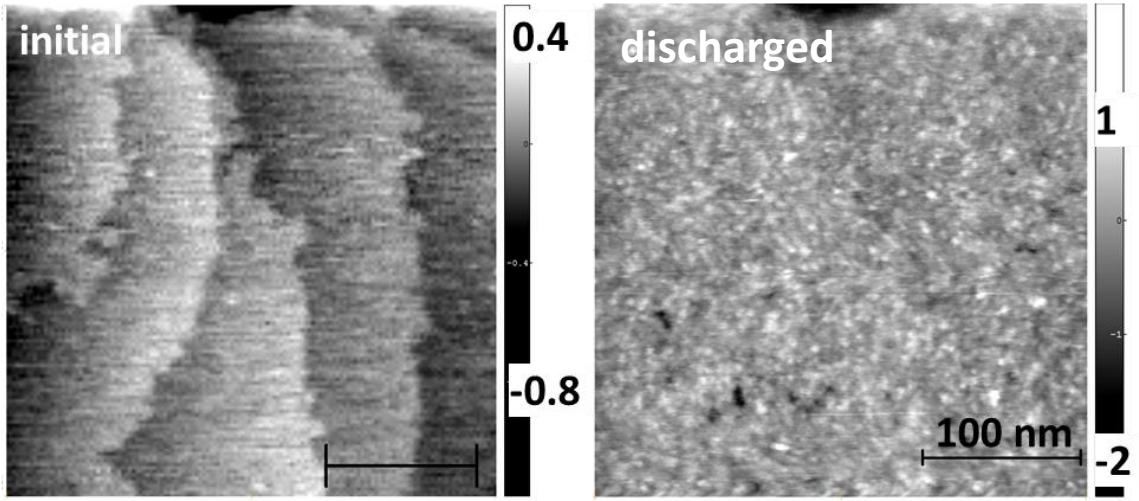
$$2LiO_2 \rightarrow Li_2O_2 + O_2\,(soln)$$



Localized: hemi-cylindrical diffusion

Uniform: semi-infinite diffusion

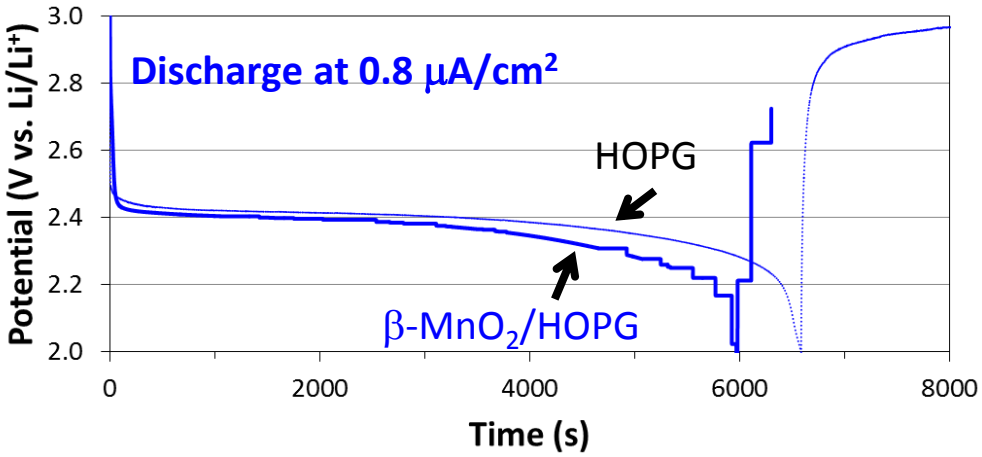
Au(111) surfaces:
minimal difference between step and terrace activity and minimal barrier for nucleation

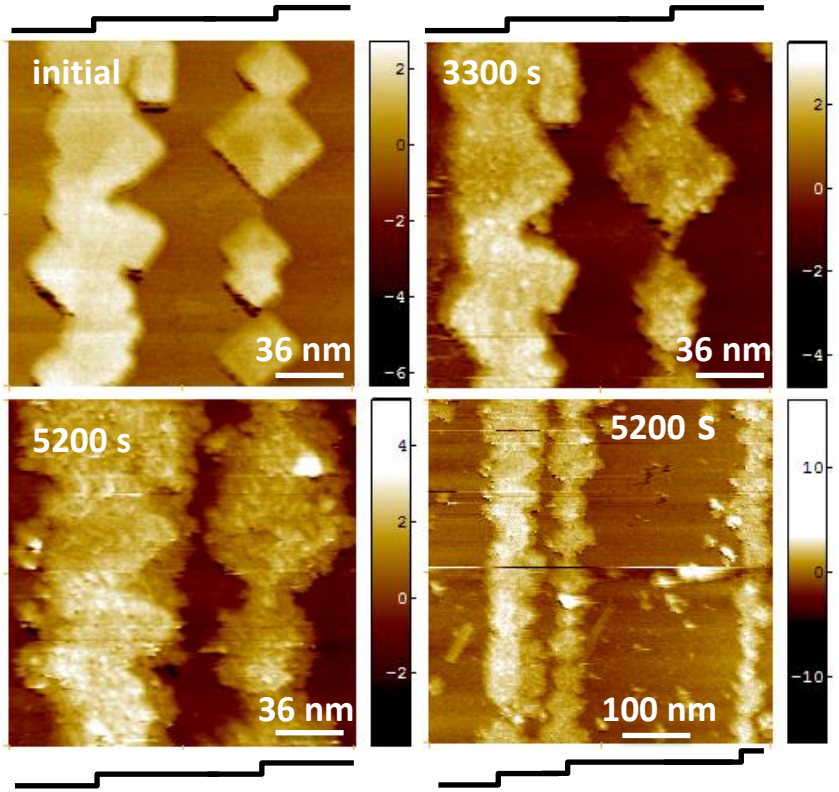


Product Nucleation and Growth Changes with an Oxophilic Surface

Co-locating an oxophilic species with step edges

step edge templated β-MnO_2 on graphite





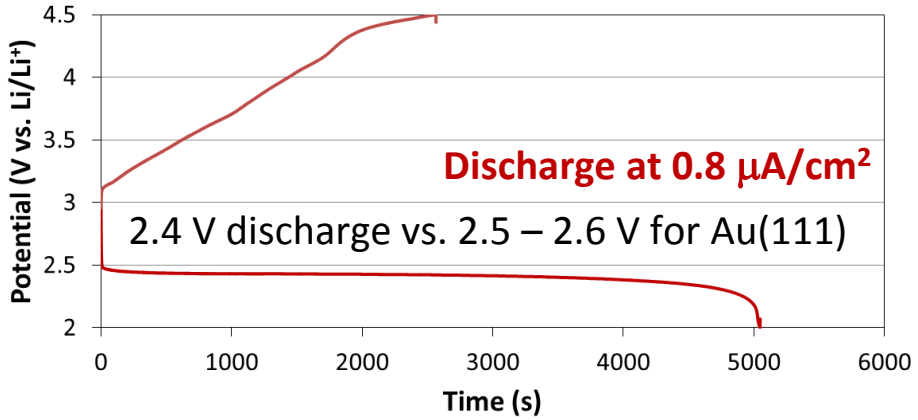
- Peroxide growth is distributed over β-MnO_2 particles
- Conformal and lateral growth vs. large particle growth at the step edges

- Eventual passivation produced by thin conformal film growth on the basal plane

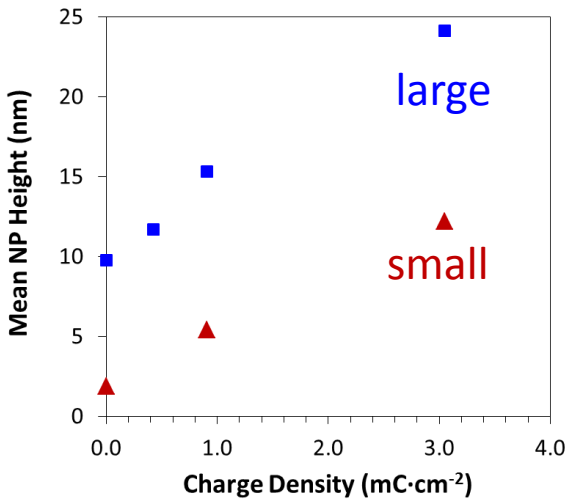
β-MnO_2 deposition by N. Hahn (SNL)

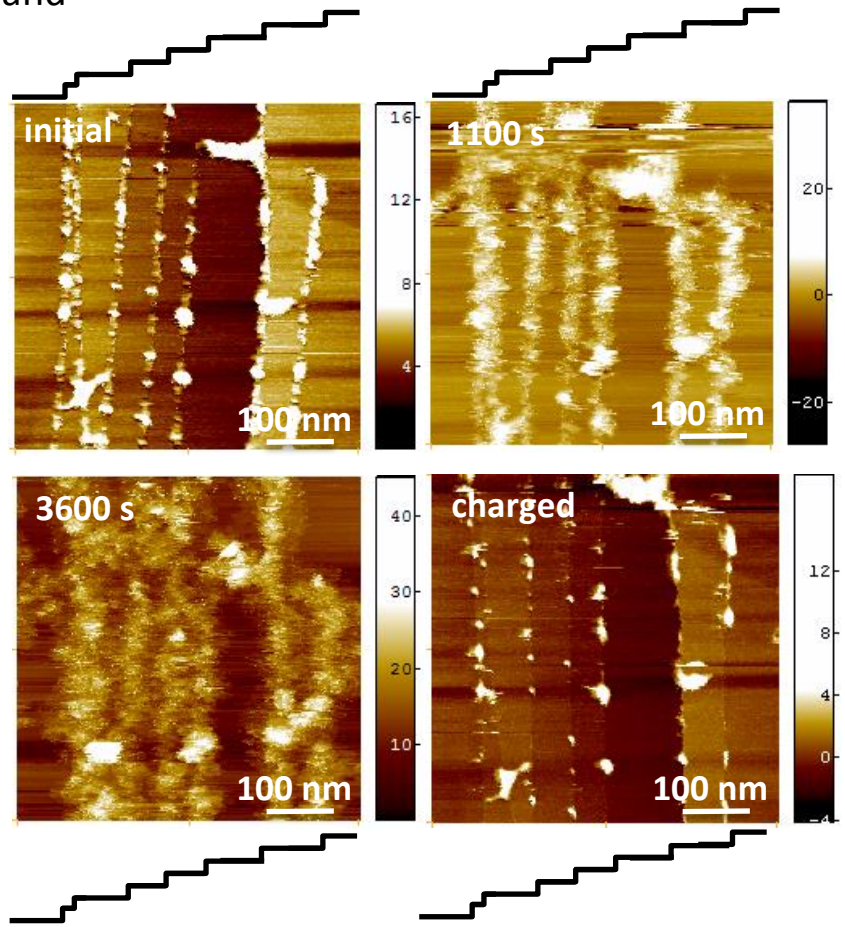
Step Edge Decoration with a High DOS Metal Yields a Similar Response

We anticipate Au NP's serving as both electron transfer and product nucleation sites



- Growth of product over and around the Au NPs
- No clear NP size effects

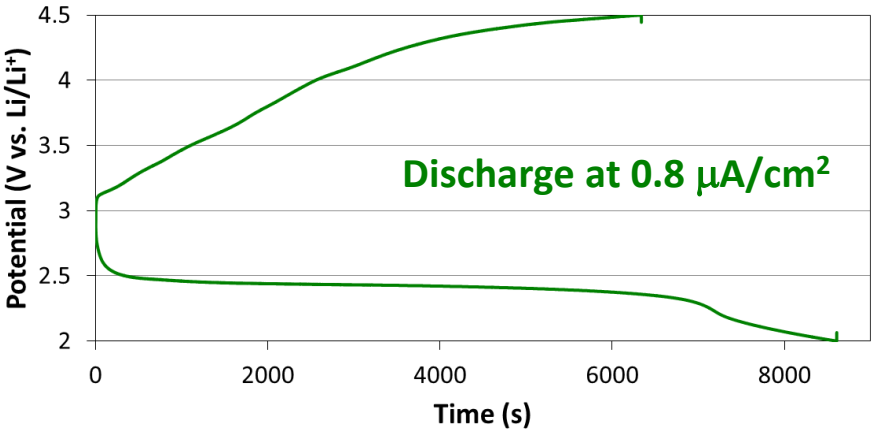




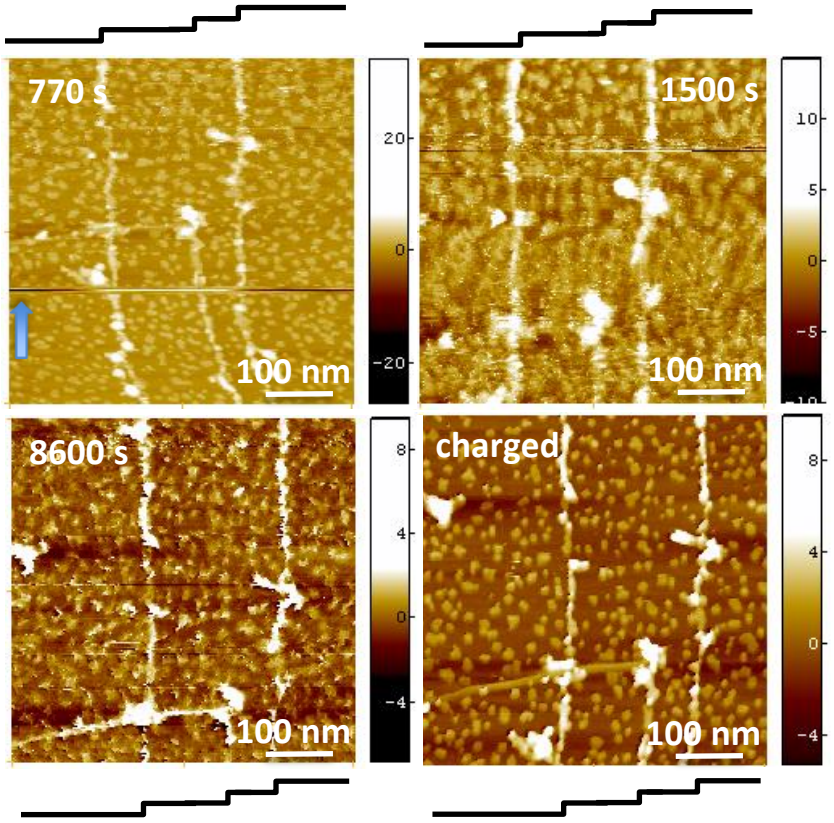
- Some NP displacement after charging – step edges minimally altered

Directing Nucleation onto the Terrace of HOPG

Backfill the terrace with β-MnO_2 to make the terrace more oxophilic – low energy ion oxygenation to pin oxide NPs at defects



2.4 V discharge potential vs. 2.6 V reported for β-MnO2 (LiTFSI, TEGDME)*

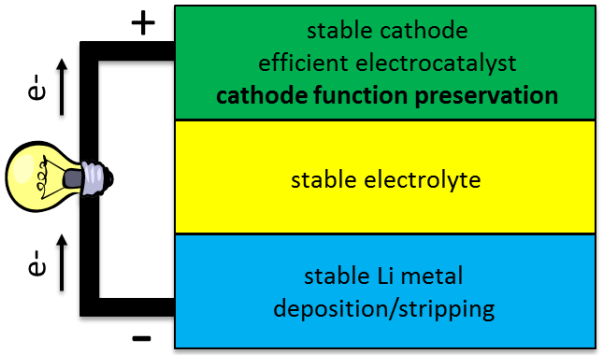


- MnO_2 particles encapsulated with product
- Inter-particle area is infilled with product
- Apparent Au NP heights remain constant – continuous film growth is occurring everywhere

*O. Oloniyo et al., *J. Electron. Mater,* DOI: 10.1007/s11664-012-2046-1

Conclusions

- Peroxide product formation is dictated by electrogeneration rate
  - High rates lead to thin films without distinction between terrace and steps
  - Low rates lead to large particle nucleation on the steps and a thin film between the large particles
  - The HOPG surface eventually passivates as a result of compact film formation
- Steps are the active nucleation sites
  - Steps not the dominant e- transfer sites
  - Nucleation and growth can be spatially directed by controlling the oxophilicity of the surface



Acknowledgements

Experimental advice from J. Jirkovsky (ANL) and B. Adams (U. Waterloo)
Distillation guidance from D. Wheeler (SNL) and characterization by T. Alam (SNL) and T. Borek (SNL)
XPS data from M. Brumbach (SNL) and ToF SIMS data from T. Ohlhausen (SNL)
Discussions with L. Nazar (U. Waterloo) and L. Curtiss (ANL)
β-MnO_2 deposition by N. Hahn (SNL)