SAND2013-10352C

JCESR | JOINT CENTER FOR ENERGY STORAGE RESEARCH

Dynamics of Lithium Peroxide Formation on Graphite and Gold Electrodes Imaged through Electrochemical Scanning Probe Microscopy

Kevin R. Zavadil and Katherine L. Harrison

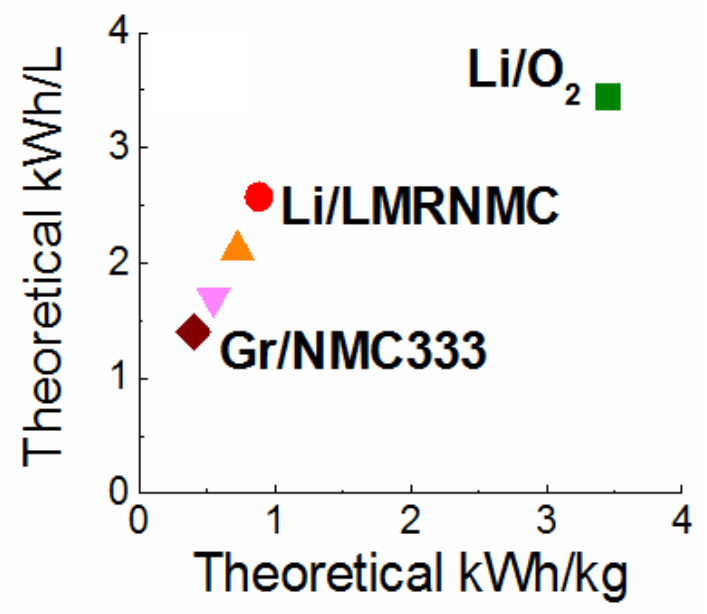
Sandia National Laboratories

2013 Fall MRS 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.

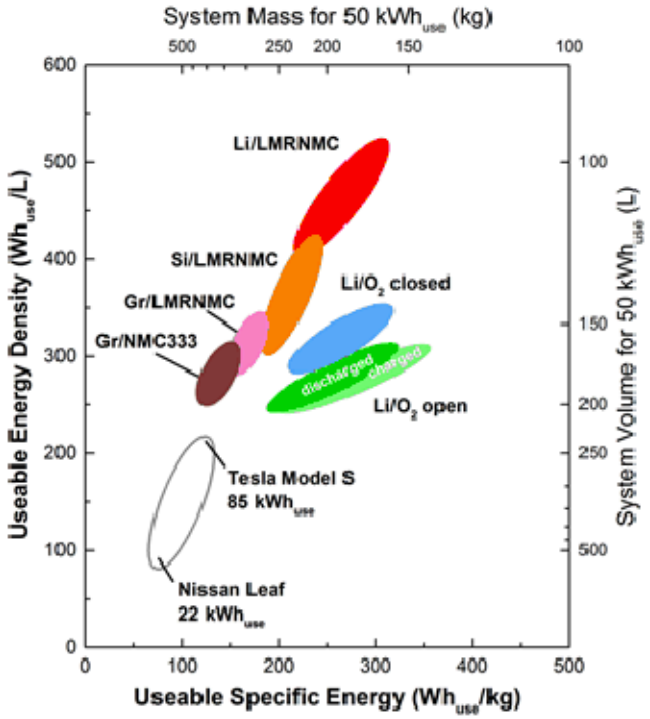
Li-O_2 Batteries Show Promise as Enhanced Energy Density Storage Systems

the promise



Full scale systems analysis

the reality



K.G. Gallagher et al. ECS 224th Meeting, submitted to *Energy Environ. Sci.*

Li-O_2 could delivery specific energy density gains 2-5X beyond state of art Li Ion

Challenges to Achieving Efficient O_2 Electrochemistry for Li-O_2 Batteries

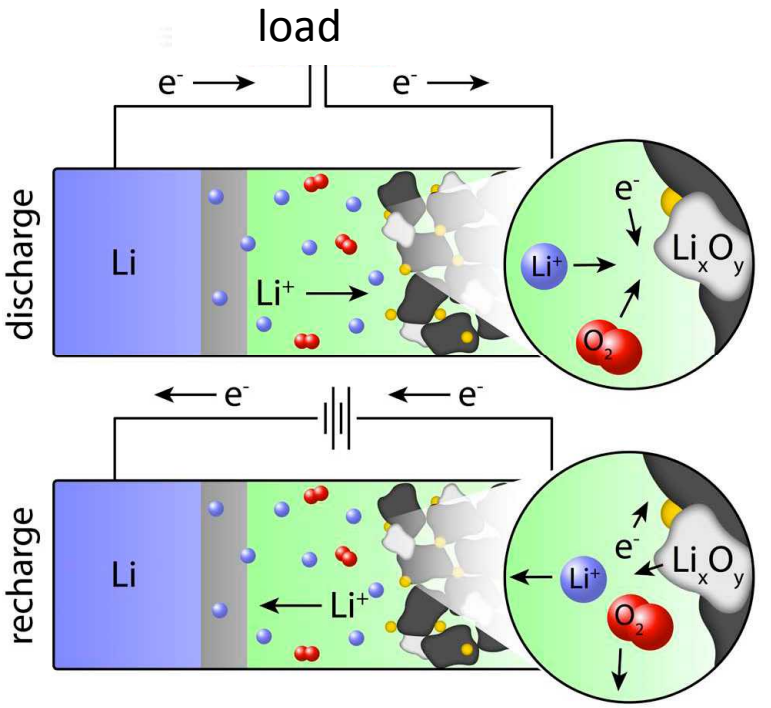


image courtesy of M. Radin and D. Siegel, U. Mich.

ORR Discharge

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

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

disproportionation

$2LiO_2 \rightarrow Li_2O_2 + O_2$

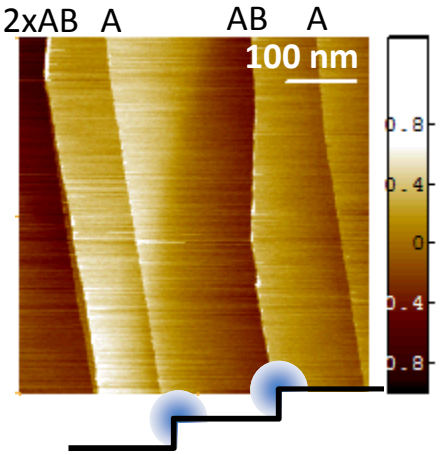
OER Charge

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

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

O_2 Cathode Function and HOPG as a Constitutive Electrode

- monitor impact of ORR – image solid peroxide formation pathway and processes using EC-AFM
- readily identifiable electron exchange sites - separable from nucleation sites
  - RRDE shows O_2^- has residence time in TEGDME (e.g. Jirkovsky and Markovic, 242th ECS)
  - TEGDME exhibits stability toward O_2^-
  - Peroxide solubility in dry TEGDME?
- possibility of creating nucleation sites
- do not have the structure factor of a mesoporous carbon
- can introduce catalysts to a graphite surface - see N. Hahn's presentation
- Not the first – several reports exist for Li_xO_y formation on graphite and Au (Wen et al. JACS 2013)



nanoband electrode

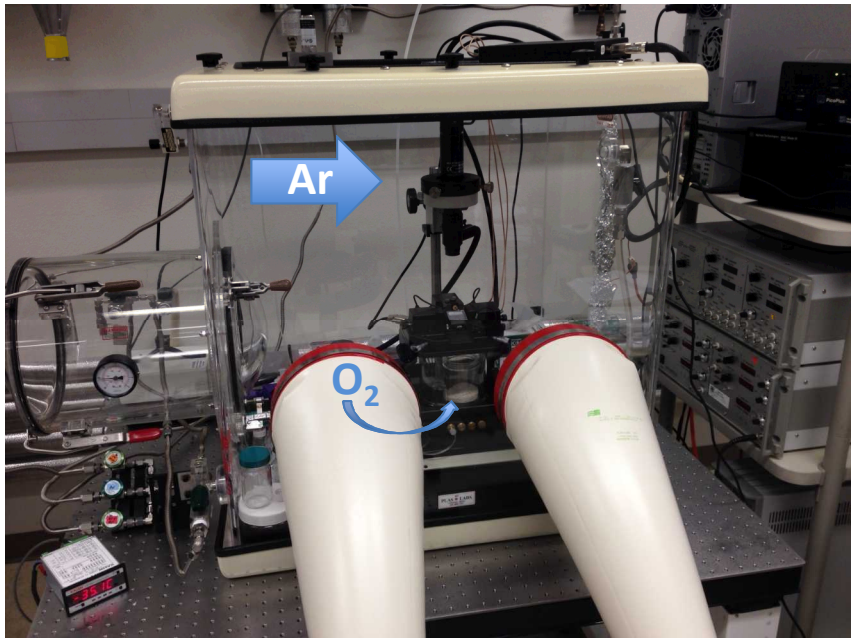
O_2^{ads} as the critical precursor – $k^o_{step} >> k^o_{basal}$ (McCreery et al. *Anal Chem* 2012)

Our goal is to understand the role of electrogeneration rate on product distribution (Adams et al. *Energy Environ Sci* 2013)

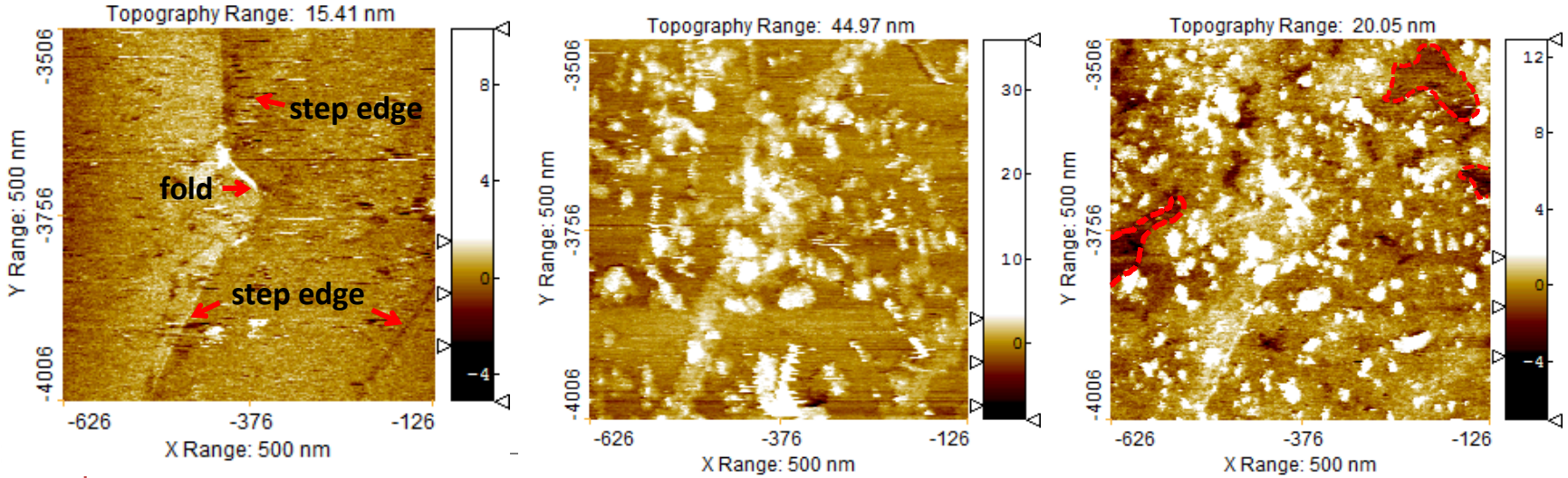
A Few Key Experimental Details

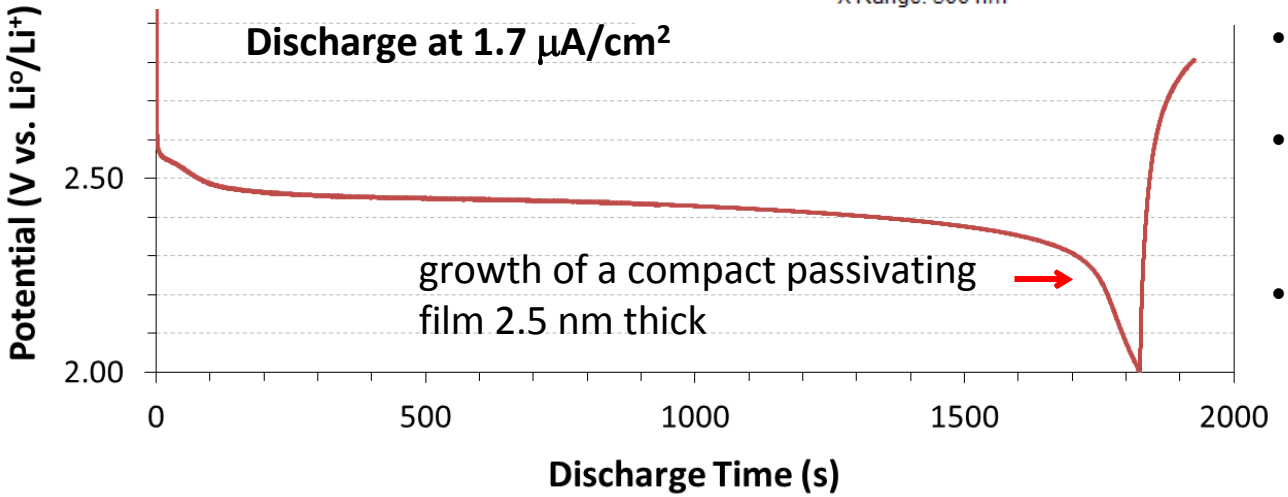
- Electrochemical AFM
  - 0.4 ml electrolyte volume : 1.2 cm^2 electrode area
  - Three electrode, both Li and Au (convenient) CE
  - galvanostatic – rate
  - swept and static potential - regimes

- TEGDME + $LiNTf_2$
  - distillation, drying, characterization



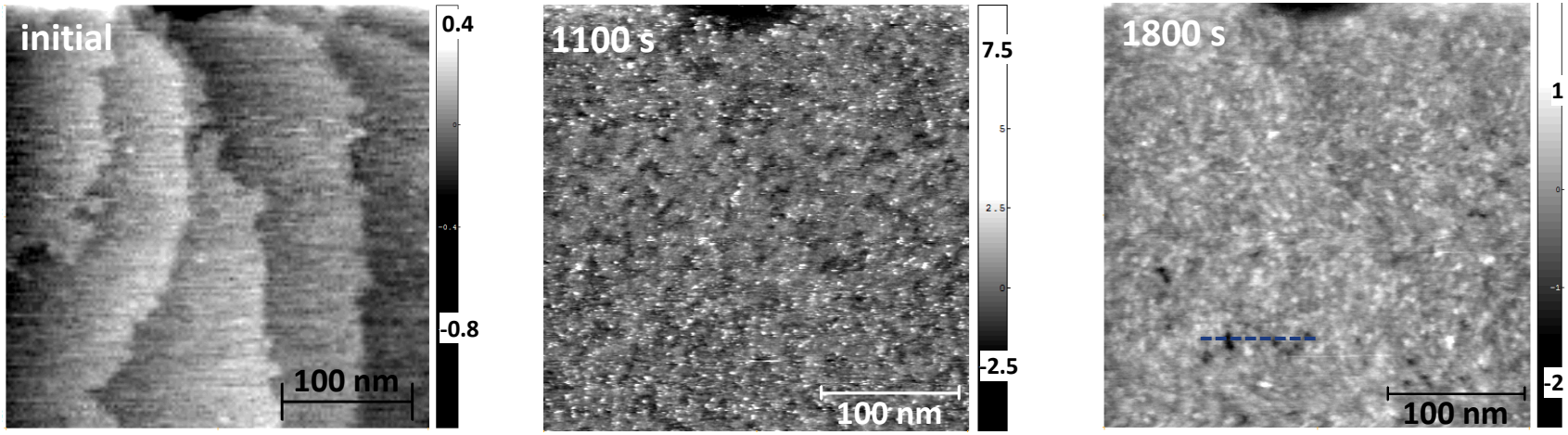
Solid Product Nucleation Occurs at Distances Away from Step Edges – Solution or Surface Mediated Transport

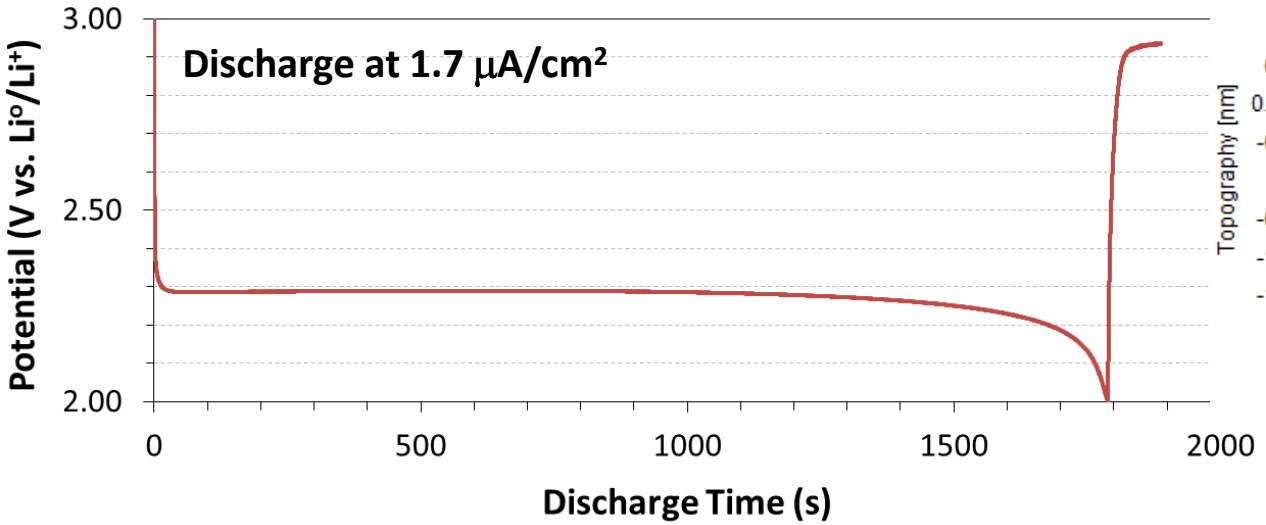


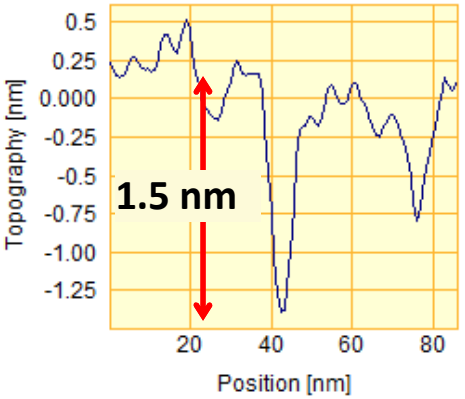


- Combination of step edge and terrace nucleation
- Terrace particles are more susceptible to tip displacement
- Additional cathodic polarization is driven by compact film formation

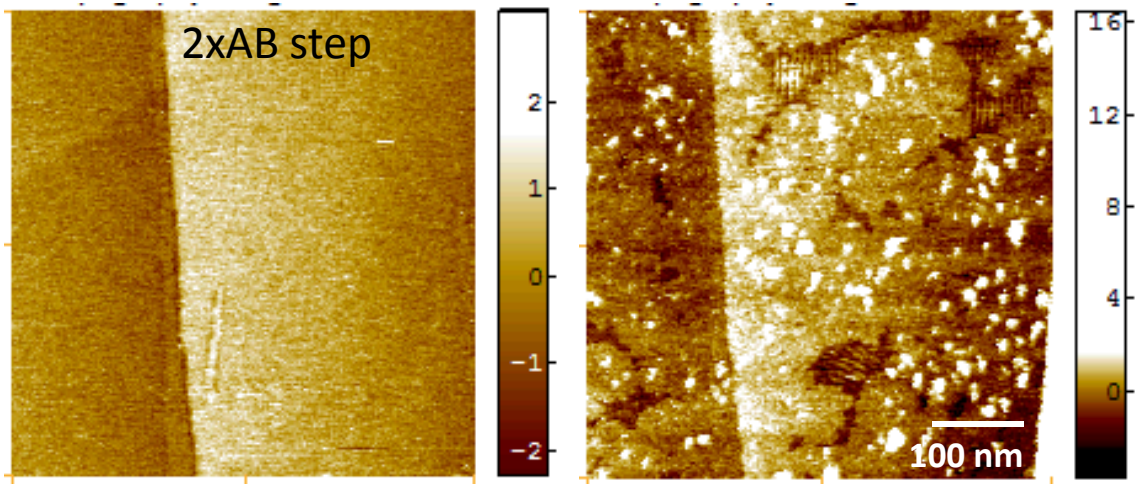
Eliminate Structural Defects Responsible for Enhanced Electron Transfer and Compact Films Form: Au(111)



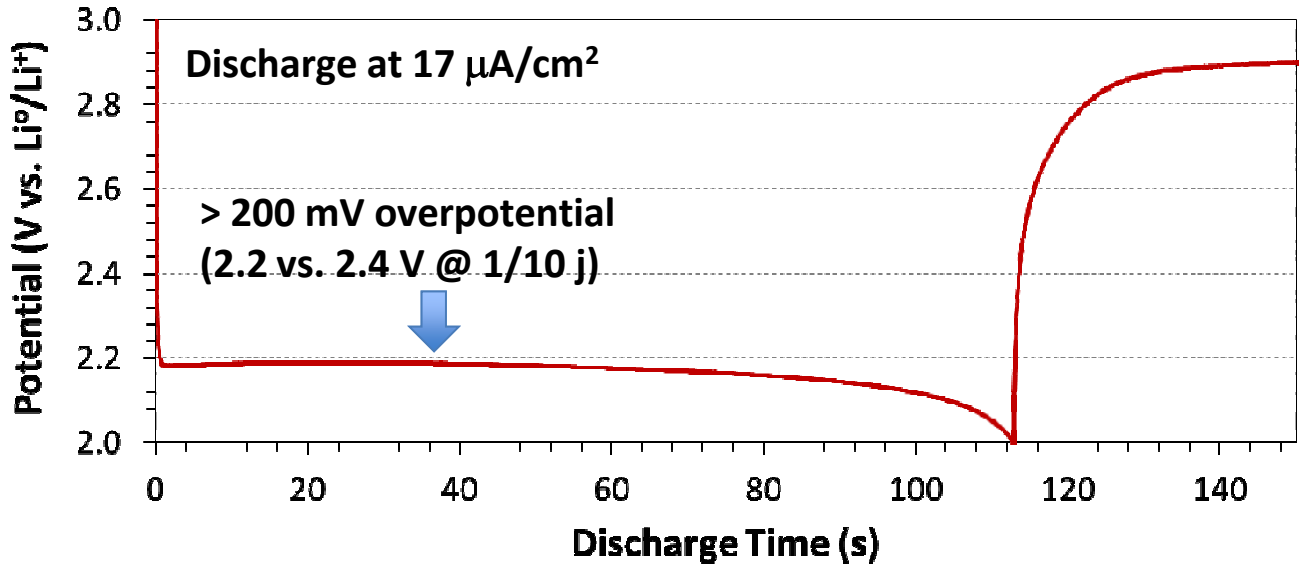


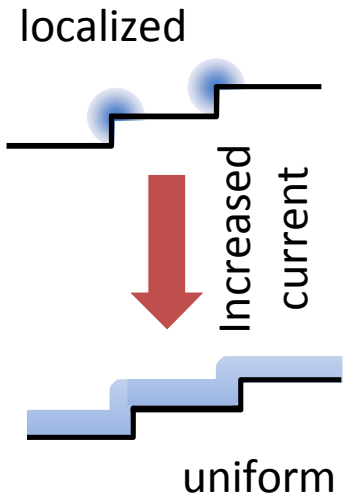


Rate Dependence: Steps are not Necessarily Preferred Early Stage Nucleation Sites

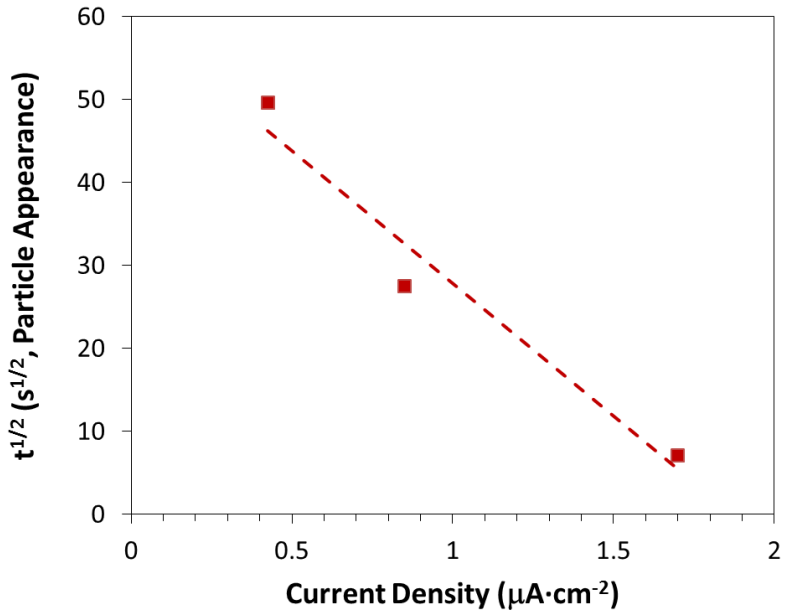


- Randomly dispersed 8 – 10 nm particles
- 2.5 nm thick continuous film
- Open terrace with self-assembled structures





A Snapshot of Rate Dependency

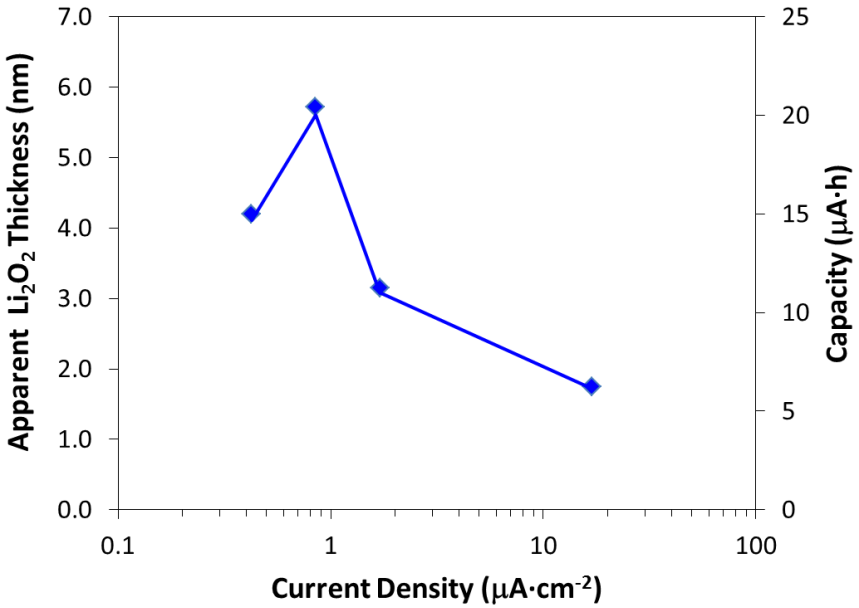


Particle nucleation is diffusion controlled

- square root dependence between electrogeneration rate and time of first particle appearance

Peroxide capture at the graphite surface appears efficient:

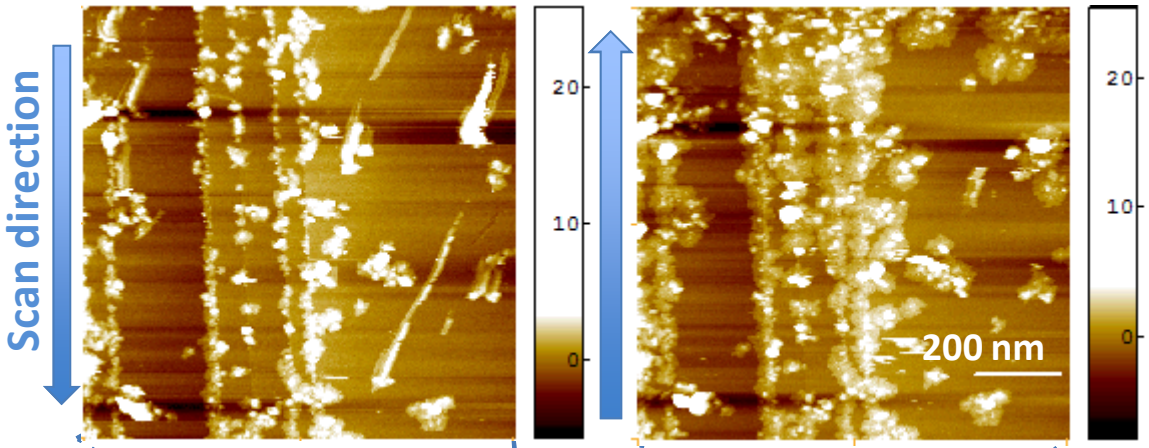
- calculated electrogenerated peroxide thickness approximates the average estimated thickness



Rate Dependence: Step Edge Appear to Passivate First under Slow Rate Discharge

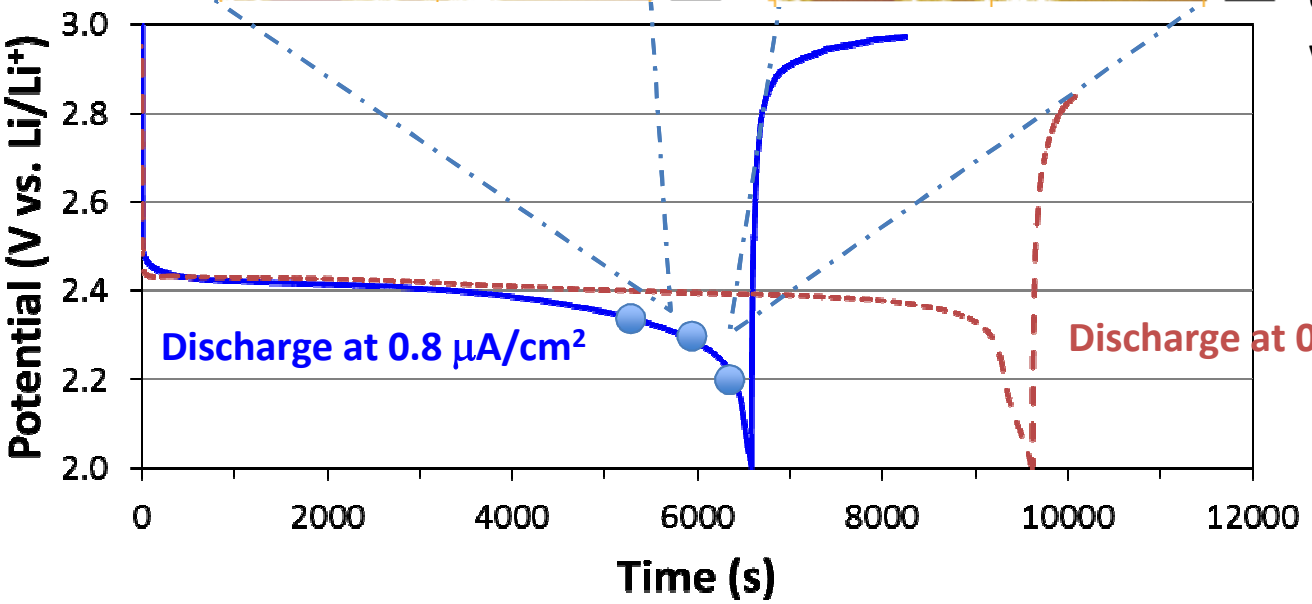
Displacement of terrace particles

Particles do not appear to block access of O_2



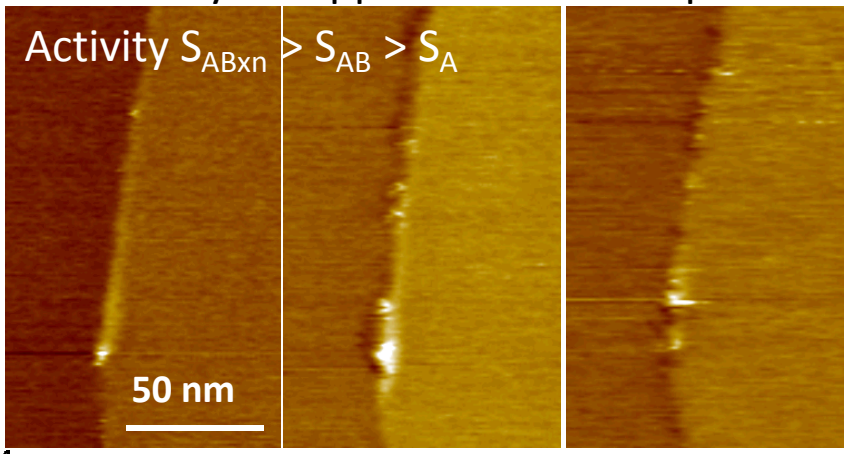
Compact film formation starts at the steps

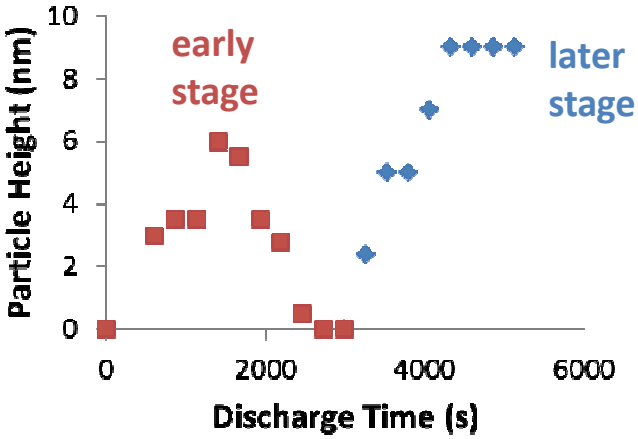
Progression of step edge encapsulation with peroxide



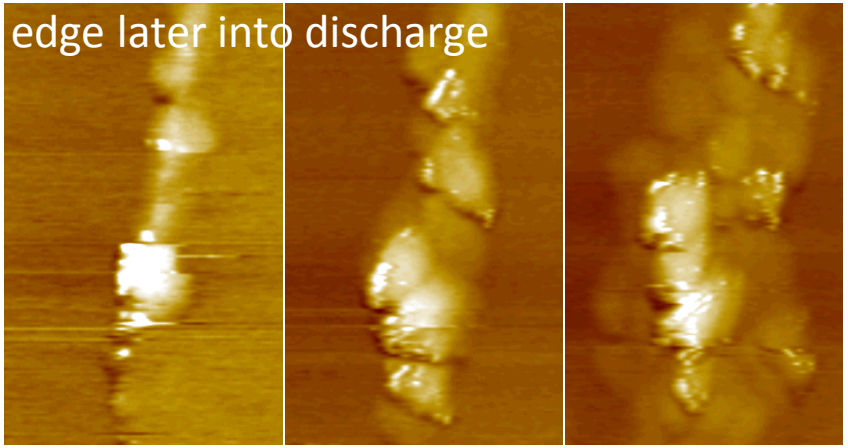
Particle Formation Correlates with Activity and Time

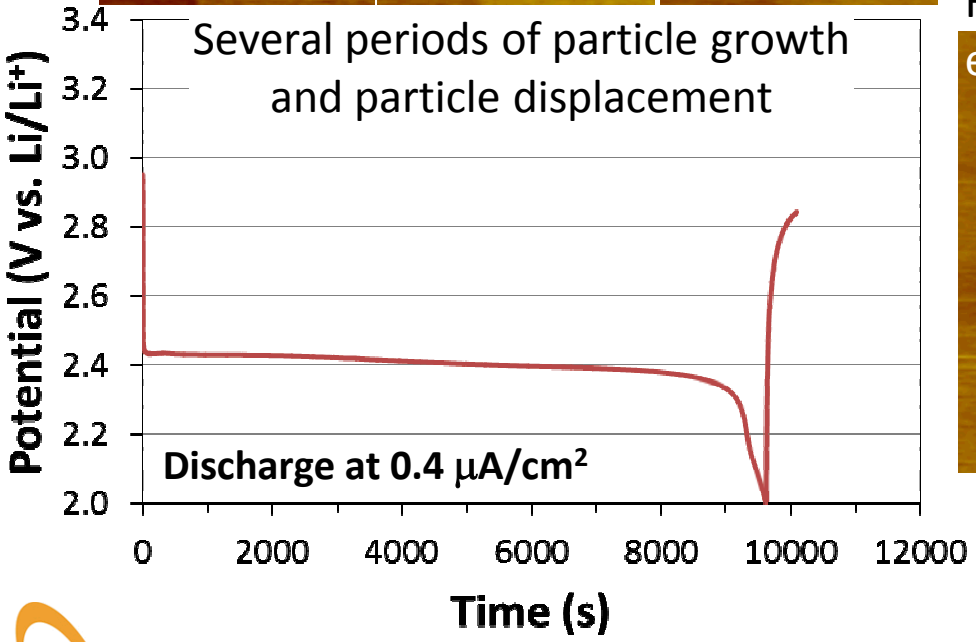
Time delay for appearance of first particles





Higher density of particles form at a step edge later into discharge





Larger scale lateral particle growth
Growth of an infilling compact film

Conclusions

- Peroxide particle nucleation and growth appears to be a solution mediated process
  - Clear evidence of diffusion control of initial growth
  - driven by some degree of peroxide solubility
  - or solution mediated disproportionation

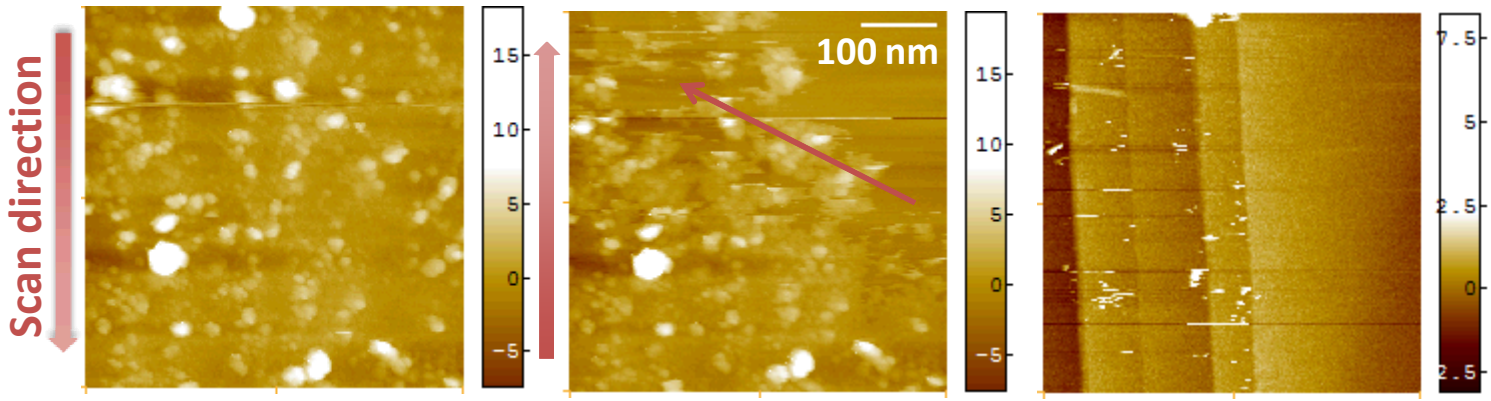
- Steps as superoxide/peroxide sources are not preferential sites for product nucleation and growth

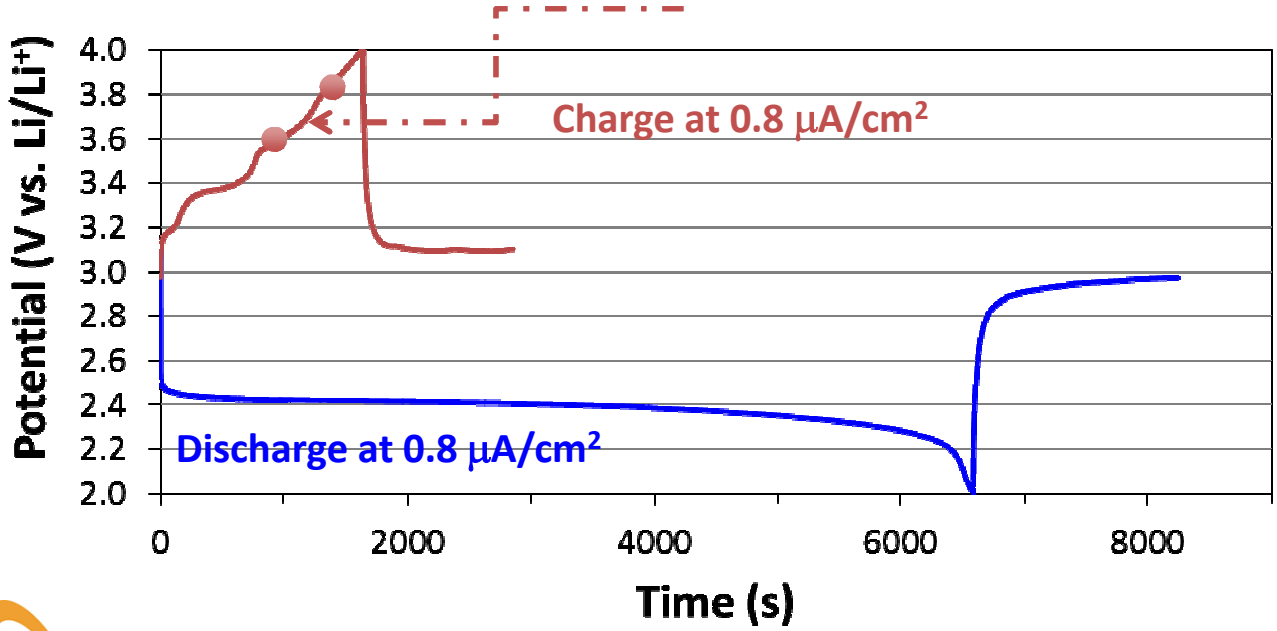
- Step edges eventually passivate – very high step edge are normalized current densities

Acknowledgements

Experimental advice from J. Jirkovsky (ANL), B. Adams (U. Waterloo)
Distillation guidance from D. Wheeler (SNL) and NMR analysis by T. Alam (SNL)
Discussions with L. Nazar (U. Waterloo) and L. Curtiss (ANL)

Film Loss during Charging (OER)





The compact film appears to be the material that electrodissolutes first

Dissolution progresses from terrace toward step