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

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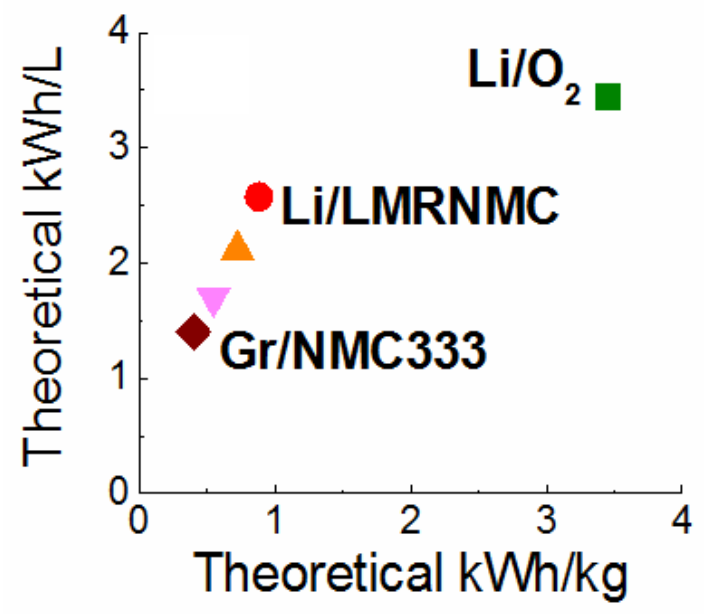
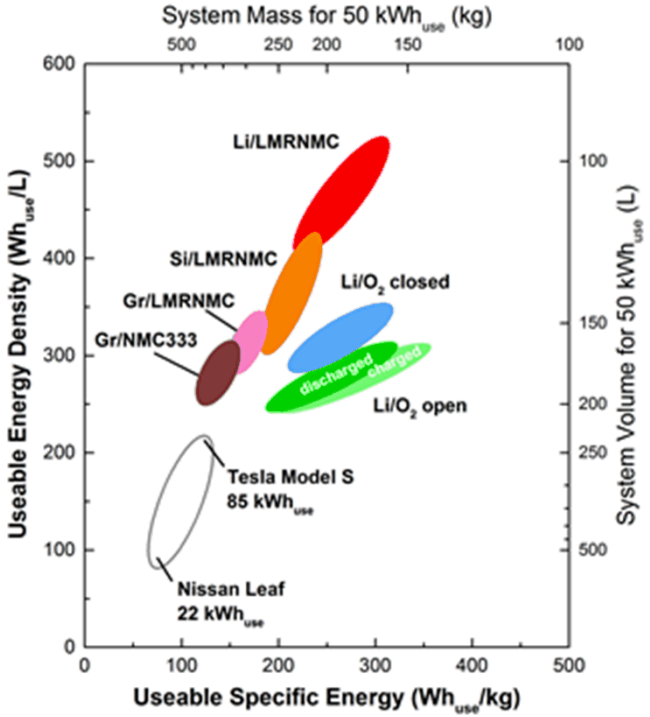
Li-O_2 Batteries Show Promise as Enhanced Energy Density Storage Systems

the promise



Full scale systems analysis

the reality



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

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

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

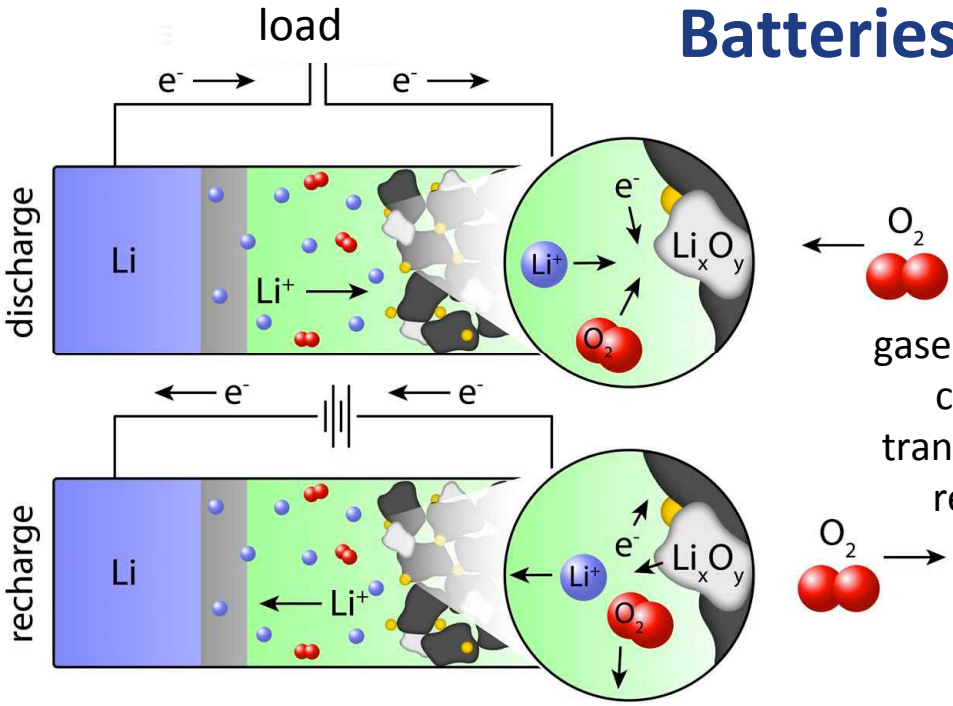


image courtesy of M. Radin and D. Siegel, U. Mich.

ORR Discharge

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

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

disproportionation

$2LiO_2 \rightarrow Li_2O_2 + O_2$

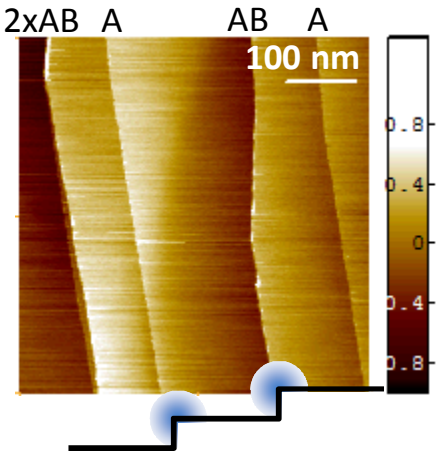
OER Charge

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

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

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
- Not the first – several reports exist for Li_xO_y formation on graphite and Au (Wen et al. JACS 2013)



nanoband electrode

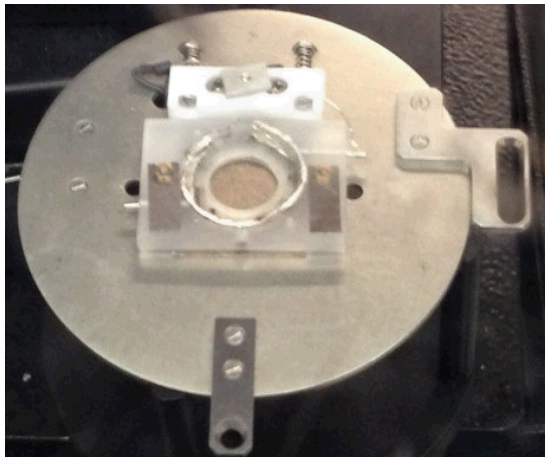
O_2^{ads} as the critical precursor – k^o_{step} >> k^o_{basal} (McCreery et al. *Anal Chem* 2012)

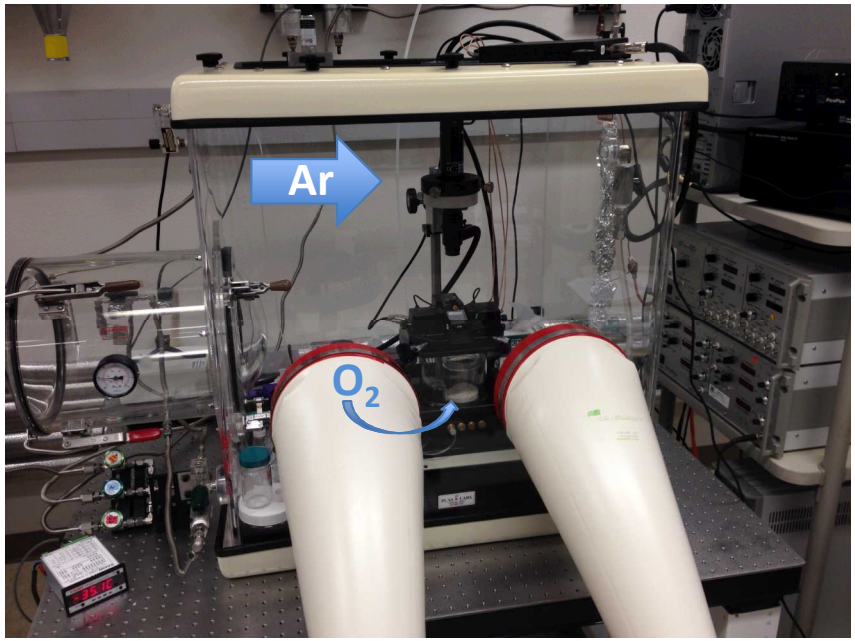
Our goal is to understand the role of electrogeneration rate on product distribution (Adams et al. *Energy Environ Sci* 2013)

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 & voltammetry – focus on rate dependence
  - swept and static potential - regimes

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



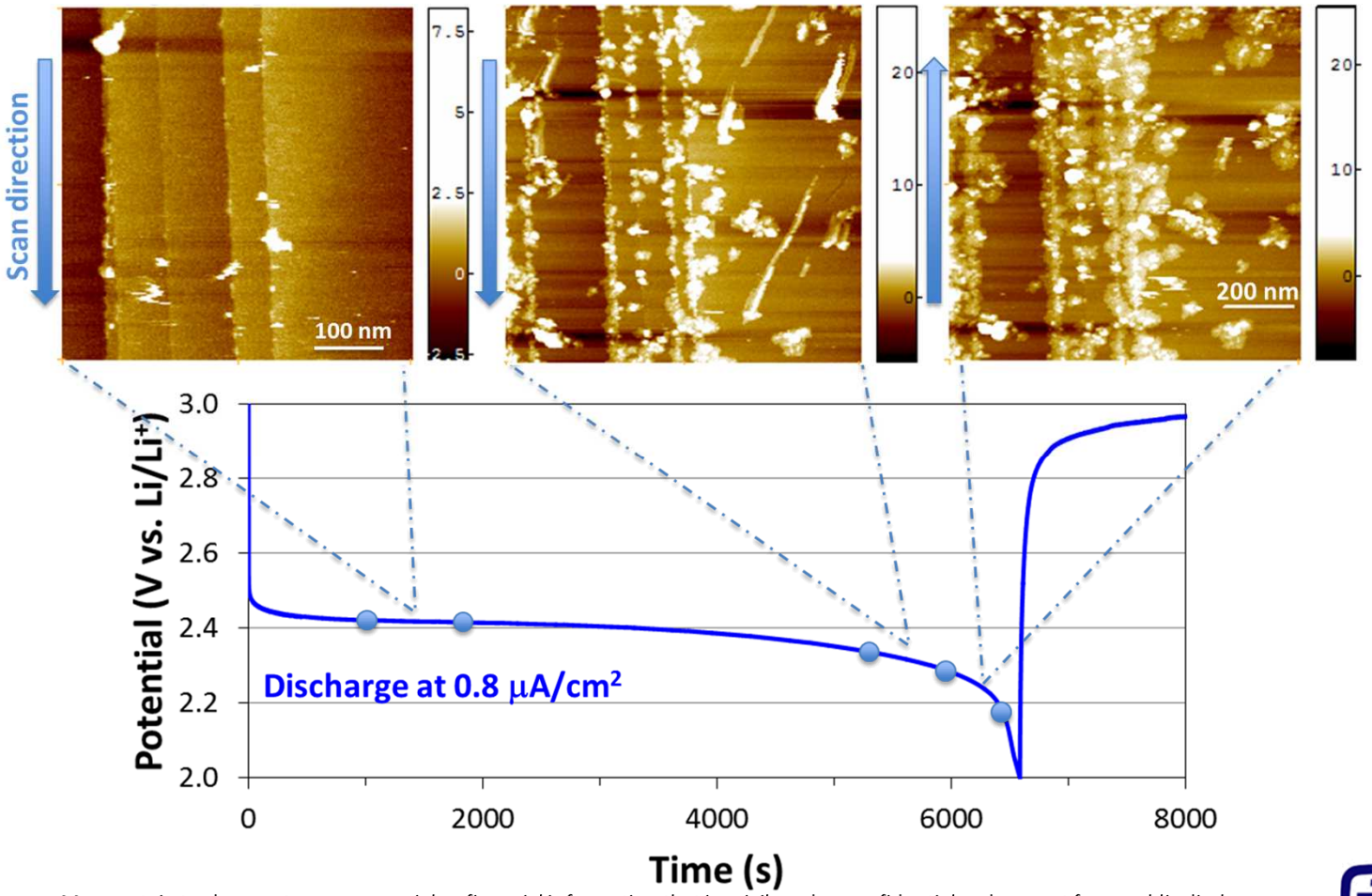


A Reproducible Product Growth Sequence is Observed

Delayed product particle nucleation and growth

Continuous growth of particles - step edge preference

Compact film growth & passivation

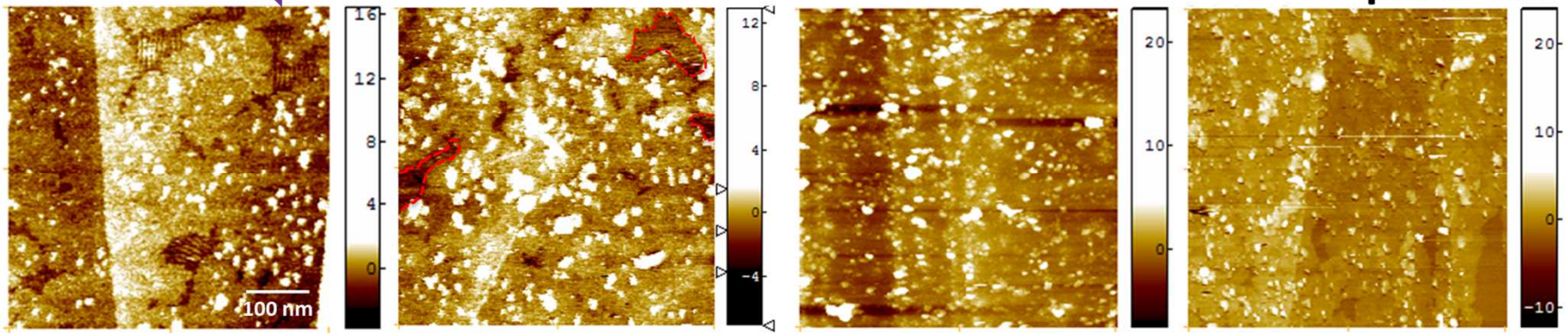


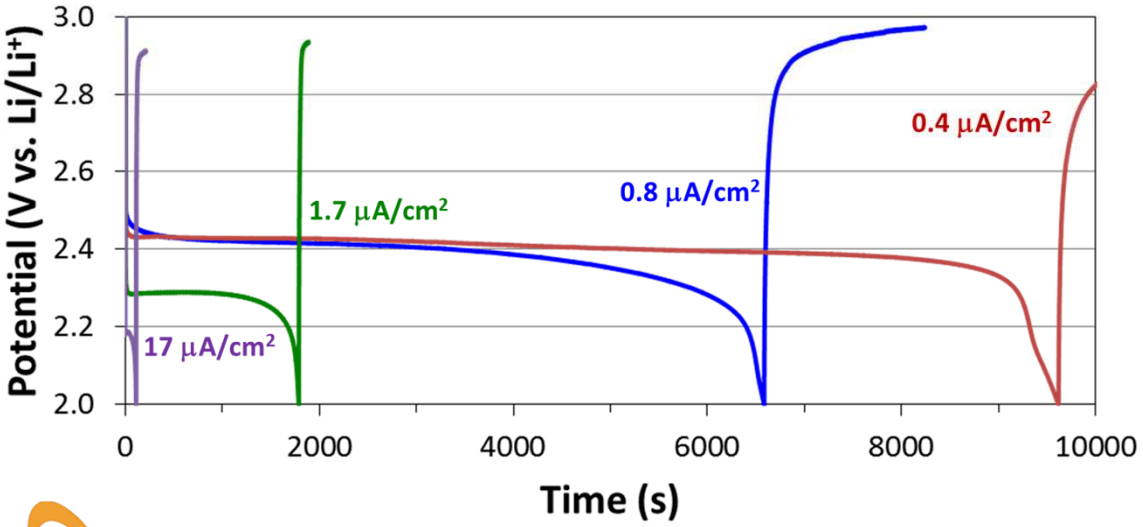
Increasing Rate Forces an Early Transition to Compact Film Formation and Passivation

smaller peroxide particles

Discharge Rate

larger peroxide particles



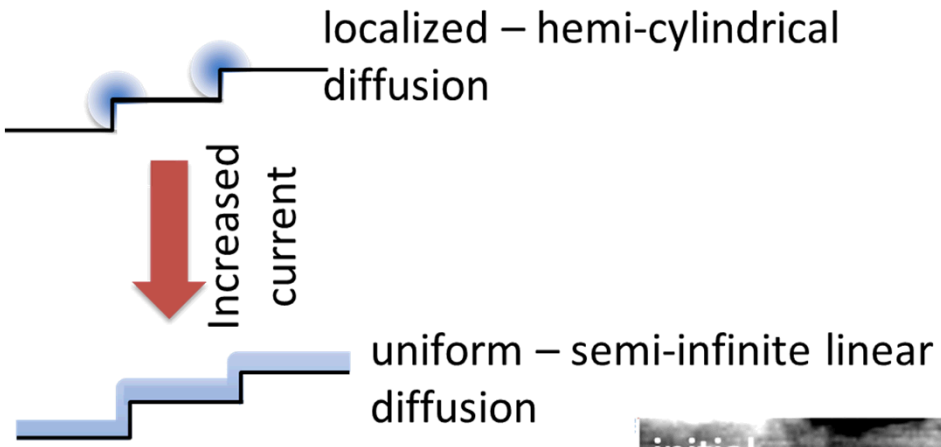


Forcing a high rate discharge shifts the current load from step edge to terrace - e^- transfer site isolation is lost favoring film formation

Step Edges as Favored Sites for Product Formation

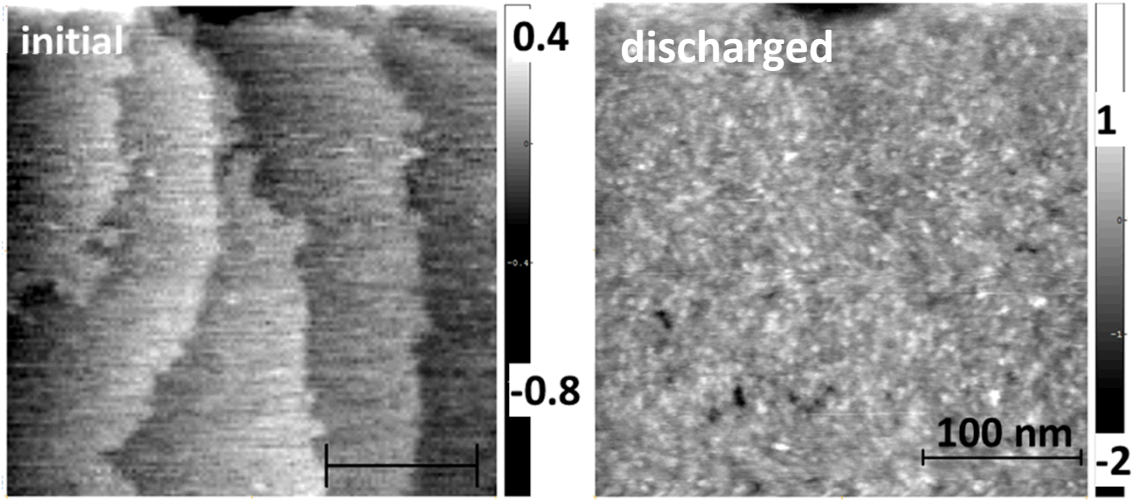
Observations consistent with: $O_2 + e^- + Li^+ \rightarrow LiO_2$ (soln)

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

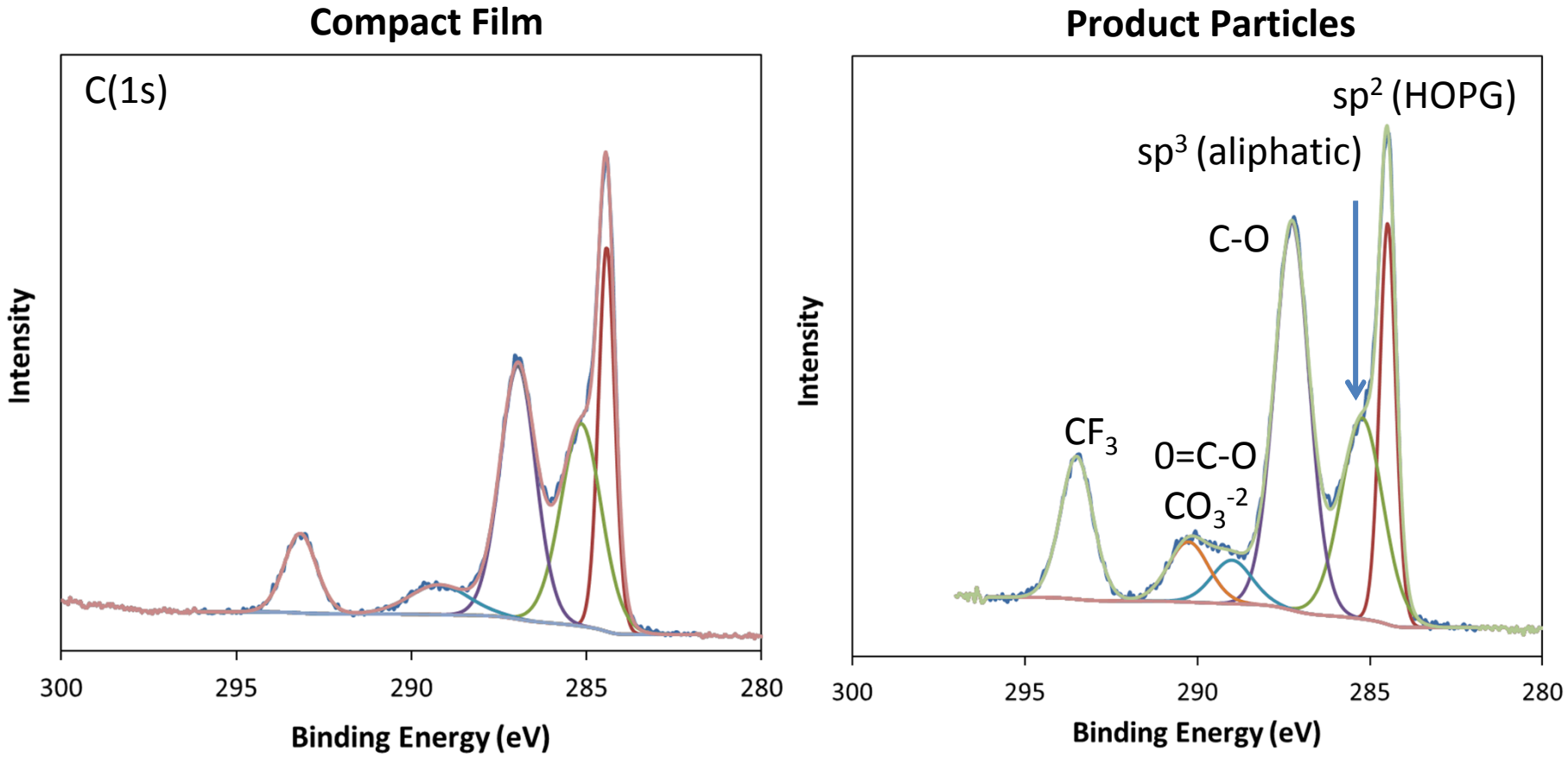


Step edges support high localized current densities
Interfacial saturation due to mass transport
Lower barrier for nucleation

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



Nature of the Passivating Compact Film

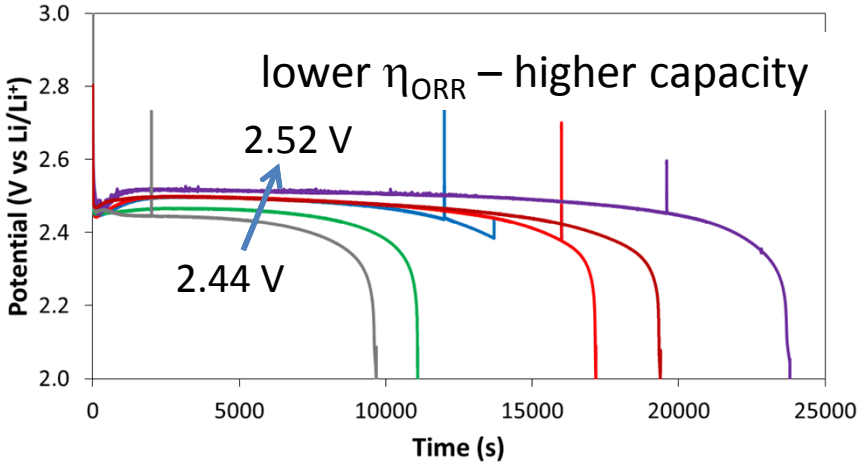


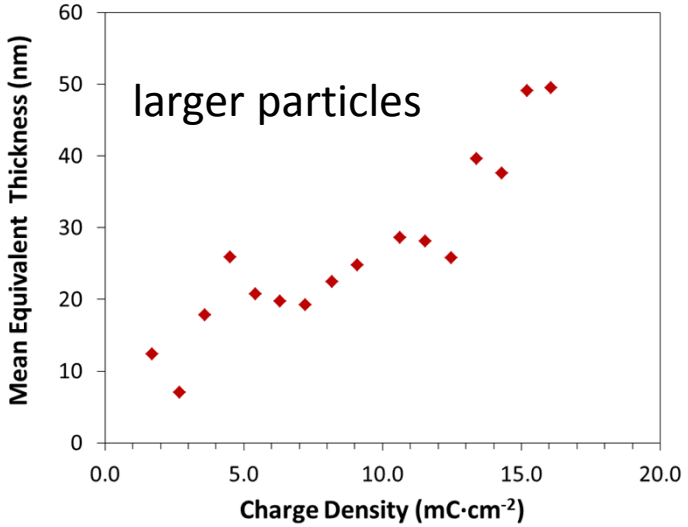
Film composition = Li_xO_y w/ organic

- ToF-SIMS - $Li_xO_y(H)^{\pm}$ manifolds up to x=3 & $LiCO_3^-$
- XPS – carbonate, high C-O content
- Residual (incorporated) TFSI

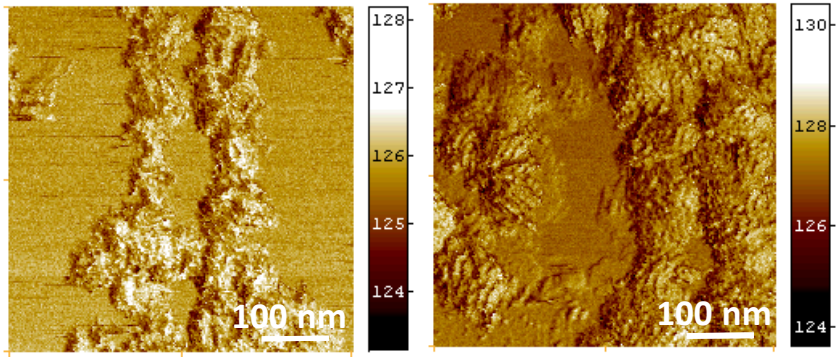
Product Quantity – Surface Capacity are Linked to Discharge Overpotential

Surprising variance for a “defined and reproducible” HOPG electrode surface – mechanically induced defects?*





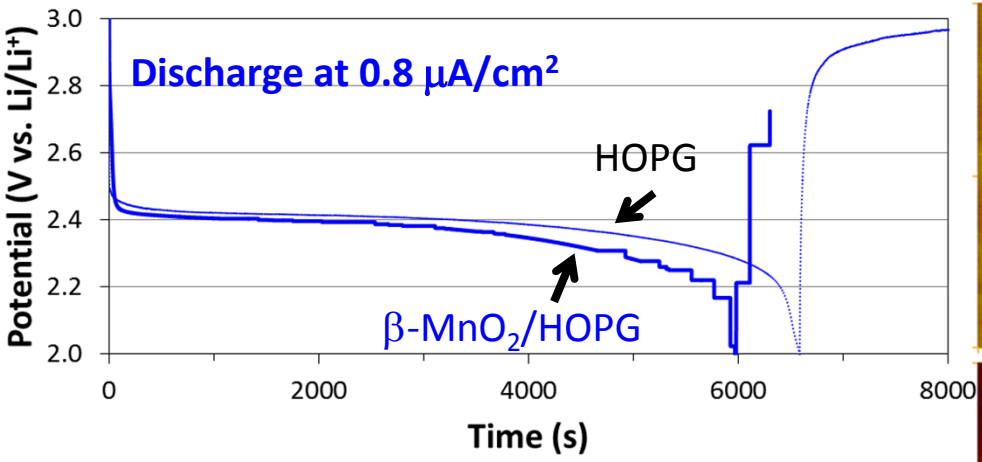
larger particles have the appearance of assembled structures

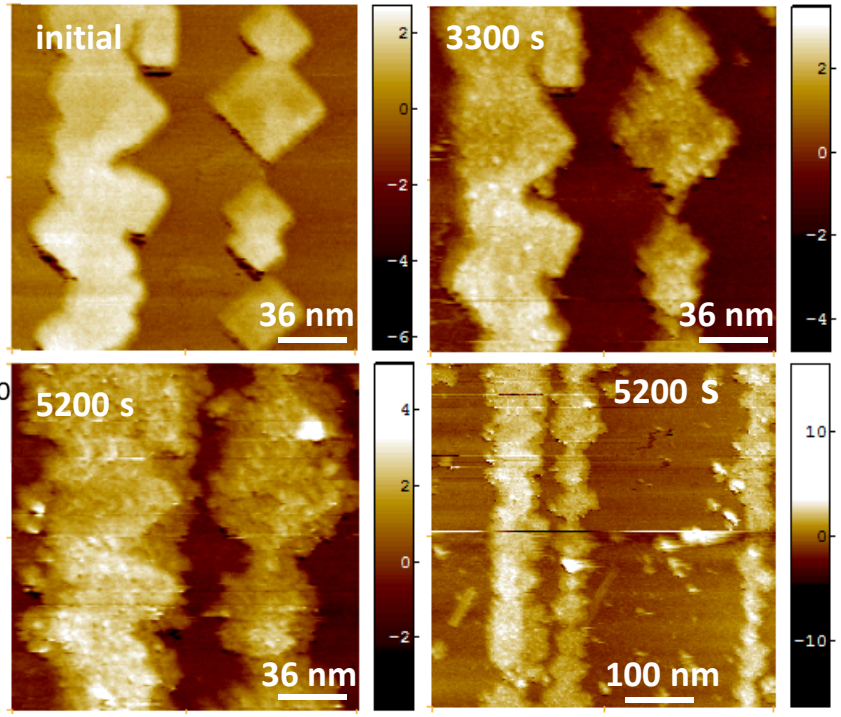


Product Nucleation and Growth Changes with an Oxophillic Surface

Co-locating an oxophillic surface with electron transfer site location

step edge templated β-MnO_2 on graphite

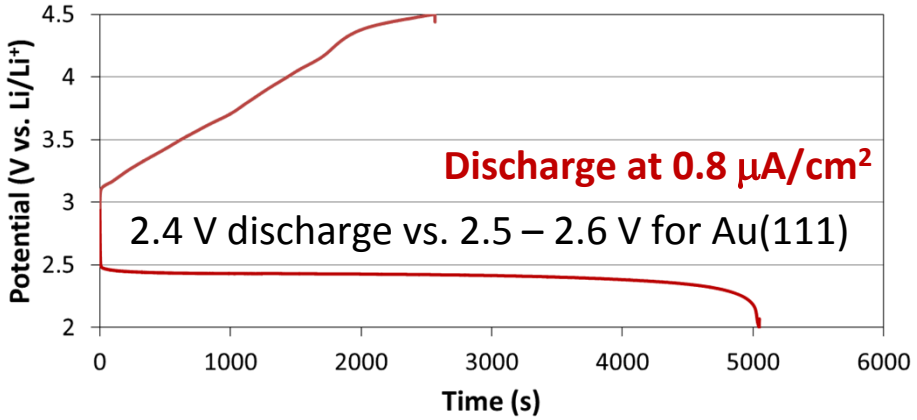


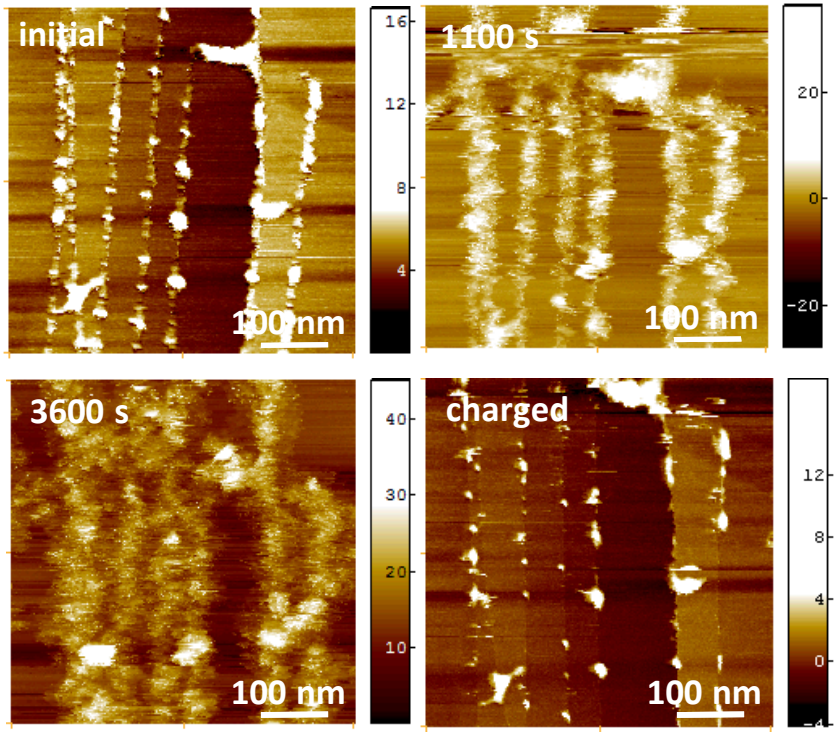


- Peroxide growth is distributed over β-MnO_2 particles
- Conformal and lateral growth vs. large particle growth at the step edges
- Eventual passivation produced by thin conformal film growth on the basal plane

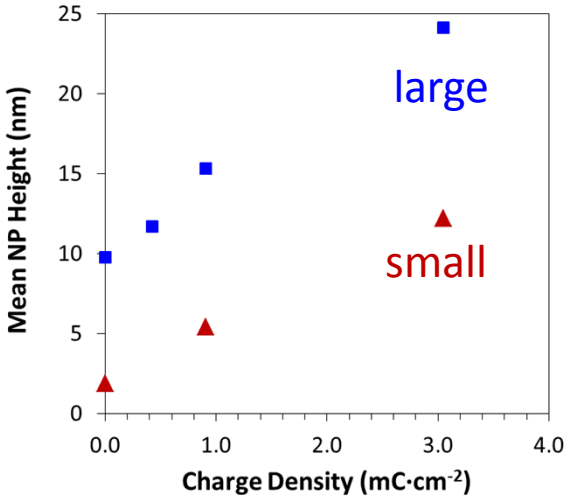
Step Edge Decoration with a High DOS Metal Yields a Similar Response

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





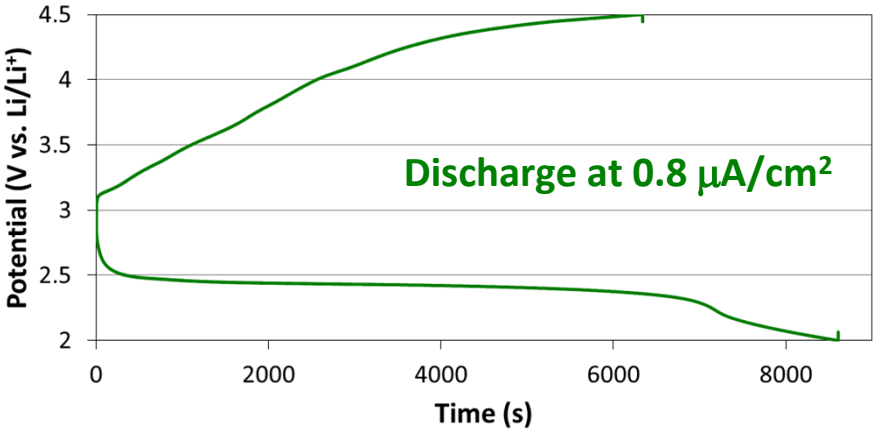
- Growth of product over and around the Au NPs
- No clear NP size effects



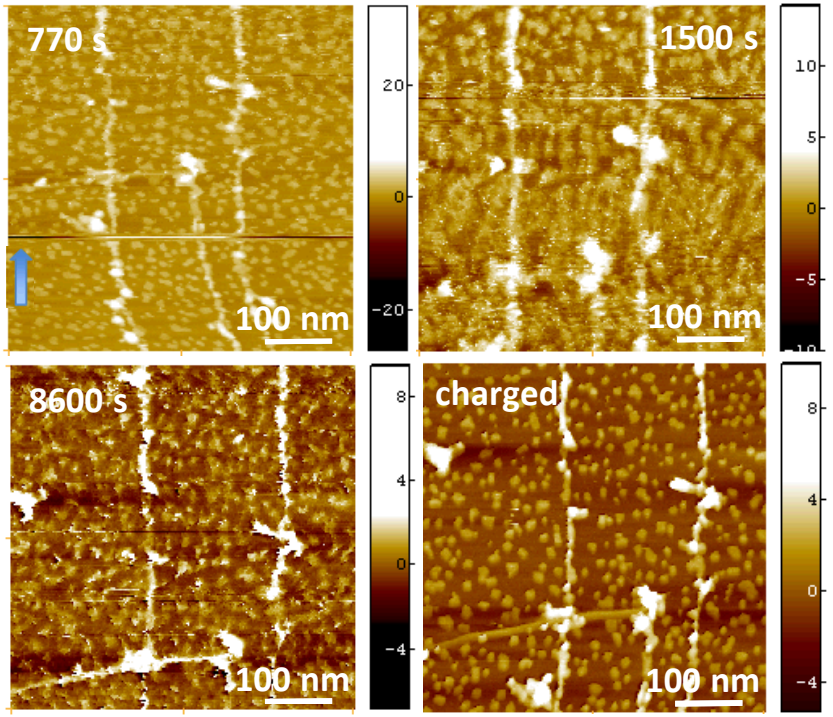
- Some NP displacement after charging – step edges minimally altered

Directing Nucleation onto the Terrace of HOPG

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



2.4 V discharge potential vs. 2.5 – 2.6 V observed for Au(111) – no clear catalytic role



- MnO2 particles are encapsulated with product
- Inter-particle area is infilled with product
- Apparent Au NP heights remain constant – continuous film growth is occurring everywhere

Conclusions

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

- Steps are the active nucleation site
  - oxide and metal nanoparticles change the product growth profile
  - nucleation can be spatially directed by controlling surface energy

- The HOPG surface eventually passivates as a result of formation of a compact film

Acknowledgements

Experimental advice from J. Jirkovsky (ANL) andB. Adams (U. Waterloo)
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