

Materials for Energy Applications

Catalysts for

Renewable Hydrogen & Oxygen from Water

Carbon Dioxide to Fuels

Hydrocarbon Oxidation

Charles Dismukes



http://chem.rutgers.edu/dismukes_charles

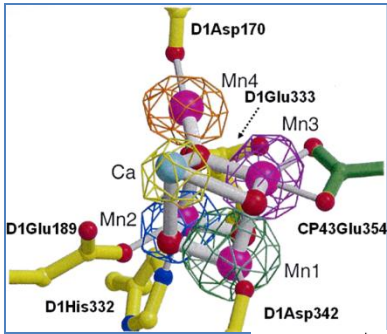
June 2012

Intellectual Property

- **M4O4-cubane Type Catalysts**, US Patent: 6,316,653
G.C. Dismukes and W.F. Ruettinger
- **M4O4-cubane Type Catalysts**, US Patent: 6,803,474
G.C. Dismukes and W.F. Ruettinger
- **Membranes and Photo-electrochemical Devices for Carbon-Neutral Renewable Hydrogen Generation from Water**,
US Provisional Patent 60/896841
G.C. Dismukes, G.F. Swiegers, L. Spiccia and R. Brimblecombe
- **Spinel Catalysts for Water and Hydrocarbon Oxidation**
US Provisional Patent 61/358292
G.C. Dismukes and M. Greenblatt
- **“High efficiency bubble-free electrolyzer for energy storage and renewable hydrogen from water”**
ARPA-E invited application (pending)
- **“Green” Synthesis: Chlorine Dioxide from Sustainable Feedstocks”**

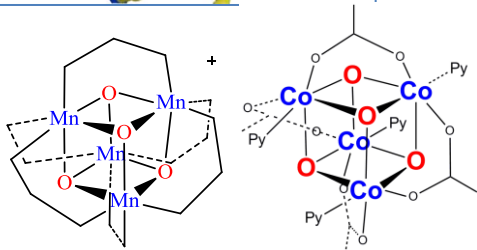
Noble Metal Free Bioinspired Electro-catalysts for Water Oxidation

Photosynthetic
Water oxidation center

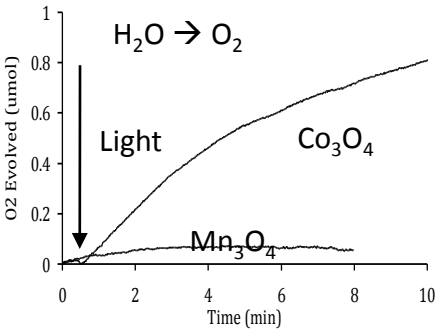
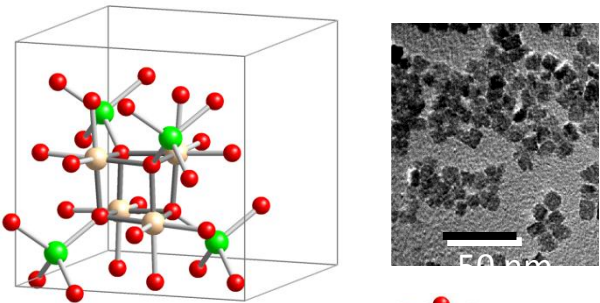


- 3 billion years evolution refinement
- TOF = 500 s⁻¹
- TON > 10⁶

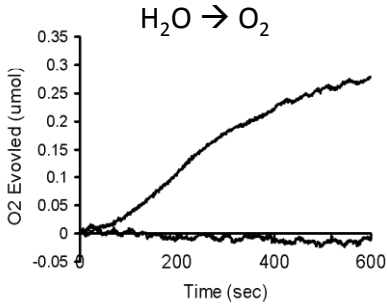
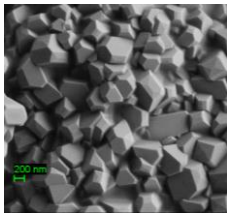
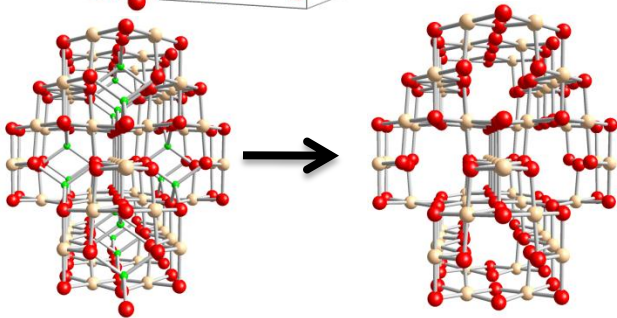
Organometallic Molecular
“cubes” [Mn₄O₄(R₂PO₂)₆]⁺
Co₄O₄(Ac)₄(Py)₄



Inorganic solid
Spinel **Nanoparticles** :
Mn₃O₄ , Co₃O₄

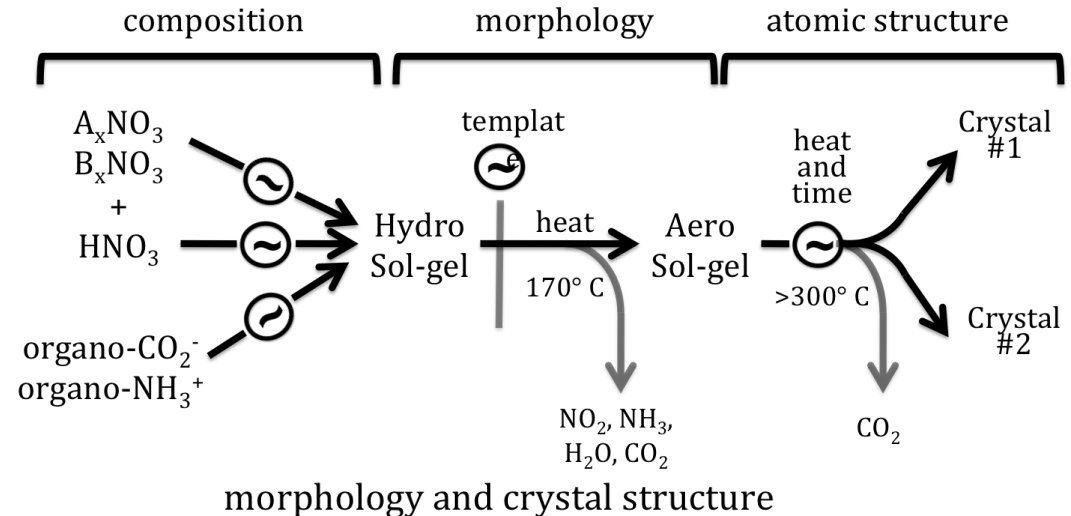


Inorganic solid
Delithiated Spinel :
LiMn₂O₄ → λ-MnO₂
A₂B₂O₄ → AB₂O₄

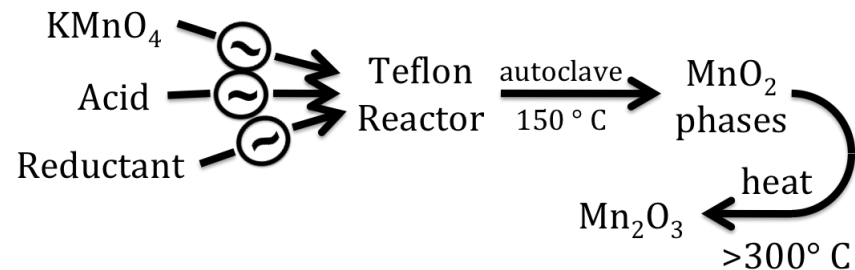


Synthetic methods for nanomaterials

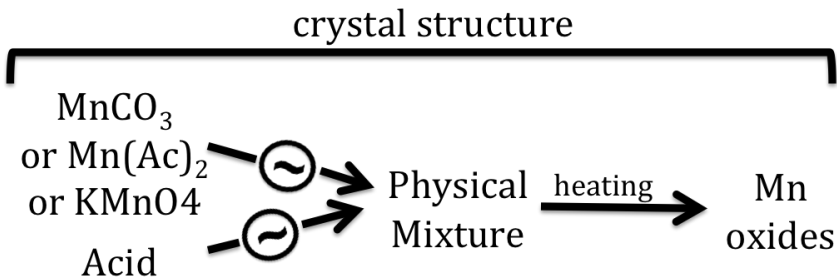
Sol Gel



Hydrothermal

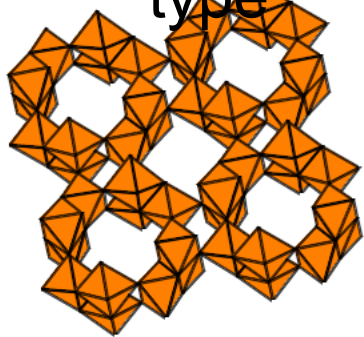


Solid State

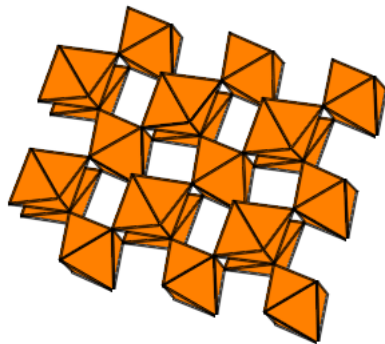


Manganese oxide polymorphs

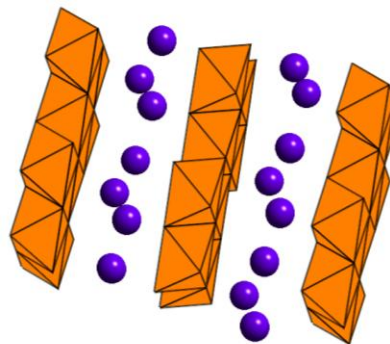
α - MnO_2
“Cryptomelane-
type”



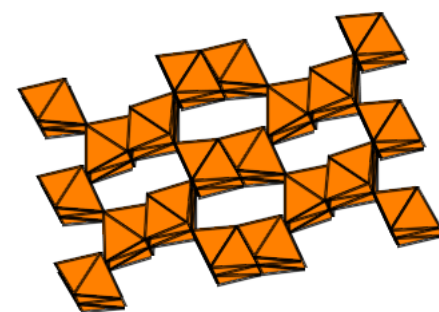
β - MnO_2
Pyrusolite



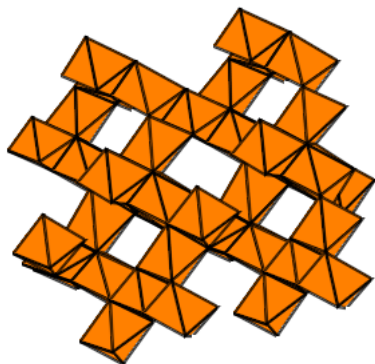
δ - MnO_2
“Birnessite-type”



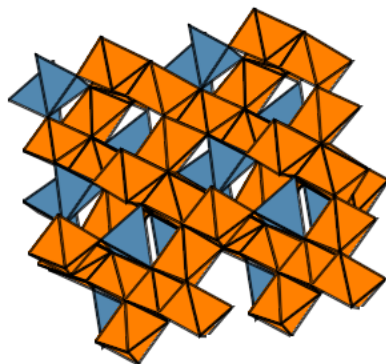
R- MnO_2
Ramsdellite



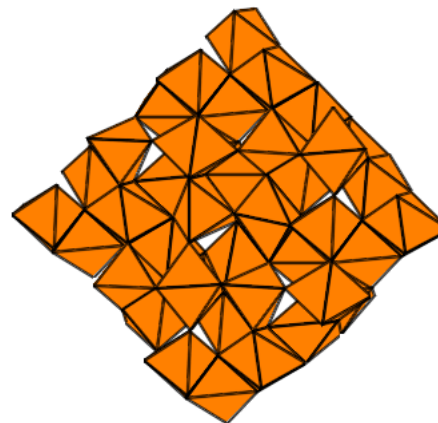
λ - MnO_2
Delithiated Spinel



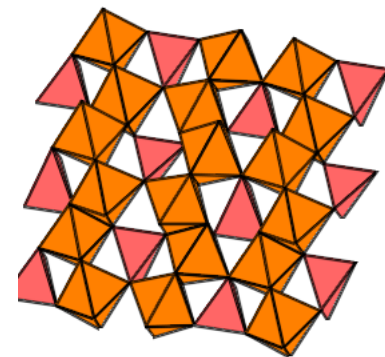
LiMn_2O_4
Spinel



Mn_2O_3
Bixbyite



Mn_3O_4
Hausmannite

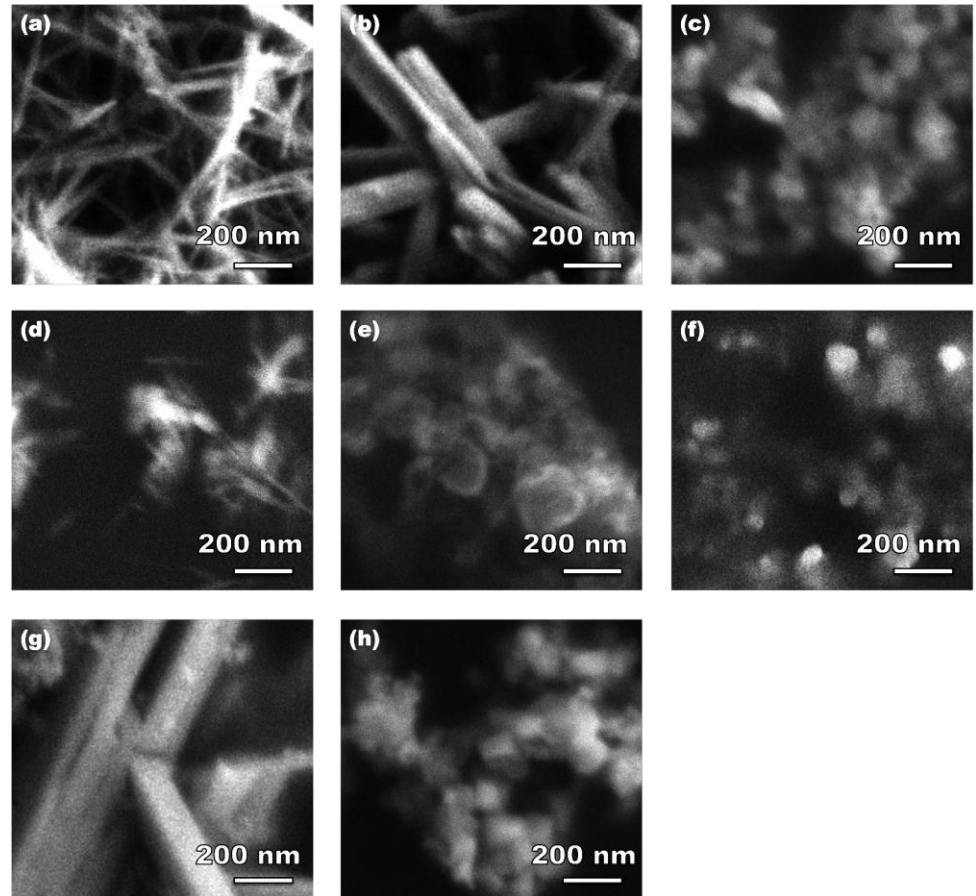
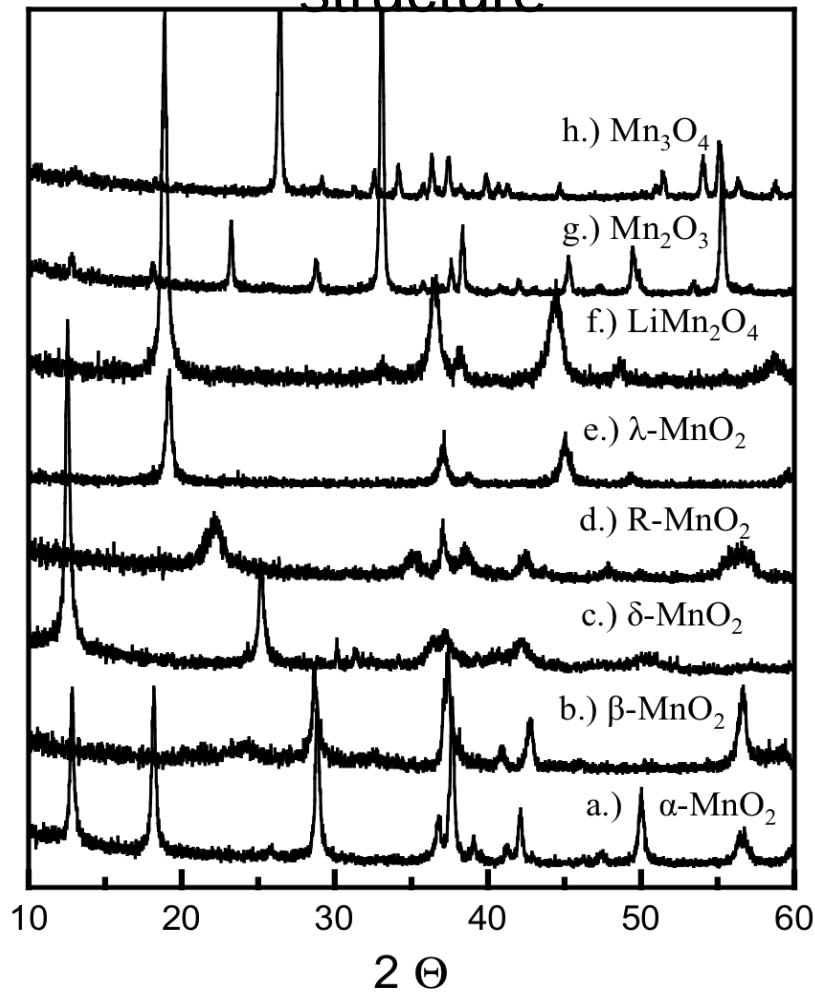


Controlling both atomic & long range (hierarchical) structure

PXRD for crystal

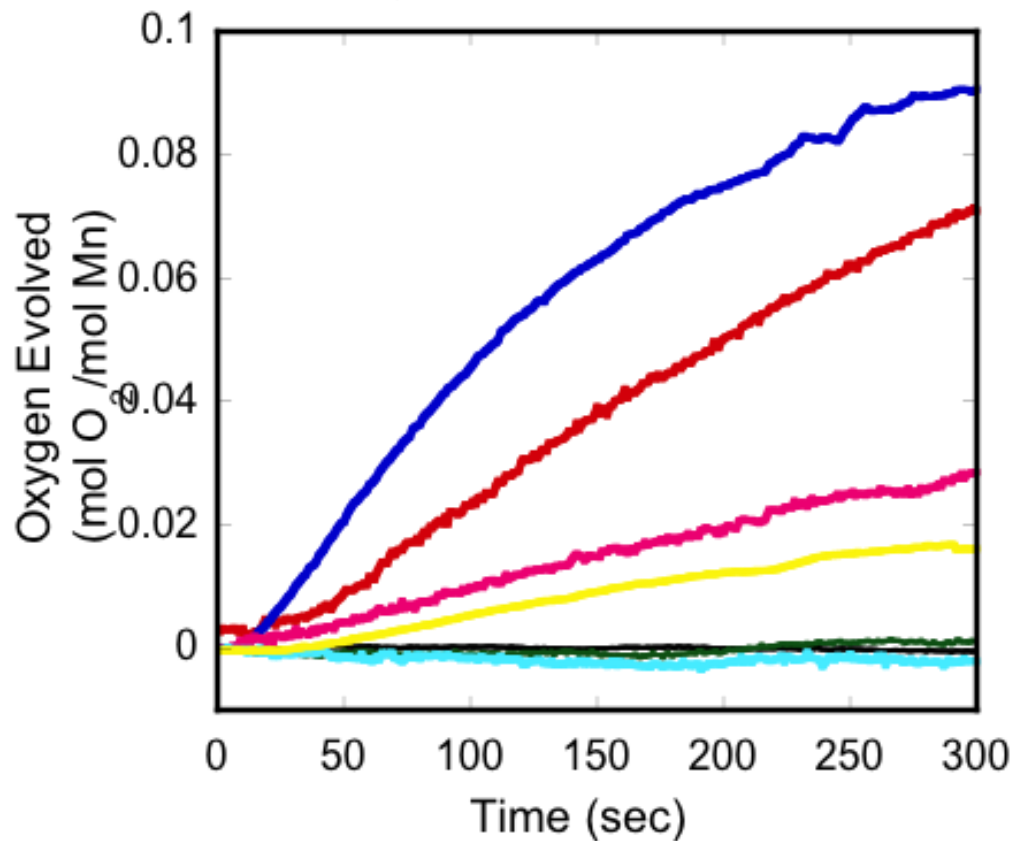
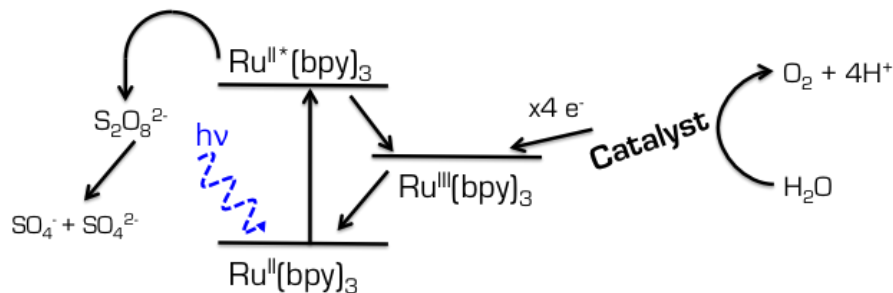
SEM for morphology

structure

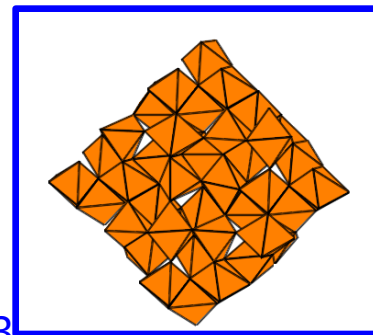


Catalytic potential for water oxidation

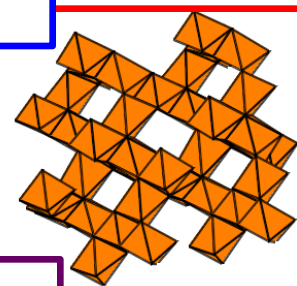
$\text{Ru}(\text{bpy})_3/\text{S}_2\text{O}_8^{2-}$ photooxidant system



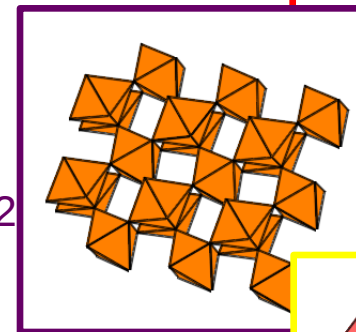
Mn_2O_3



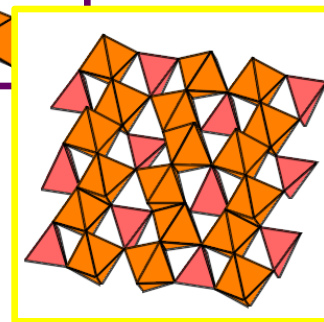
$\lambda\text{-MnO}_2$



$\beta\text{-MnO}_2$



Mn_3O_4



LiMn_2O_4 , $\delta\text{-MnO}_2$, R-MnO_2 , $\alpha\text{-MnO}_2$

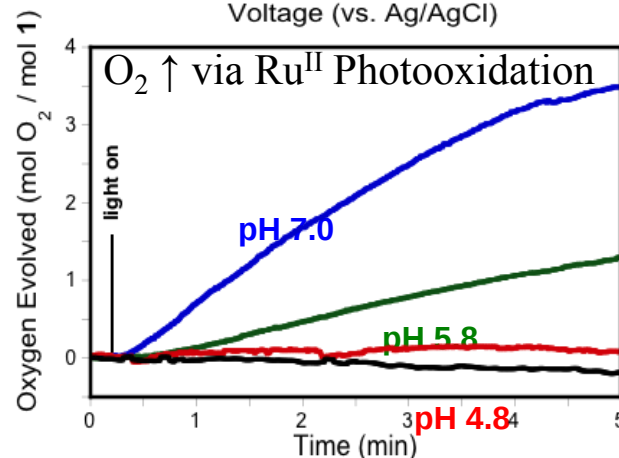
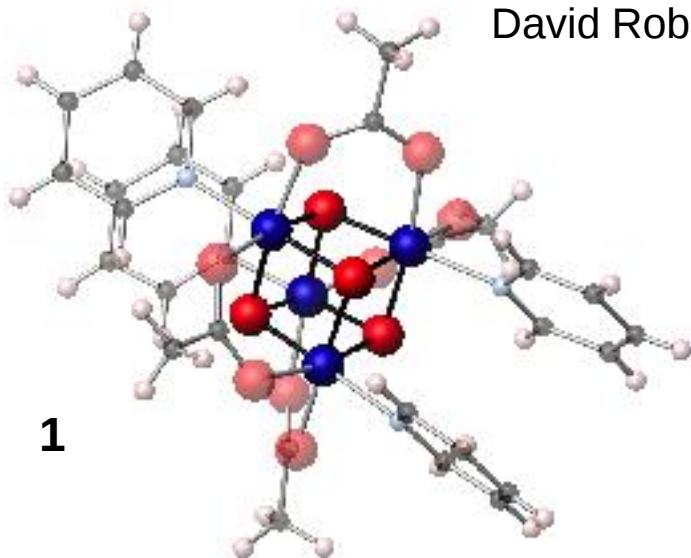
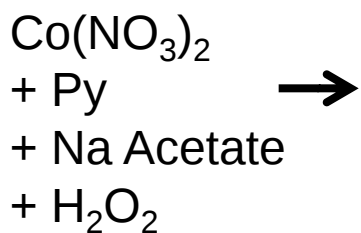
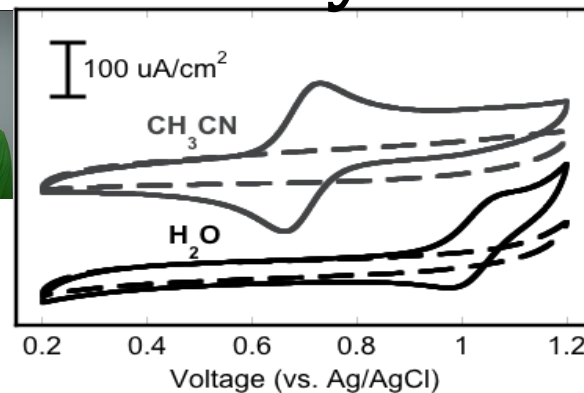
Co₄O₄ Molecular “Cubane” Catalyst



McCool, *JACS* 2011



Nick McCool
David Robinson



Catalyst



in Nafion/GC

TOF (s⁻¹)

2.0x10⁻²

2.4x10⁻⁴

TON

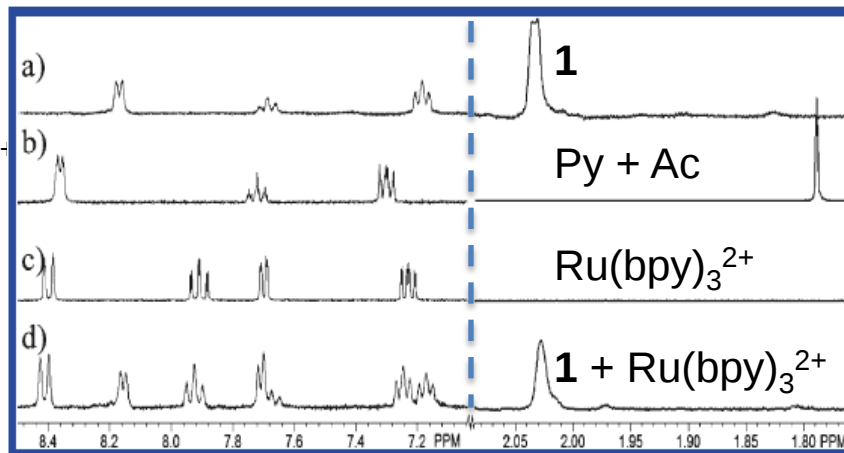
>40*

>10³

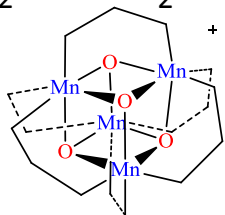
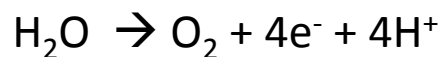
Oxidant



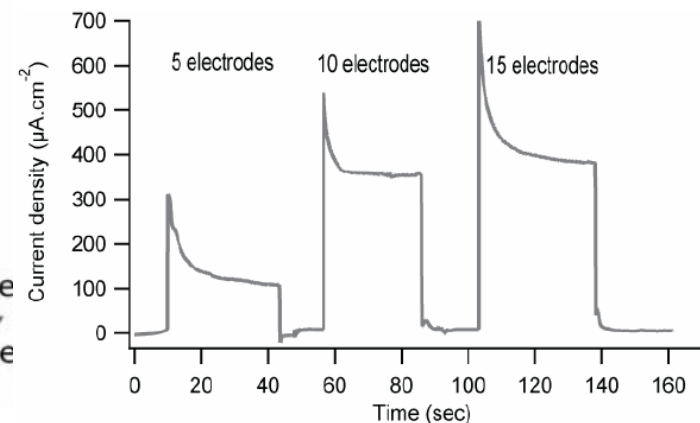
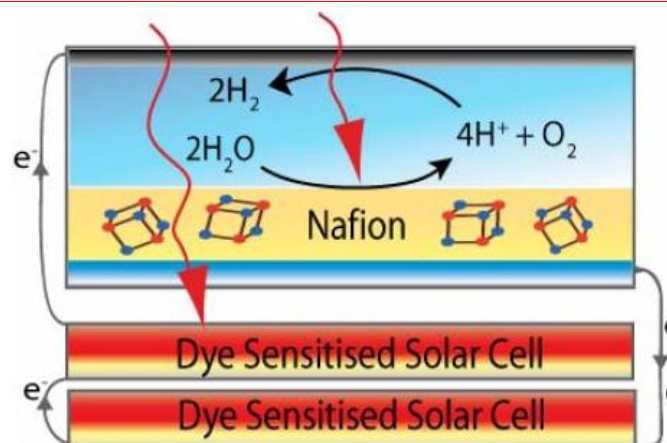
GC @1.2 V



Multi-layer Cubane/Nafion Performance at no external potential



Organometallic
Molecular "cubium"



Demonstrated Performance*:

- Photocurrent = 0.5 mA/cm² at 1.3V DSSC at 1 sun (275-750 nm)
- Peak Solar-to-O₂ Eff. η = 1.1% (0.1 sun)
- TOF = 1.4 mol O₂/cm² h
- TOF' = 0.5 mol O₂/mol Mn h
- * Nafion limits catalyst $\sim 6 \times 10^{-2}$ catalysts/ 10³ Å³

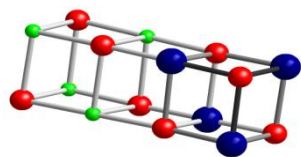
Future Anode Improvements:

- ↑Cubium loading, 3D-electrodes
- ↓diffusion: covalent attachment
- ↓Eliminate Light pre-activation
- ↓Energy barrier (E_{act})
- Bimetallic cubanes AB₃O₄
- Replace Nafion: solid acids

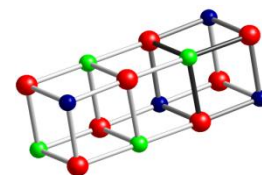
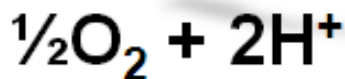
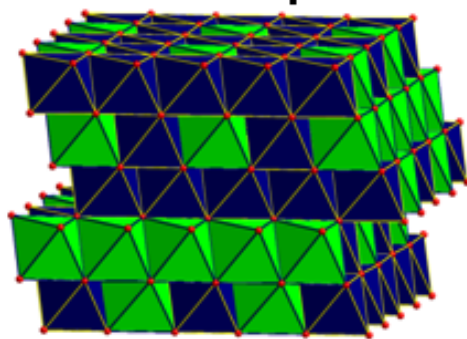
Brimblecombe et al (2009) *Dalton Perspsective*. ; Dismukes et al. (2009) *Acc. Chem Res*.

Brimblecombe et al. (2010) *JACS*; Brimblecombe et al. (2010) *ChemSusChem* , 3, 1–5

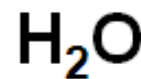
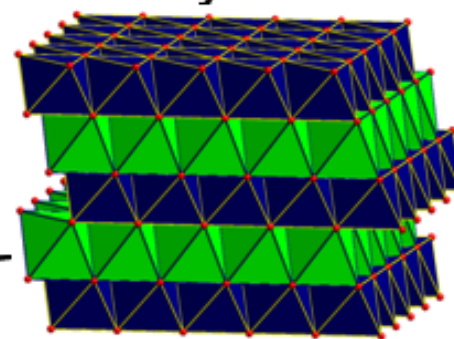
Bioinspired Catalyst for Water Oxidation



Cubic Spinel



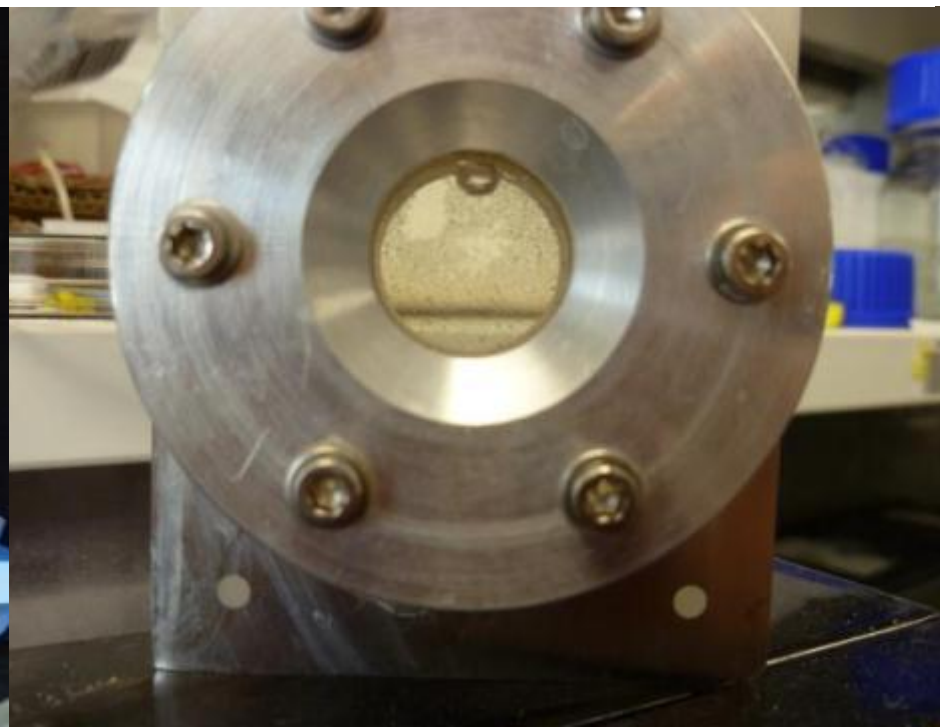
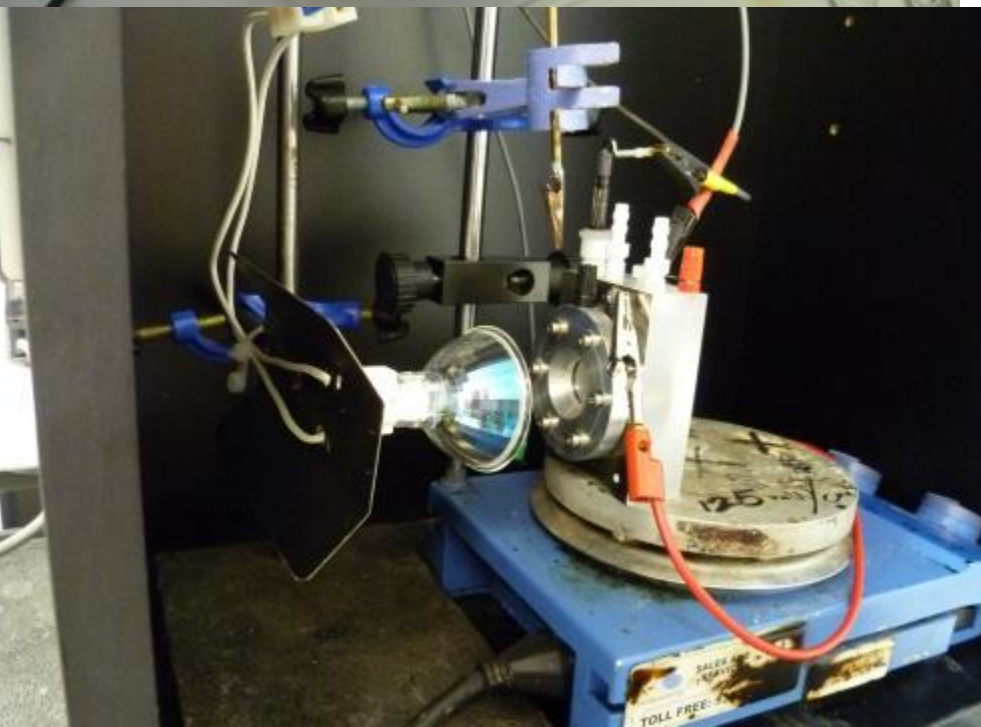
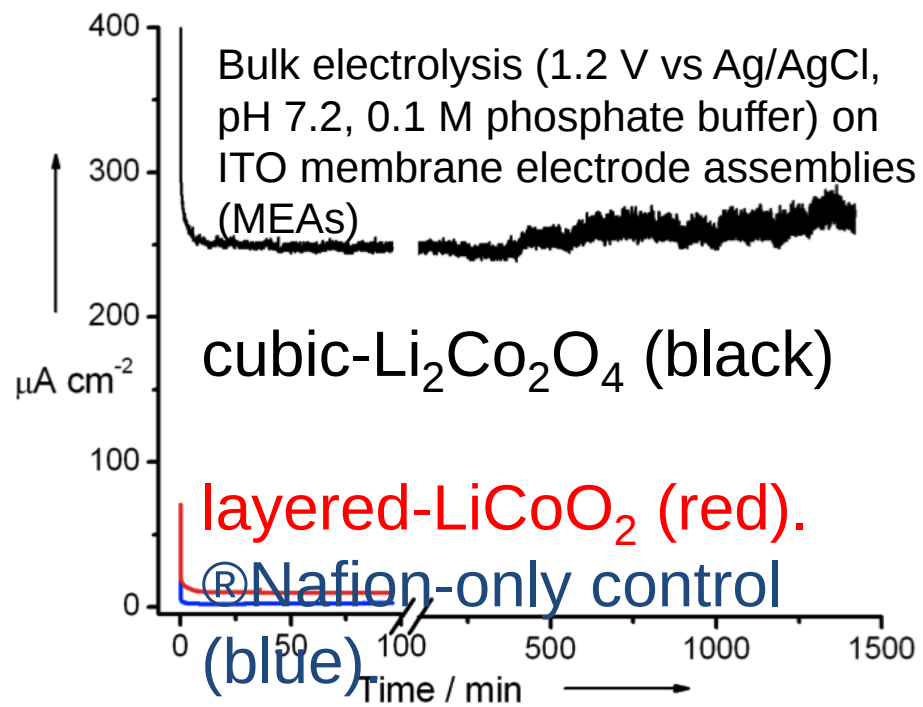
Layered



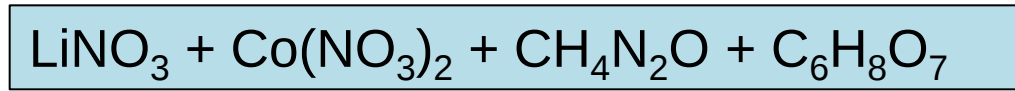
Crystal structure transformation of lithium cobalt oxides Only the cubic polymorph is an active **water oxidation catalyst**



Gardner, Robinson, Smith, Go, Greenblatt, Dismukes (2012) *Angew Chemie*, 51, 1616.
Pill millipede: http://photos.wildmadagascar.org/images/pill_millipede_ball_0142.shtml



Sol-Gel Nanophase TMO Preparation*



A

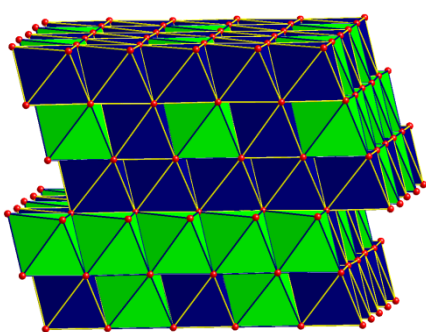
Solvent Evaporation,
- NH_4NO_3 , $\text{NH}_4(\text{citrate})$

LiCo(citrate) precursor

400 ° C,
2 hours

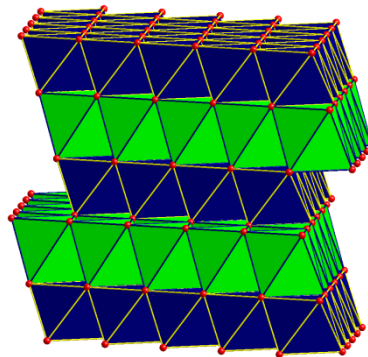
- CO_2
B

700 ° C,
1-2
hours

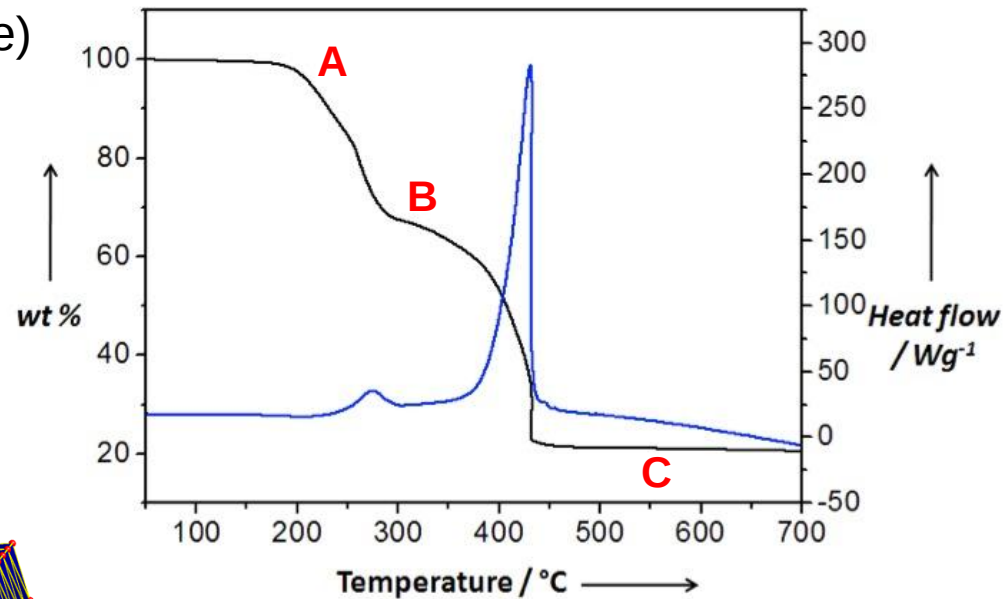


$\text{Li}_2\text{Co}_2\text{O}_4$ Cubic

C

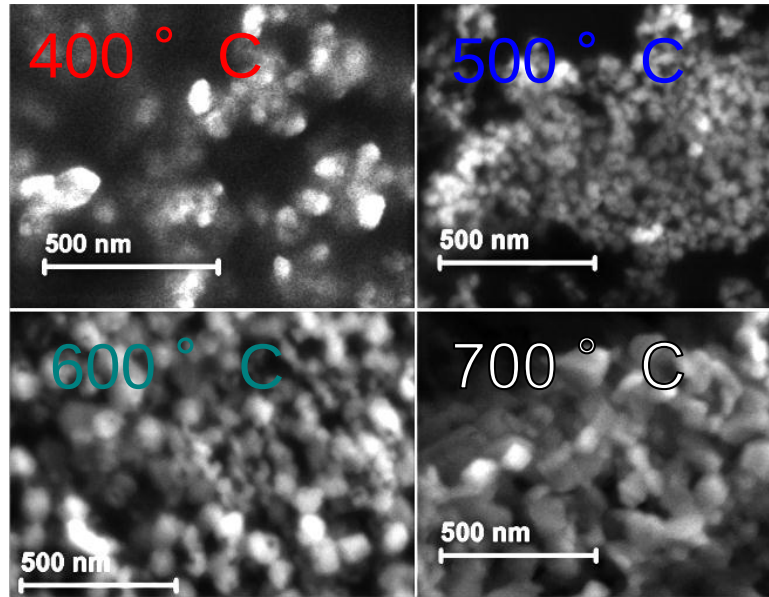


LiCoO_2 Layered



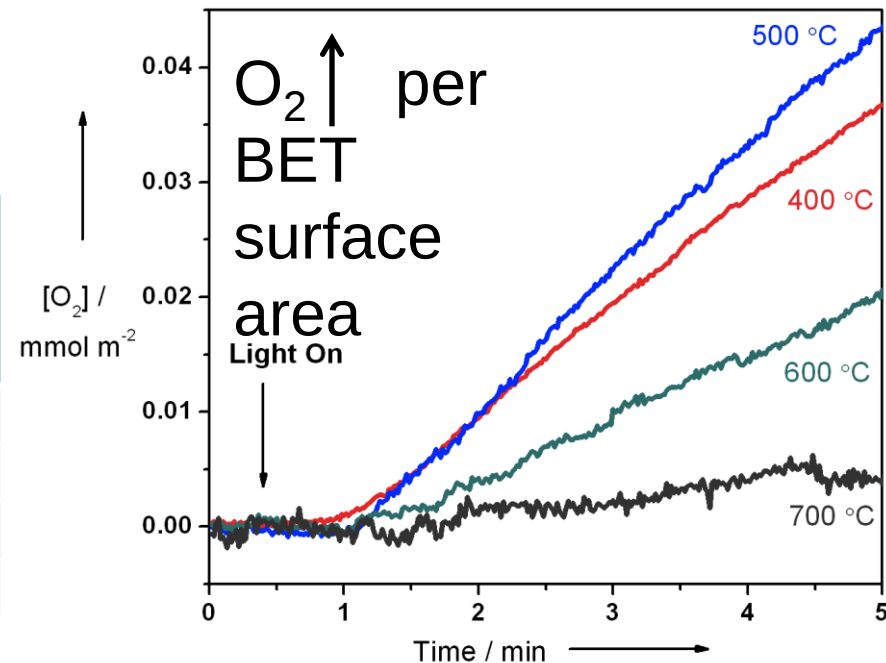
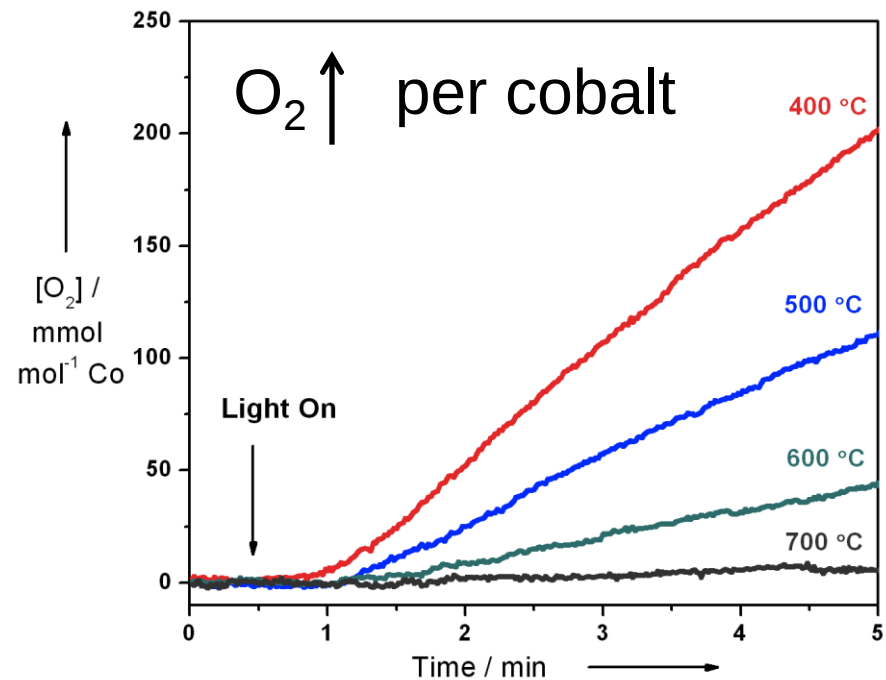
* With Prof. Martha Greenblatt

Water Oxidation catalyzed by two LiCoO_2 polymorphs



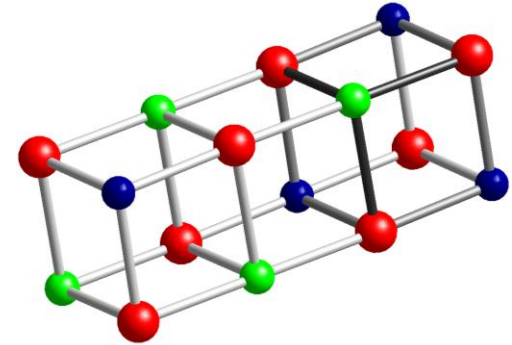
Calcination Temperature	BET Surface area (m^2/g)	Average particle size (nm)
400 ° C	56.19	50
500 ° C	26.30	50
600 ° C	21.83	75
700 ° C	14.24	100

Gardner et al (2012) ACI

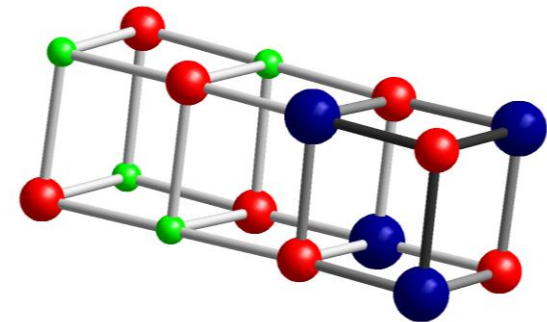


Only the spinel LiCoO_2 has Co_4O_4 cubes which is essential for catalysis

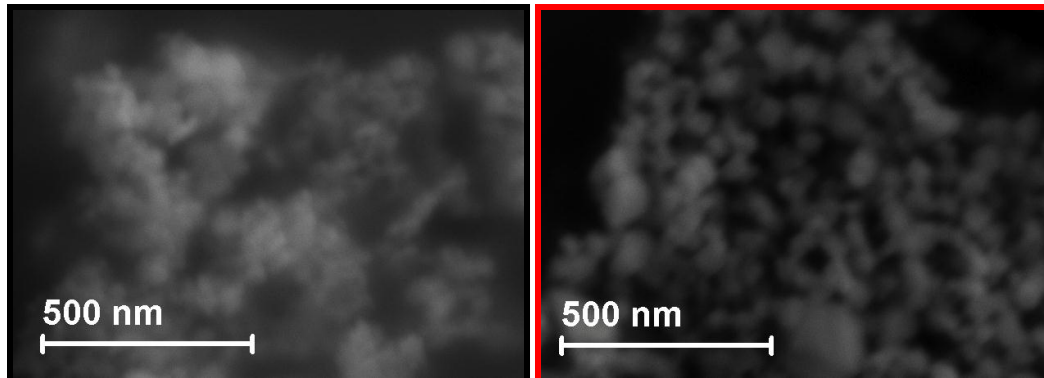
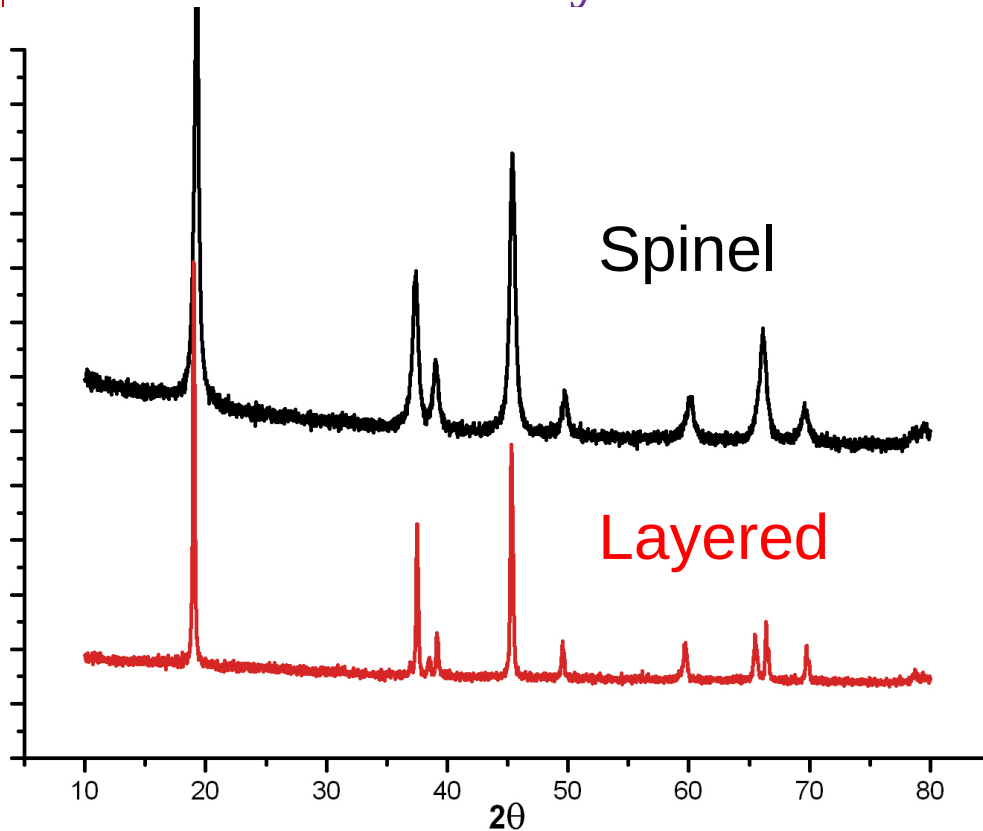
Layered ($R-3m$) LiCoO_2



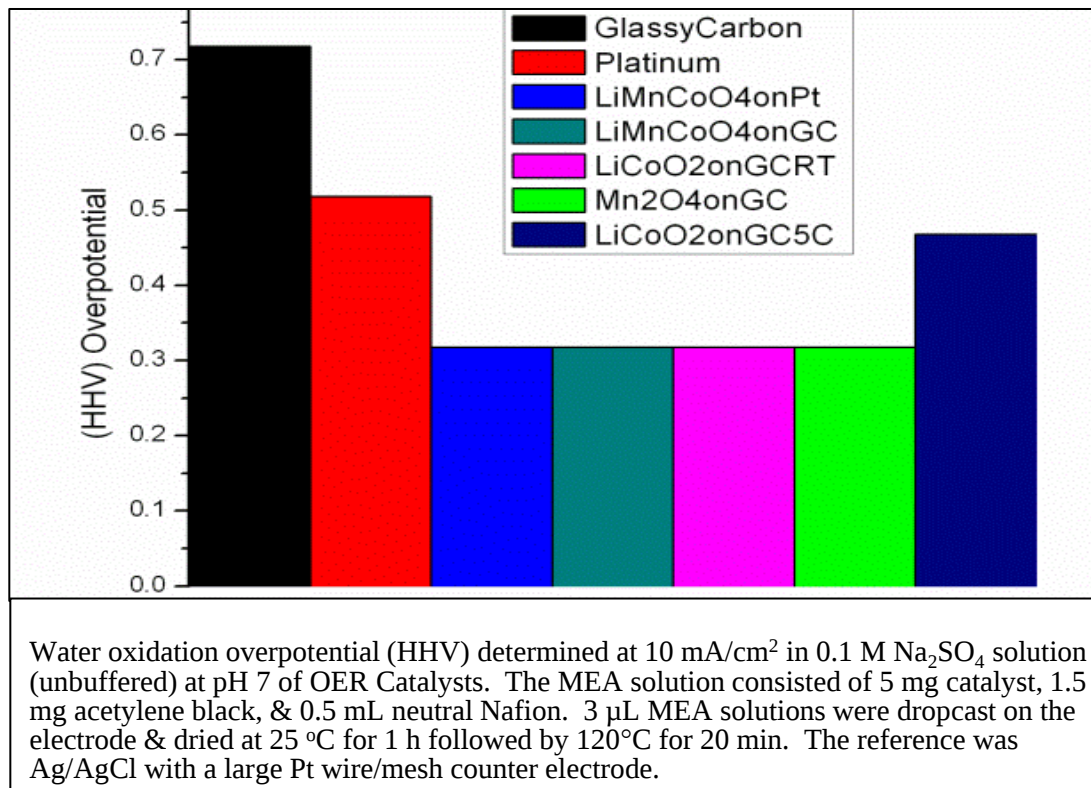
Spinel ($Fd-3m$) LiCoO_2



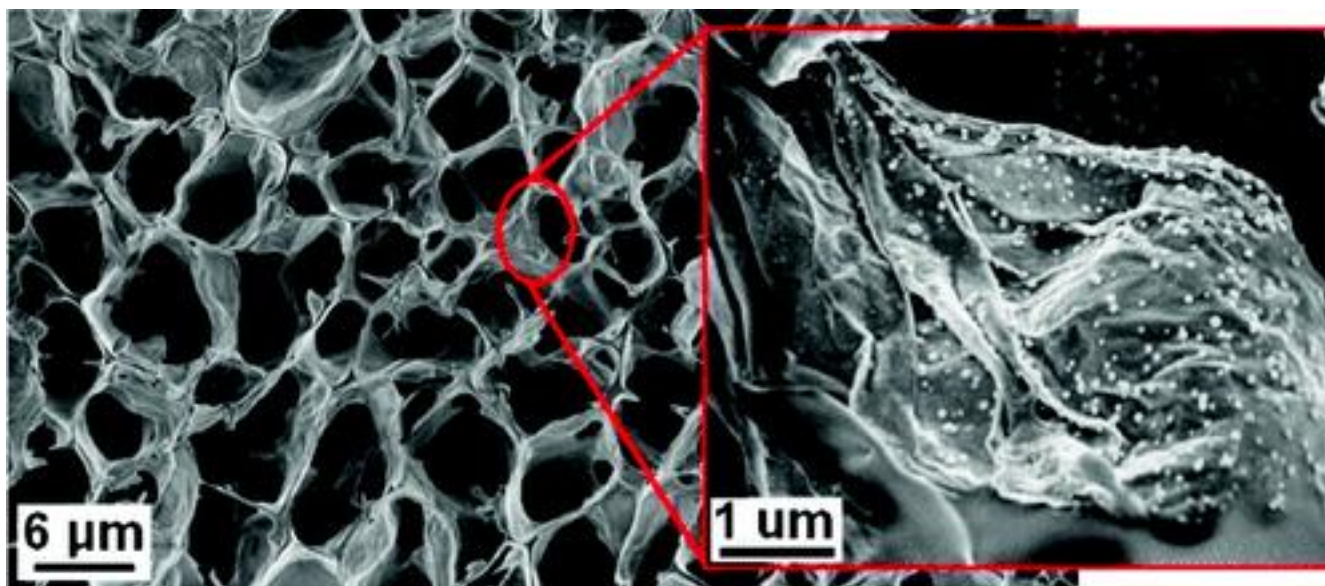
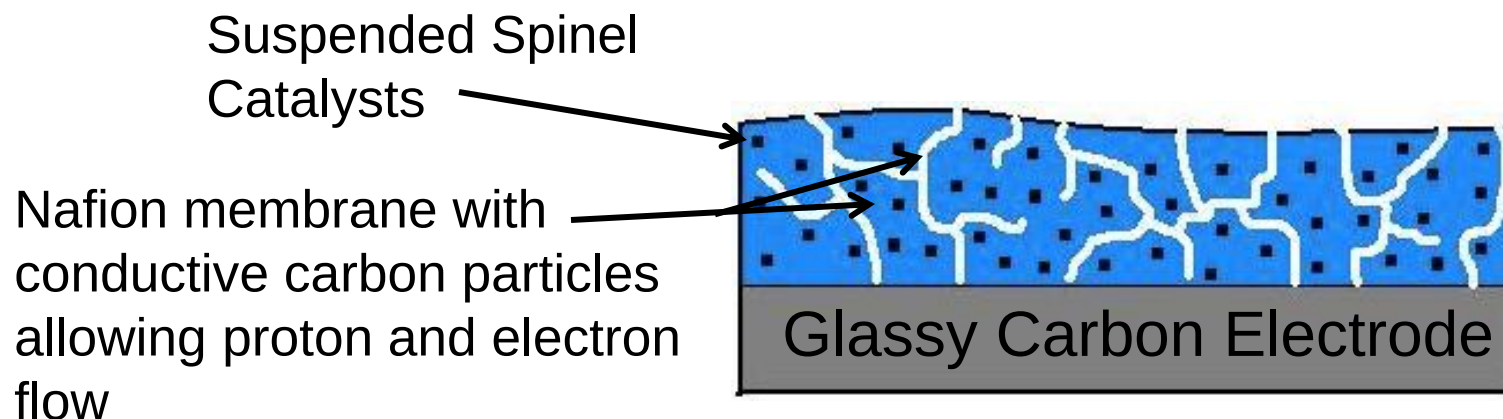
↑
 Co_4O_4



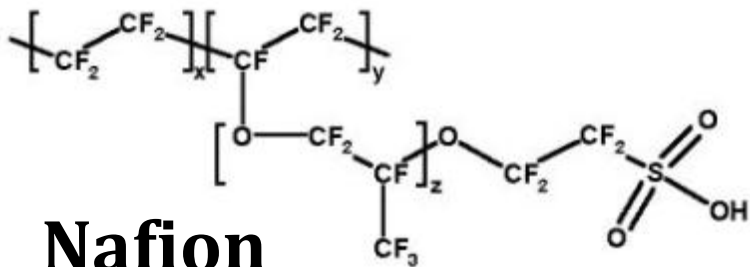
Overpotential for water electrolysis: $\text{LiMM}'\text{O}_4$ binary spinels ($\text{M} = \text{Co}, \text{Mn}$) and spinel $\lambda\text{-Mn}_2\text{O}_4$ consistently outperform Platinum as OER catalyst



Membrane coated electrodes



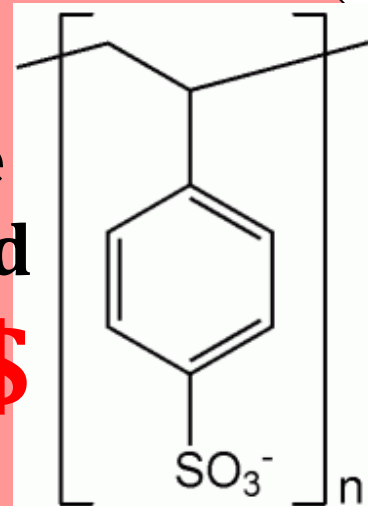
Replacing Nafion:Fuel Cells & Electrolyzers



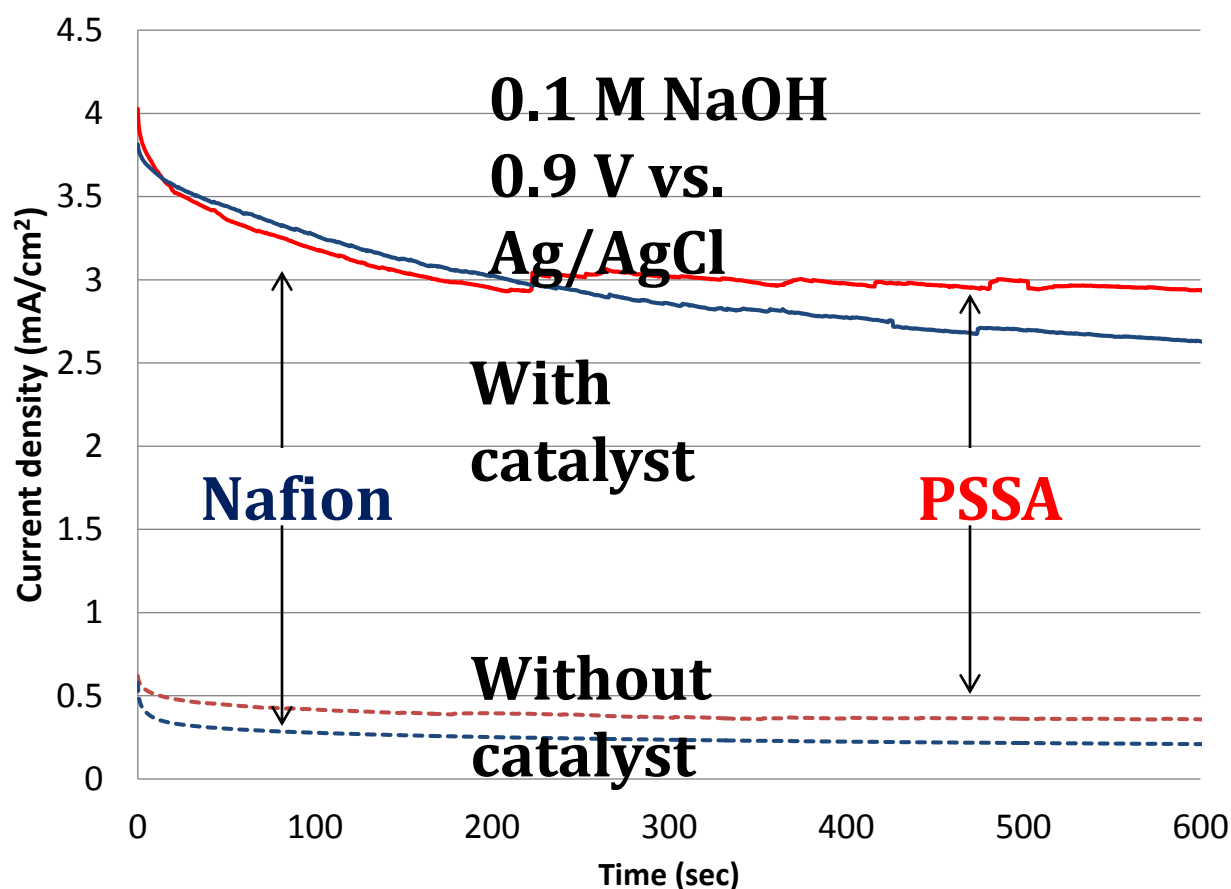
Nafion

\$\$\$

**Polystyrene
sulfonic acid**



\$



Rutgers infrastructure used for these projects:

- [Institute for Advanced Materials, Devices and Nanotechnology](#) (IAMDN),
- Department of Chemistry
- Materials Science and Engineering Dept.
- [Nanofabrication Laboratory](#);
- Microelectronics fabrication and characterization ([MERL clean room](#))
- [Surface Characterization Laboratory](#)
- Thermal Analysis Laboratory;
- [X-ray Scattering Analysis](#)
- [Electron Microscopy Laboratory](#);
- Instrumentation for particle and pore sizes, patterning, lithography, printing
- BET Nitrogen adsorption analyzer (NOVA 2000 BET)

Princeton Team

Wolfgang Ruettinger

Tom Carrell

Rob Brimblecombe

John Sheats

Patrick Baesjou

Marcelo Maneiro

Masayuki Yagi

Jian-Zhong Wu

Ying Yu

Greg Felton

Johanna Scarino

Matt Lin

Joe Dennes

Emilie Bourles

Shari Cohen

Calvin Sung

Rutgers Team

Clyde Cady

David Robinson

Graeme Gardner

Paul Smith

Nick McCool

John Sheats

Princeton Collaborators:

Steve Bernasek

Kurt Wolf

Roberto Car

Filippo DeAngelis

George McLendon

Rutgers Collaborators

Martha Greenblatt

Yong Bok Go

Collaborators

Monash U.

Leone Spiccia

Rob Brimblecombe

Alan Bond

Univ. Wollongong

Gerry Swiegers



\$

NIH-GM, AFOSR, DOE

Lemberg Award, Fullbright

ARC Australia

