SAND2015-1125PE

Exceptional service in the national interest

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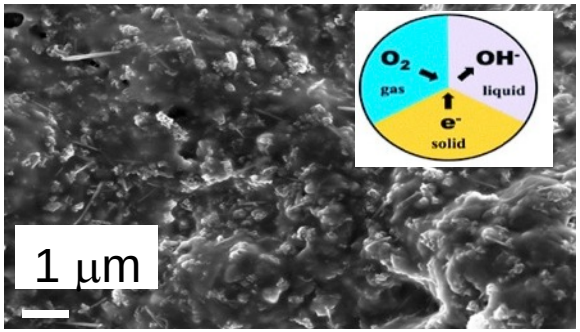
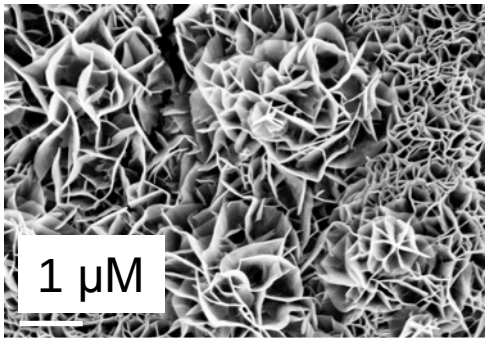
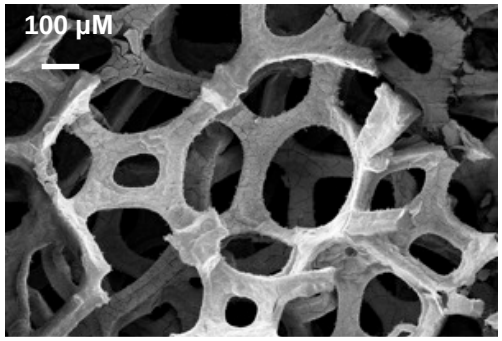
$$O_2 + 2H_2O + 4e^- = 4OH^-$$







Materials for Energy Storage and Conversion

Timothy N. Lambert

(Electrocatalysts and Electrodes for Batteries, Fuel Cells)

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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SNL – Materials, Devices & Energy Technologies

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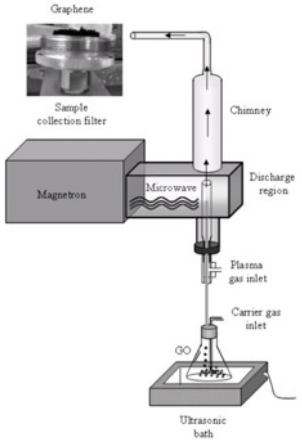
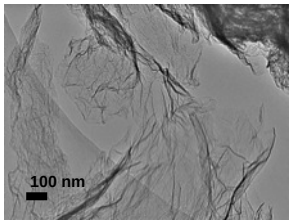
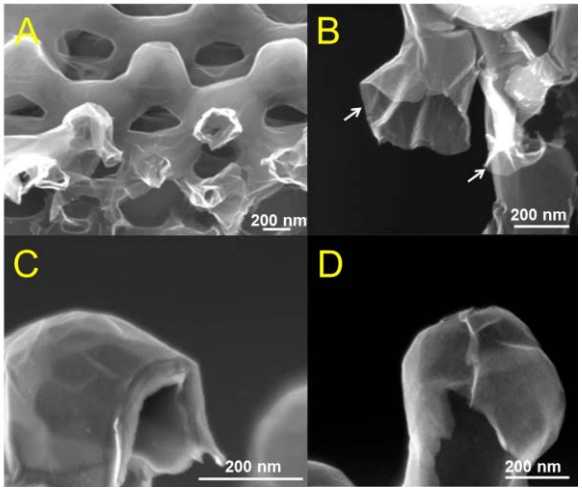
Graphene Materials and Composites





T. N. Lambert *et al. Nanoscale* **2011** *3(1)*, 188-191.
T. N. Lambert *et al. J. Phys. Chem. C.* **2009** *113 (46)*, 19812-19823.
T. N. Lambert *et al. Carbon* **2010** *48*, 4081-4089

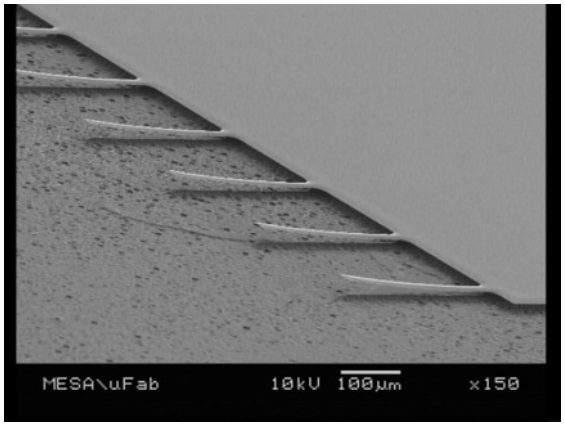
3D Graphene Electrodes



X. Xiao *et al. J. Mater. Chem.* **2012** *22*, 23749-23754.

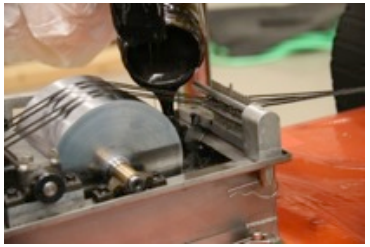
X. Xiao *et al. ACS Nano* **2012** *6(4)*, 3573-3579.

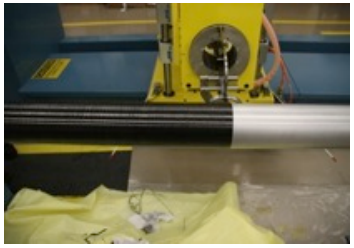
Carbon-based MEMS Devices

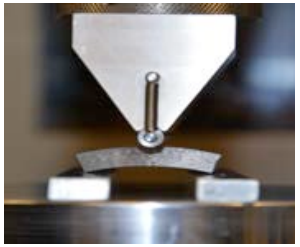


C. Washburn *J. Electrochem. Soc. Trans.*, **2012** *50(12)*, 423-434.

Improved Flywheel Materials







- Building and Testing Prototype Flywheels with US Company

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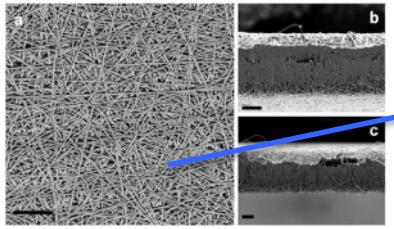
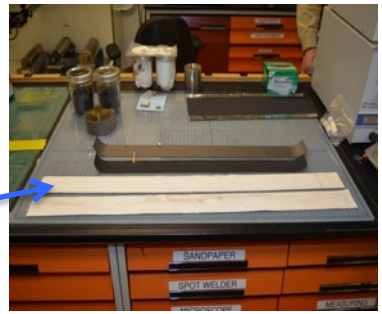
Lithium Ion Battery Safety

Electrospun Poly(terephthalate) Separators



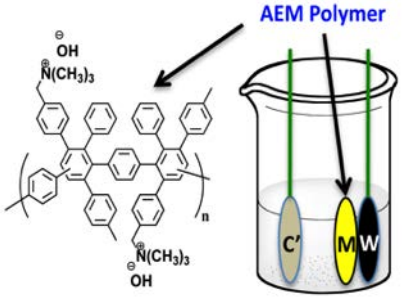


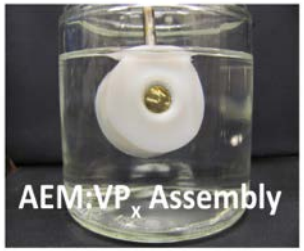
C. Orendorff *Adv. Energ. Mater.* **2013** *3(3)*, 314-320.

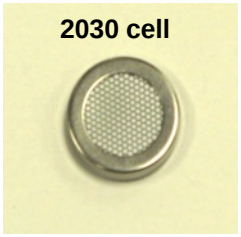
- NMC/graphite lithium-ion cells, results show comparable performance to commercially available polyolefin separators (rate, capacity fade, and reactivity)
- 75% porous with improved thermal stability to >200 °C
- Developed to 18650 size separator films
- Low flammable electrolyte/solvents

Ceramic-air Batteries and Anodes

$$VP_4 + 40\ OH^- \rightarrow VO_4^{3-} + 4\ PO_4^{3-} + 20\ H_2O + 25\ e^-$$







T. N. Lambert *et al. Chem. Commun.* **2011**, *47(34)*, 9597-9599
(Patent submitted)

- Development of multi-electron anodes
  e.g. VP_4 (25 e^- or 3832 mAh/g),
  VB_2 (11 e^- or 4060 mAh/g)
- High Discharge Capacities (80-90%) obtained
- Coin cell battery development
- Organic polymer anion exchange membranes (AEMs) used as hydroxide shuttles/corrosion barriers (for VP_x)

<u>Practical volumetric capacities</u>:

- Gasoline = 2.7 kWh L^{-1}
- Li-ion = 0.5 kWh L^{-1}
- Zn-Air ~ 1.75 kWh L^{-1} (1.3V)
- VP-Air = 4.3 kWh L^{-1}

Importance of O_2 Electrochemistry

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A. Multi-electron ceramic/air batteries (Primary)

1. $VP + 16\ OH^- \square VO_4^{3-} + PO_4^{3-} + 8\ H_2O + 10\ e^-$; $E^0 = 1.07$ V vs NHE
2. $O_2 + 2\ H_2O + 4\ e^- \square 4\ OH^-$; $E^0 = 0.40$ V vs NHE
3. $VP + 6\ OH^- + 5/2\ O_2 \square VO_4^{3-} + PO_4^{3-} + 3\ H_2O$; $E^o = 1.47$ V

VP/air ~ 4.3 kWh L^{-1}
vs.
Gasoline 2.7 kWh L^{-1}

TN Lambert *et al. Chem. Commun.* **2011** *47*, 9597-9599.

B. Sodium/air batteries (Secondary)

Anodic half-reaction: $Na = Na^+ + e^-$ $E^0 = 0.00$ V/Na
Cathodic half-reaction: $O_2 + 2H_2O + 4e^- = 4\ OH^-$ $E^0 = +3.1$ V/Na
Full cell reaction: $4Na + O_2 + 2H_2O = 4Na + 4OH^-$

Na/air ~ 1690 Wh kg^{-1}
vs.
Li-ion 200-250 Wh kg^{-1}

Review: J. Power Sources **2011**, *196(16)*, pp 6835-6840

C. Alkaline Fuel Cells (Bi-directional beneficial)

Anodic half-reaction: $2\ H_2 + 4\ OH^- \square 4H_2O + 4e^-$
Cathodic half-reaction: $O_2 + 2\ H_2O + 4e^- \square 4\ OH^-$
Full cell reaction: $2\ H_2 + O_2 \square 2\ H_2O$

Proc. Nat. Acad. Sci. **2008**, *105(52)*, pp 20611-20614

D. Solar Fuels Synthesis

Fuel Generation: $2H^+ + 2e^- \square H_2$ $E^0 = 0.00$ V/RHE
or $CO_2 + 6H^+ + 6e^- \square CH_3OH + H_2O$ $E^0 = +0.05$ V/RHE

Source of protons: $2H_2O \square 2O_2 + 4H^+ + 4e^-$ $E^0 = +1.23$ V/RHE **Water Electrolysis**

Gorlin *et al. J. Am. Chem. Soc.* **2010**, 132, 13612-13614

Most effective catalysts are based on precious metals = rare, expensive

Importance of O_2 Electrochemistry

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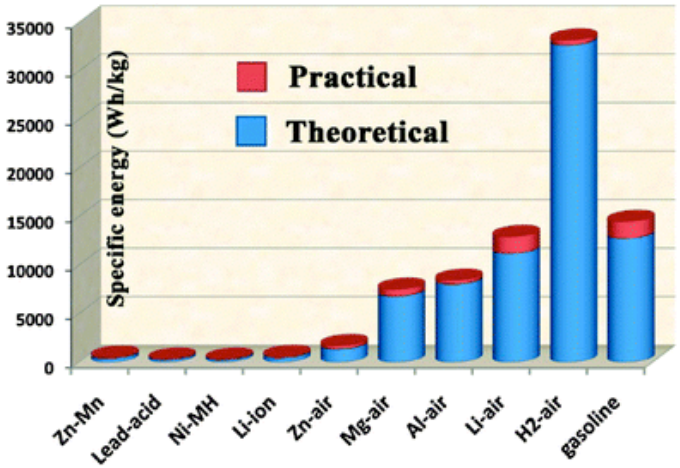
Electrical Energy Storage

Gravimetric Energy Densities



Cheng *et al. Chem. Soc. Rev.* **2012**

Multi-electron ceramic/air batteries (Primary)

1. $VP + 16\ OH^- \rightarrow VO_4^{3-} + PO_4^{3-} + 8\ H_2O + 10\ e^-$; $E^0 = 1.07$ V vs NHE
2. $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$; $E^0 = 0.40$ V vs NHE
3. $VP + 6\ OH^- + 5/2\ O_2 \rightarrow VO_4^{3-} + PO_4^{3-} + 3\ H_2O$; $E^0 = 1.47$ V

TN Lambert *et al. Chem. Commun.* **2011** *47*, 9597-9599.

Practical volumetric capacities:

- **Gasoline = 2.7 kWh L^{-1}**
- **Li-ion = 0.5 kWh L^{-1}**
- **Zn-Air = 1.75 kWh L^{-1} at 1.3 V**
- **VP-air = 4.3 kWh L^{-1} (10 e^-) at 1.47 V**
- **VB_2 = 5 kWh L^{-1} (11 e^-) at 1.3 V**

Adapted from: S Licht *et al. Chem. Commun.* **2008** 3257-3259.

Sodium/air batteries (Secondary)

Anodic half-reaction: $Na = Na^+ + e^-$ $E^0 = 0.00$ V/Na

Cathodic half-reaction: $O_2 + 2H_2O + 4e^- = 4\ OH^-$ $E^0 = +3.1$ V/Na

Full cell reaction: $4Na + O_2 + 2H_2O = 4Na + 4OH^-$

Na/air ~ 1690 Wh kg^{-1} vs. Li-ion 200-250 Wh kg^{-1}

J. Power Sources **2011**, *196(16)*, pp 6835-6840

Solar Fuels Synthesis

Fuel Generation: $2H^+ + 2e^- \rightarrow H_2$ $E^0 = 0.00$ V/RHE

or $CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$ $E^0 = +0.05$ V/RHE

Source of protons: $2H_2O \rightarrow 2O_2 + 4H^+ + 4e^-$ $E^0 = +1.23$ V/RHE

Gorlin *et al. J. Am. Chem. Soc.* **2010**, 132, 13612-13614

Manganese oxide Nanowires

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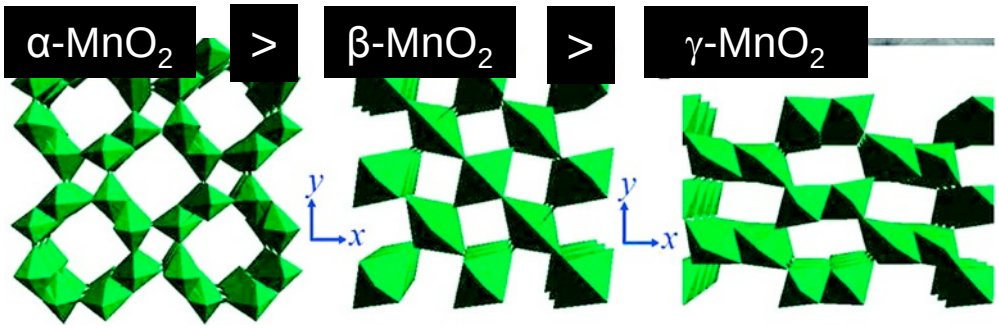
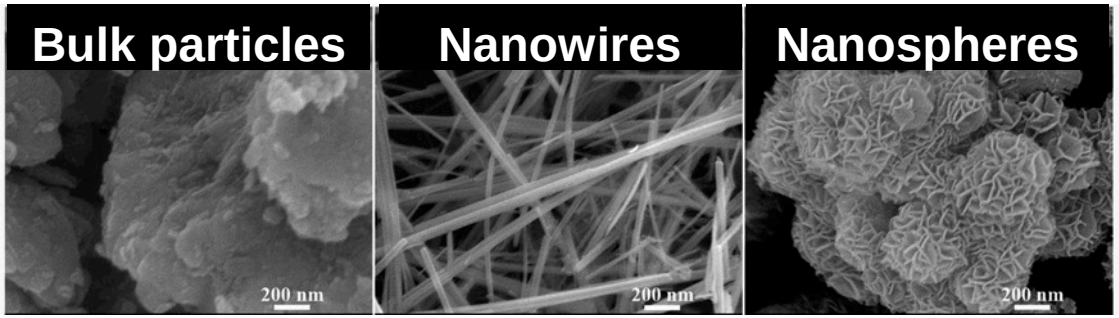
An effective catalyst must facilitate O_2 adsorption and HO_2^- decomposition

Phase



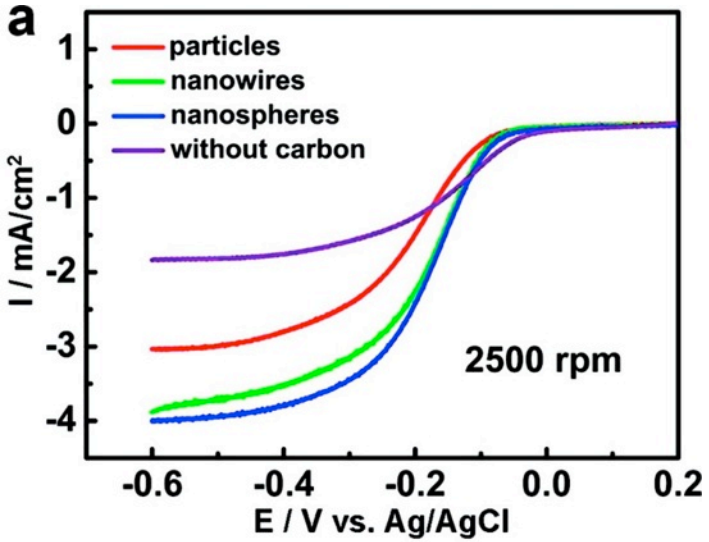
Size nm MnO_2 > μm MnO_2

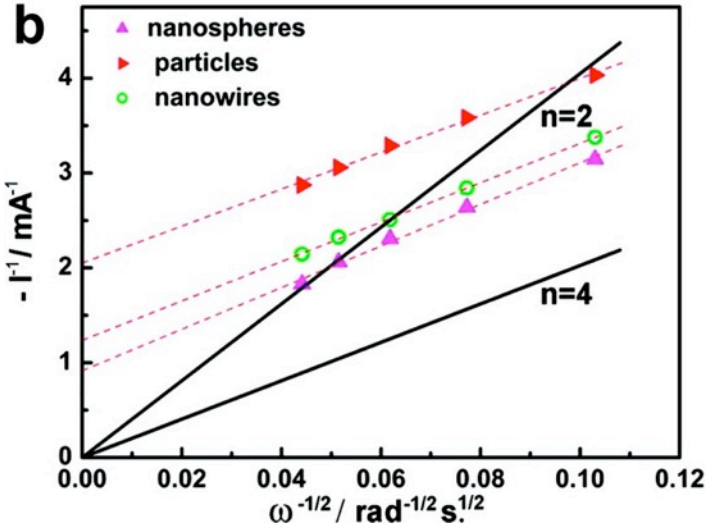
Morphology nanowires/spheres > nanoparticles



7.9 m^2/g 32.9 m^2/g 40.1 m^2/g

F. Cheng, *et al. Chem. Mater.* **2010**, *22*, 898–905





Ni- and Cu-α-MnO_2 Nanowires

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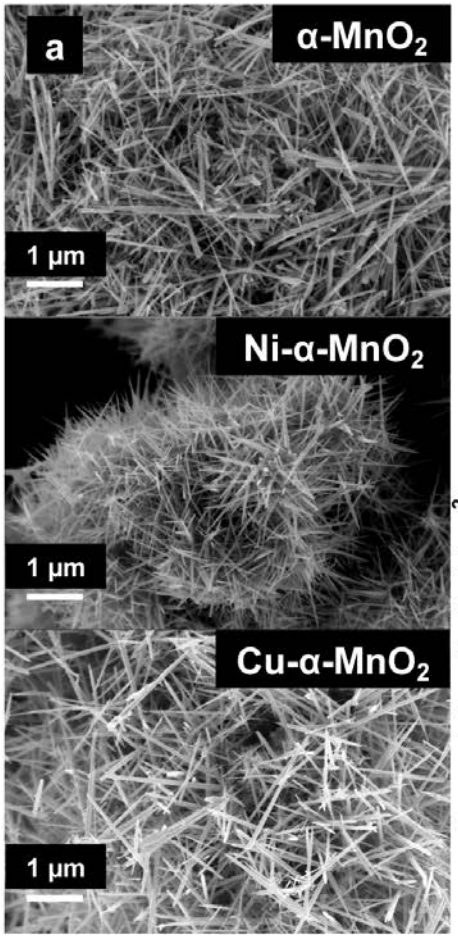
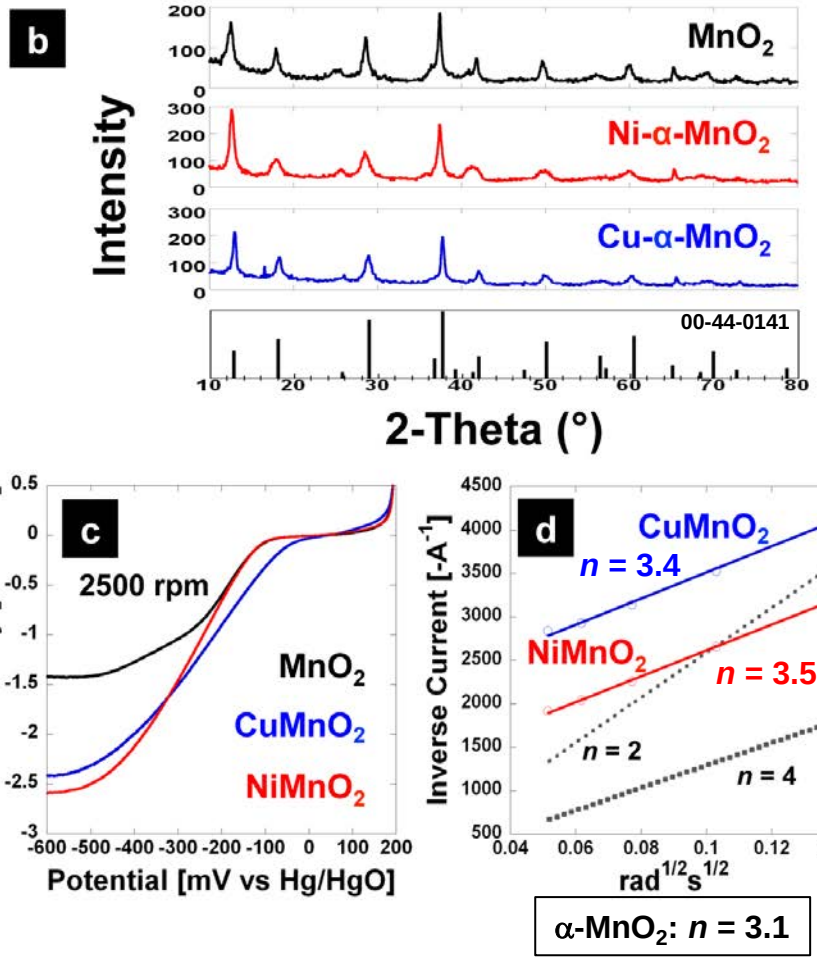
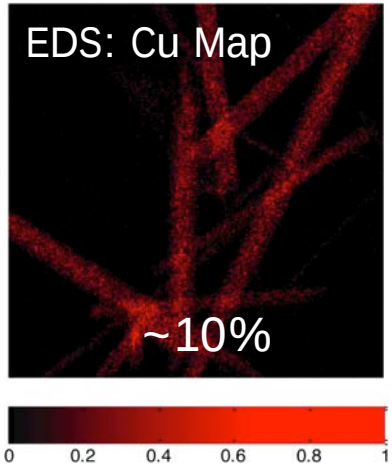
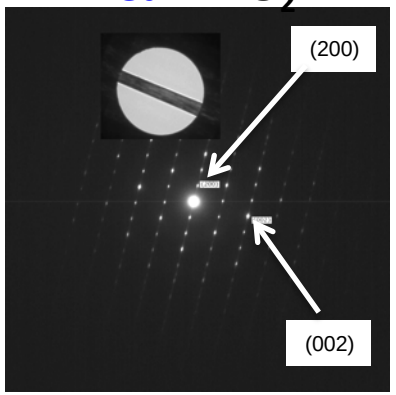
$^{II}MnSO_4 \cdot H_2O + (Ni/Cu\text{-}SO_4 \cdot H_2O) + {}^{VII}KMnO_4$ —Hydrothermal synthesis, 140° C, 12-120 h→ $^{IV}Ni\text{-}\alpha\text{-}MnO_2$ or $^{IV}Cu\text{-}\alpha\text{-}MnO_2$





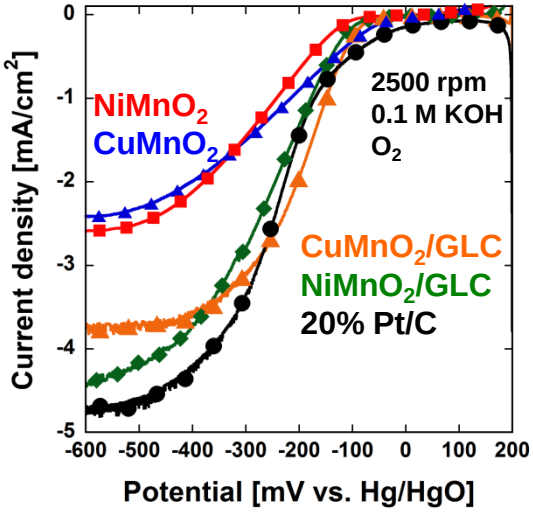




T.N. Lambert *et al. Chem. Commun.* **2012** *48*, 7931-7933

Graphene/Ni- and Cu-α-MnO_2 blends

Graphene-like carbon blends more active than Vulcan blends despite lower conductivity
= better dispersion and synergistic behavior



$CuMnO_2$ outperforms Pt/C in the potential range of -127mV to -267mV

→ 78% of current obtained by Pt/C, *n* = 3.9
→ 91% of current obtained by Pt/C
rate = 3.50 x 10^{-2} cm/s
Pt/C rate = 3.24 x 10^{-2} cm/s

For GLC (Prof. JM Tour@ Rice) synthesis see:
Z. Jin *et al. J. Am. Chem. Soc.* **2010**, 132, 15246–15251.

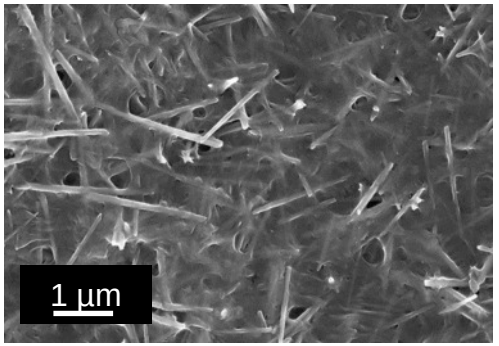
(i) Direct four electron pathway:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(ii) Indirect (peroxide) pathway:
$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$

followed by either
(a) the further reduction of peroxide:
$HO_2^- + H_2O + 2e^- \rightarrow 3\ OH^-$

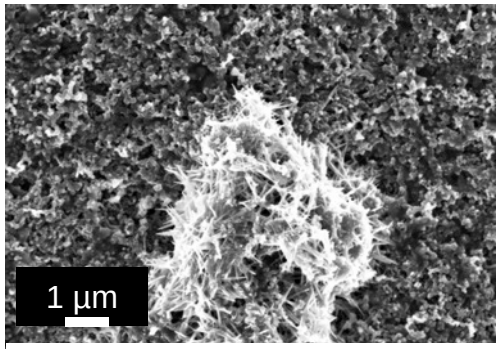
or (b) the catalytic peroxide decomposition:
$HO_2^- \rightarrow ½\ O_2 + OH^-$

Cu-α-MnO_2 NWs / GLC / Nafion



***GLC**:*
Conductivity = 2.59 S/cm
Surface Area (carbon) = 900-1000 m^2/g
Excellent Dispersion of NWs

Cu-α-MnO_2 NWs / Vulcan XC-72/ Nafion



***Vulcan**:*
Conductivity = 107.5 S/cm
Surface Area (carbon) = 230-250 m^2/g
Poor dispersion of NWs

Electrocatalytic Selectivity

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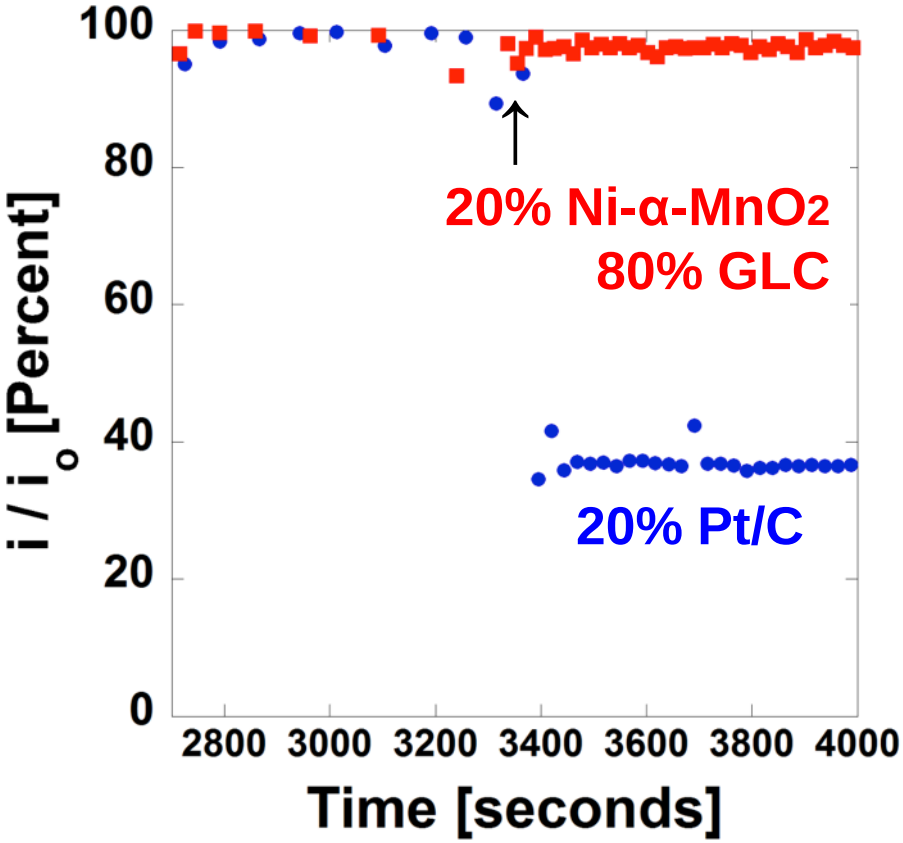
Chronoamperometric Percent Response



- Preliminary probe to examine crossover effects in alkaline methanol fuel cells
- Arrow indicates injection of 2 wt.% methanol
- 20% Pt/C suffers a ~60% decrease in current.
- 20% $NiMnO_2$/80% GLC only shows a ~5% decrease in current.

What is role of metal ion dopant ?

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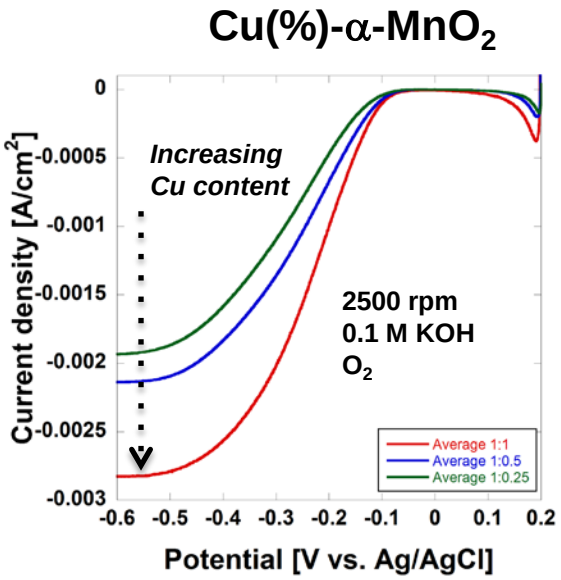

Ratio Mn:Cu	Onset (mV)	n (e-)	Current density (mA/cm²)	Half-wave (mV)	Rate (cm/s)	Rct (Ω)
1:0.25	-107.7	3.28	-1.93	-312	0.0078	5744
1:0.5	-97.3	3.31	-2.14	-303	0.0097	4380
1:1	-100.3	3.20	-2.82	-292	0.019	3430

Prepared series of Cu-doped α-MnO_2

Nanowires are highly crystalline w/ substitutional doping throughout

Reactant Ratio (Mn:Cu)	Percent Copper	BET Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)
1:0 (MnO_2)	0	73.6	13.4	0.31
1:0.25	7.5	59.1	9.4	0.14
1:0.5	7.8	80.7	9.2	0.19
1:1	9.3	83.8	11.6	0.24

Surface Area is important but not sole reason for activity > α-MnO_2

Structural Effects of Cu

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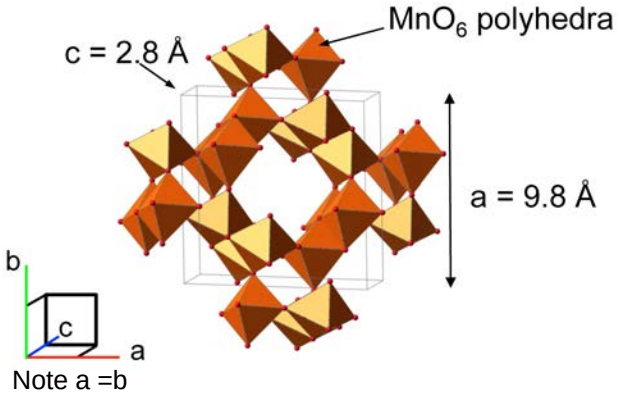
Analysis of XRD



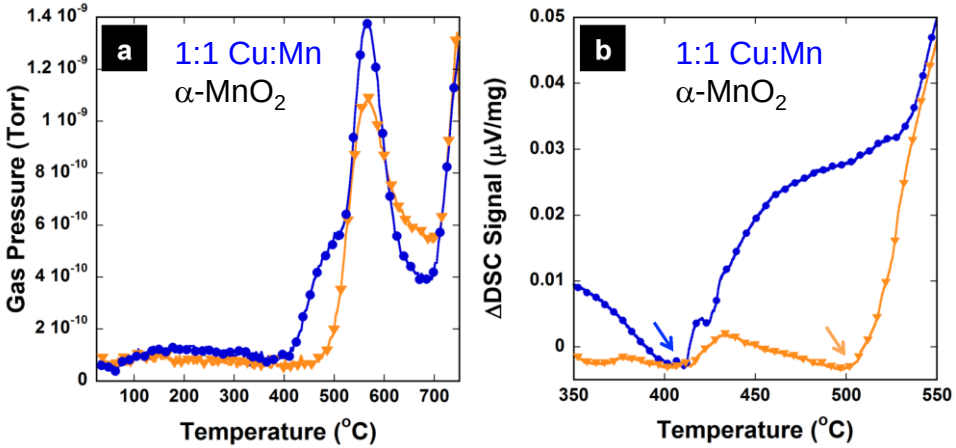
Lattice expands and becomes more covalent

- Bond Lengths: Cu-9.3-α-MnO_2 (1.900 ± 0.010 Å) *higher covalency*
  α-MnO_2 (1.915 ± 0.035 Å)
- Lattice volume: Cu-9.3-α-MnO_2 (278.12 Å^3) *lattice expansion*
  α-MnO_2 (276.45 Å^3)
- Crystallite size: Cu-9.3-α-MnO_2 (16 nm) *more edge defects*
  α-MnO_2 (36 nm)

Cu^{2+} ions (0.73 Å) in place of smaller Mn^{3+} (0.645 Å) or Mn^{4+} ions (0.530 Å) is consistent with an overall expansion in the lattice.

O_2 evolution upon heating

TGA/DSC/MS

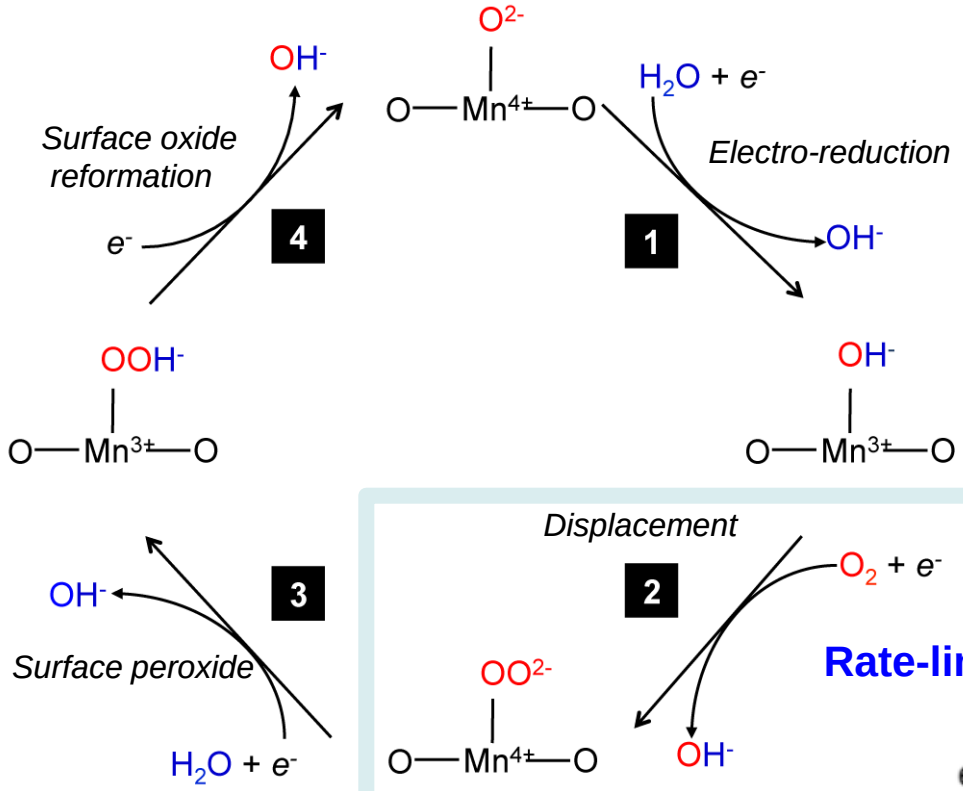


Higher number of crystalline edge defects

- O_2 release observed ~ 90 °C earlier for Cu-α-MnO_2 indicates a portion of more weakly bound O_2
- Mass losses/water content up to 700 °C:
  Cu-α-MnO_2 1.57 μmol O_2 / 4.67% H_2O
  MnO_2 1.16 μmol O_2 / 2.18% H_2O

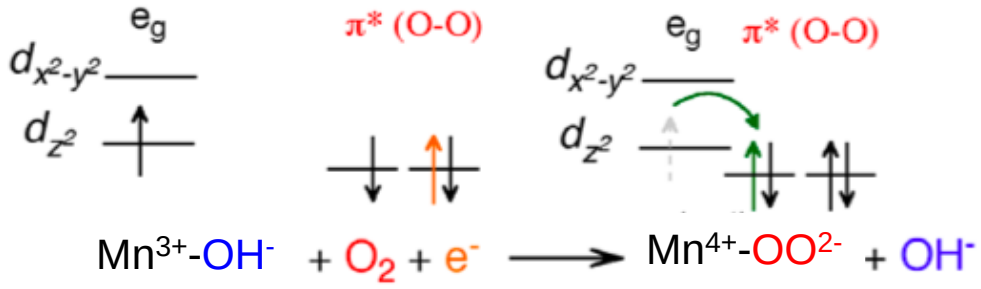
consistent with higher # edge defects and larger lattice

The role of Mn^{3+}/Mn^{4+} Couple



- **The transfer of the e_g electron during the OH^-/O_2^{2-} exchange drives the reaction forward.**
- **O_2 adsorption energy trends of B-O_2 can be approximated by those of B-O**
- **Hence more covalent structures should have faster kinetics (as observed)**

Rate-limiting step



Mn^{3+}: d4 ion = High Spin in Octahedral coordination

Adapted from: J. Suntivich *et al.* Nature Chemistry **2011** *3*, 546-550.

Electron Configuration of Mn^{3+}

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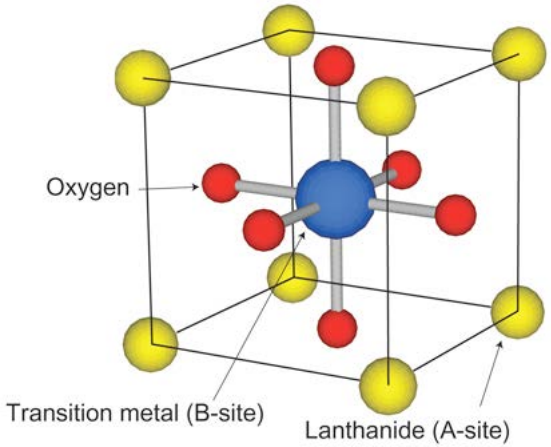
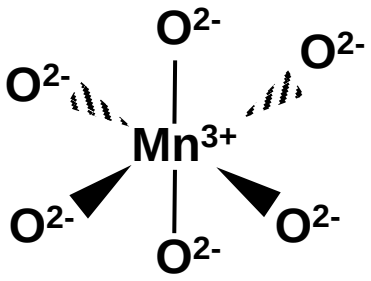
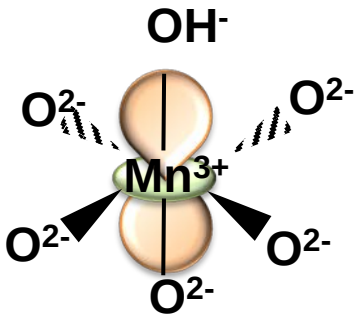
d^4 and d^7 are most active metal ions in O_h B-site of perovskite oxide catalysts
➔ relevant to our Mn^{3+} here.

d4 = High Spin in Octahedral coordination



Mn^{3+}

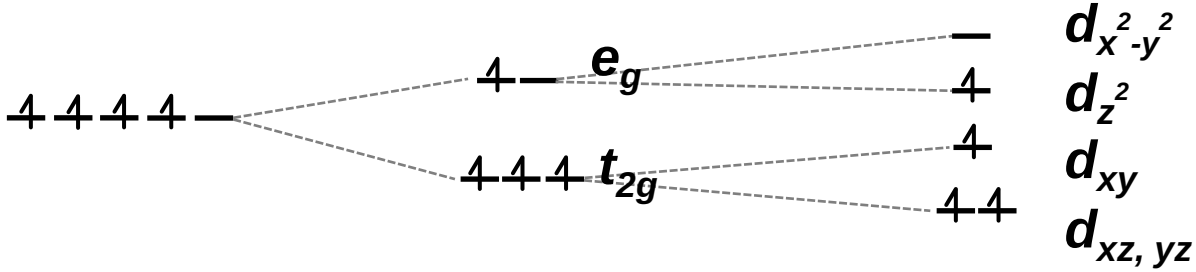


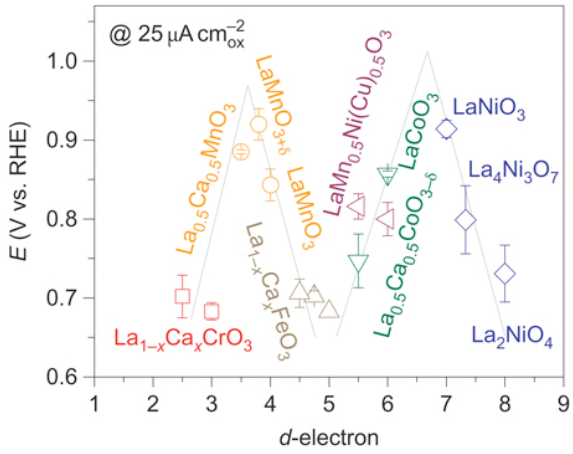


d^4 : d-manifold

d-manifold with oxygen ligands *(high spin)*

d-manifold in tetragonal symmetry *(high spin)*





Adapted from J. Suntivich *et al.* Nature Chemistry. **2011.** 3, 546-550.

Mn^{3+}/Mn^{4+} couple mediates ORR

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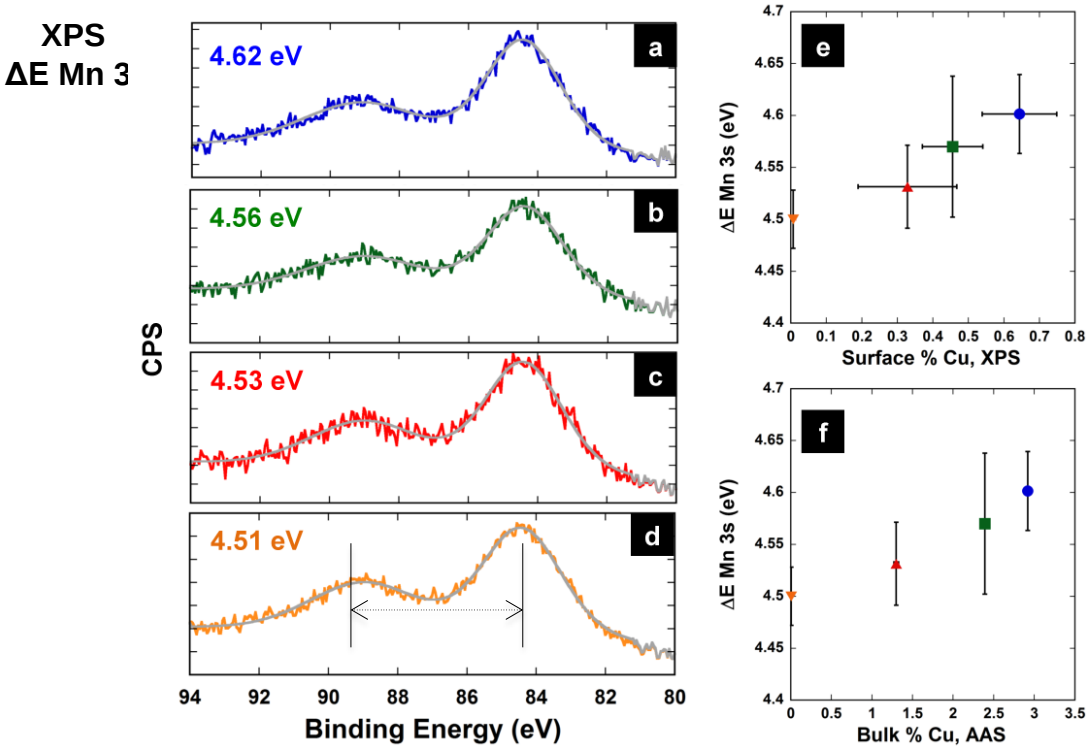
ΔE Mn 3s splitting correlates with Mn^{3+}/Mn^{4+}



- **Increasing copper (most active catalyst) leads to increasing surface Mn^{3+}**
- **Less Cu observed at surface versus bulk**

Cu-α-MnO_2 Electrocatalysts

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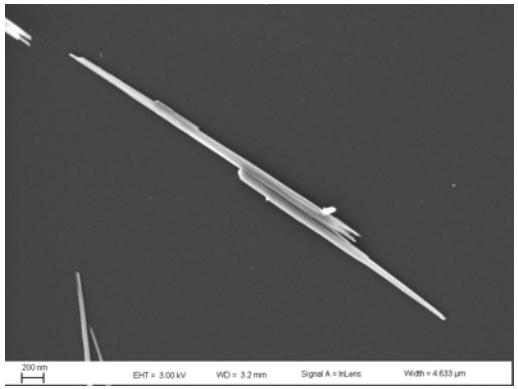
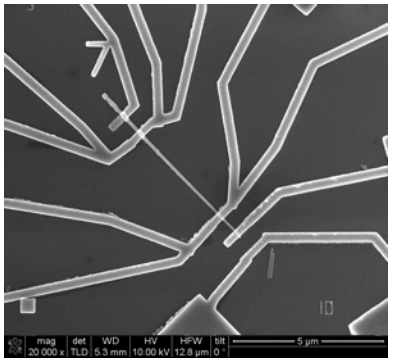
Summary

- The Cu-dopant species, when added to α-MnO_2, improves the electrochemical performance (half wave, current, kinetics) as a catalyst for ORR in alkaline media.
- Cu leads to higher Mn^{3+}/Mn^{4+} ratio *at the surface*
- Mn^{3+} plays role in mediating ORR
- Cu leads to increased covalency, smaller crystallite domain and lattice expansion
- Some O is more loosely bound – (catalytic) edge sites
- Cu-α-MnO_2 displays an (almost) apparent 4 e^- process
- Graphene/Ni/Cu-α-MnO_2 blends are highly active ORR electrocatalysts
- OER performance is ongoing
- Conductivity ?
  - Single wire conductivity

  of interest





New Sandia O_2 Electrocatalysts

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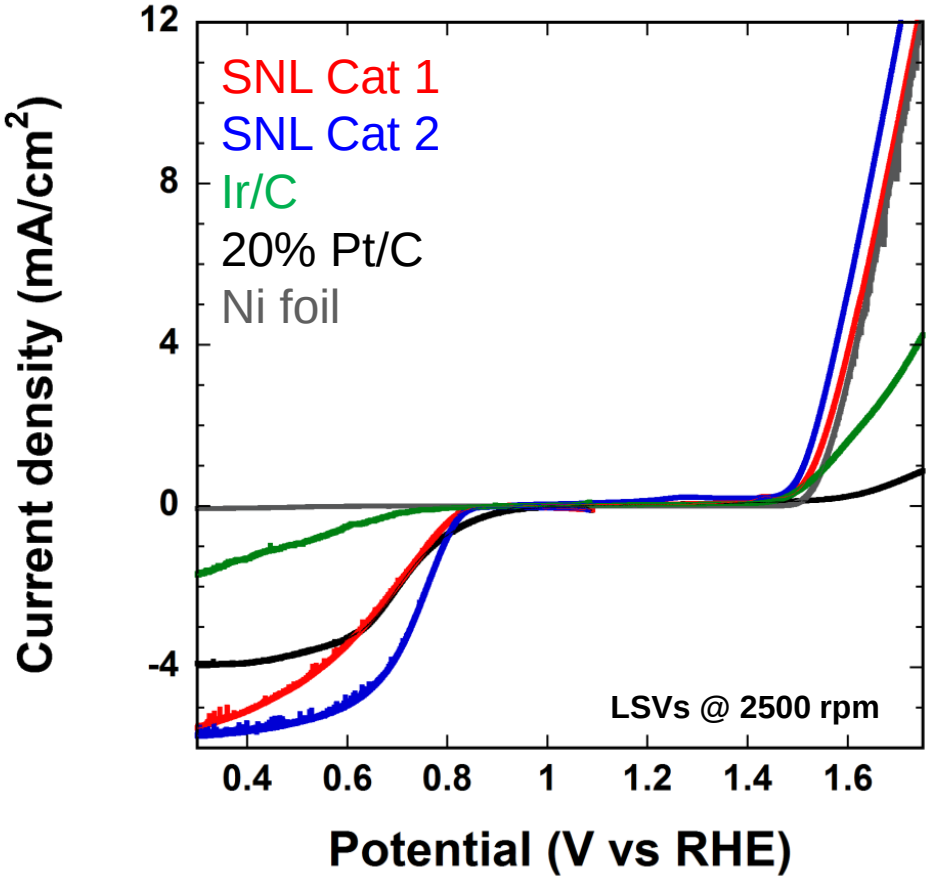
$$O_2 + 2H_2O + 4e^- = 4OH^-$$

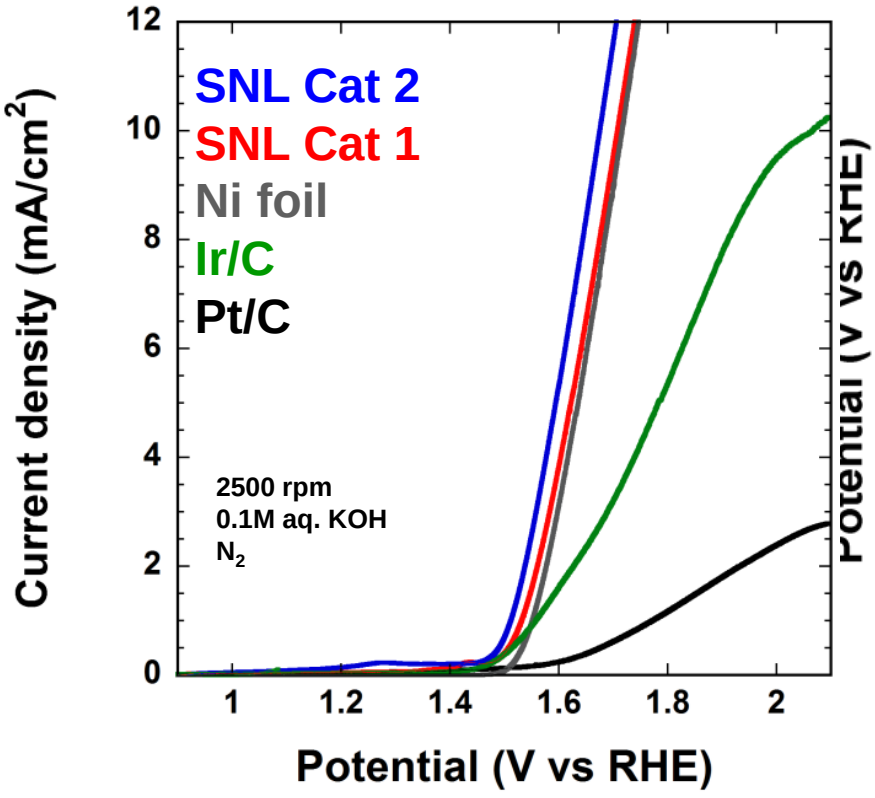


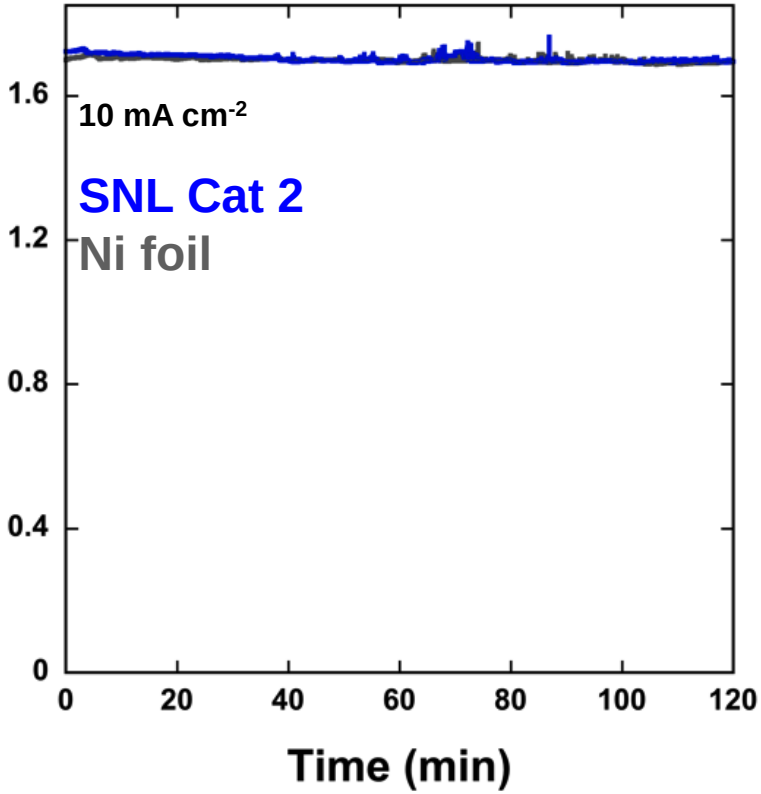
- **New cost effective bi-directional nanostructured catalysts**
- **Contain no binder, prepared w/ scalable methods**
- **Excellent performance as compared to Pt/C (ORR), n ~ 4**
- **Excellent/Good stability for ORR and OER**
- **Excellent performance as compared to Ir/C (OER)**

T. N. Lambert *et al. unpublished results*.

New Sandia O_2 Electrocatalysts

Oxygen Evolution Reaction Performance and Stability





Good Stability for OER after 2 hours

Hydrogen Evolution Reaction

HER 1600 RPM Overlay of Sandia Catalysts – non Pt based materials

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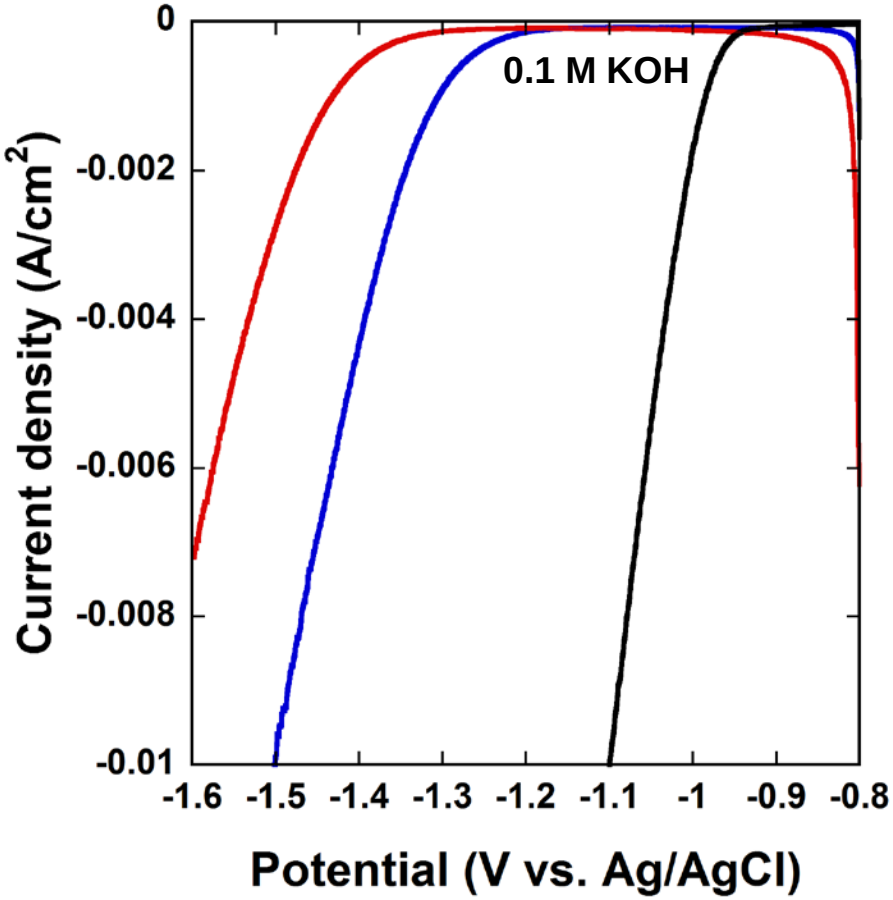
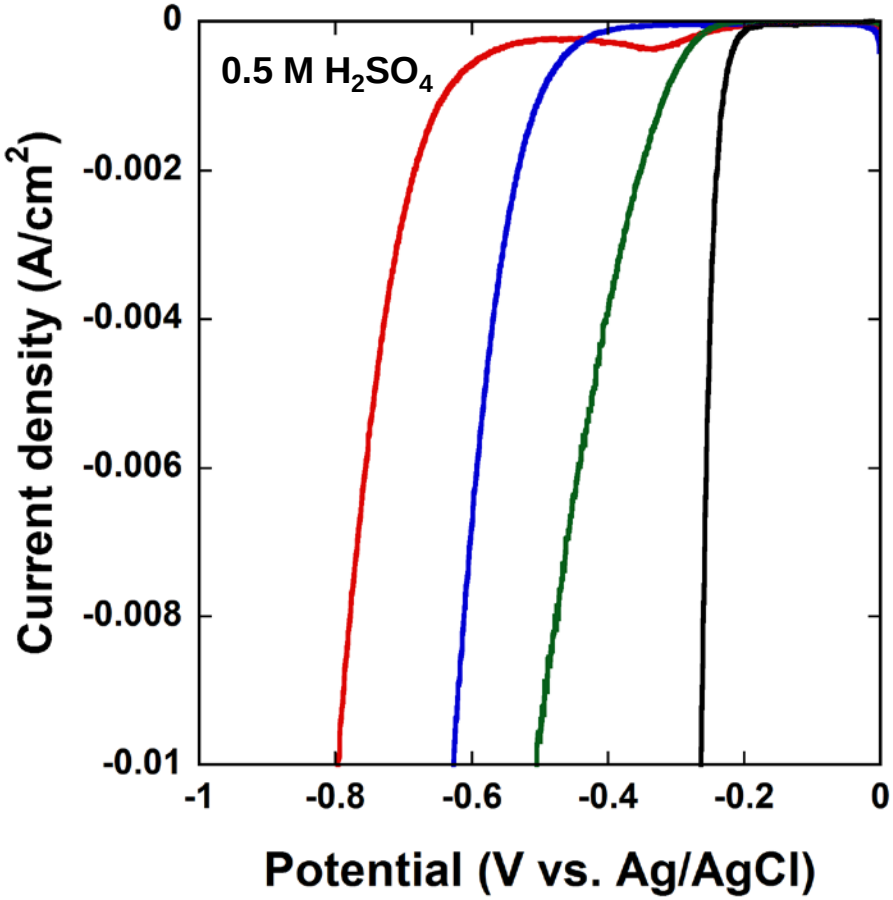
$$2H^+_{(aq)} + 2e^- \rightarrow H_{2\,(g)}$$

Catalyst 1 **Catalyst 2** **Catalyst 3** **20% Pt/C**





Preliminary results: Comparable to best non-Pt catalysts in literature

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Thank you

Analyzing the Catalytic Performance

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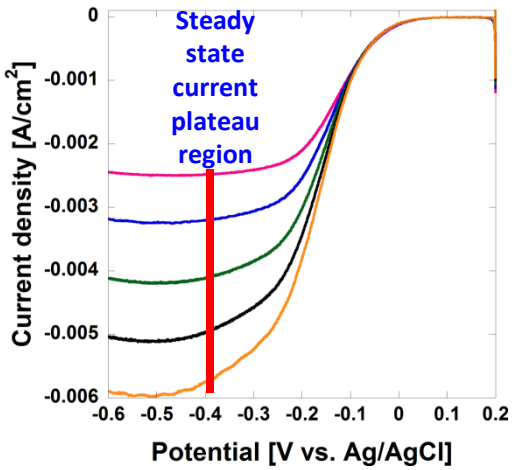
Linear Scanning Voltammogram (LSV)

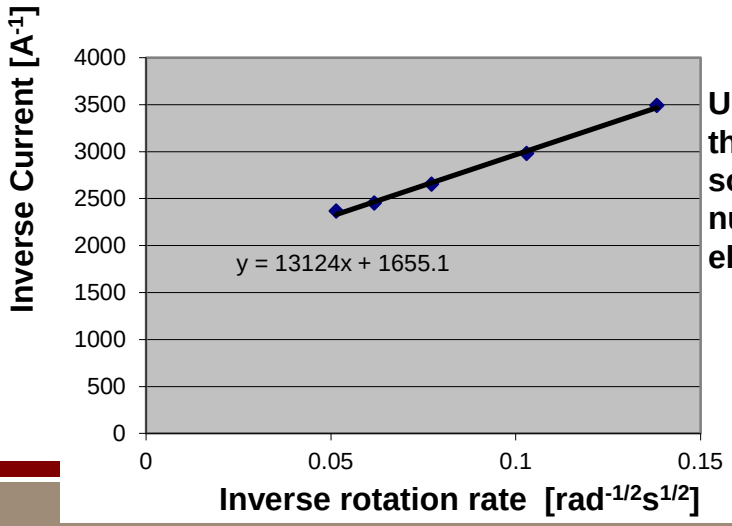


Using current density values at a constant potential for each rotation speed, construct a Koutecky-Levich plot.

Koutecky-Levich Equation

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_d}$$

$$= \frac{1}{nFAkC^0} - \frac{1}{0.62nFAD_{O_2}^{2/3}\upsilon^{-1/6}C^0\omega^{1/2}}$$



Use slope of the K-L Plot to solve for number of electrons.

***n* = number of electrons transferred**

1/*i* = slope of K-L plot

F = Faraday constant

A = geometric electrode area (cm^2)

k = rate constant for oxygen reduction

C° = saturated concentration of O_2 in 0.1M KOH

D_{O2}= diffusion coefficient of oxygen

v = kinetic viscosity of electrolyte solution

ω = rotation rate

Comparison of α-MnO_2 NW Catalysts

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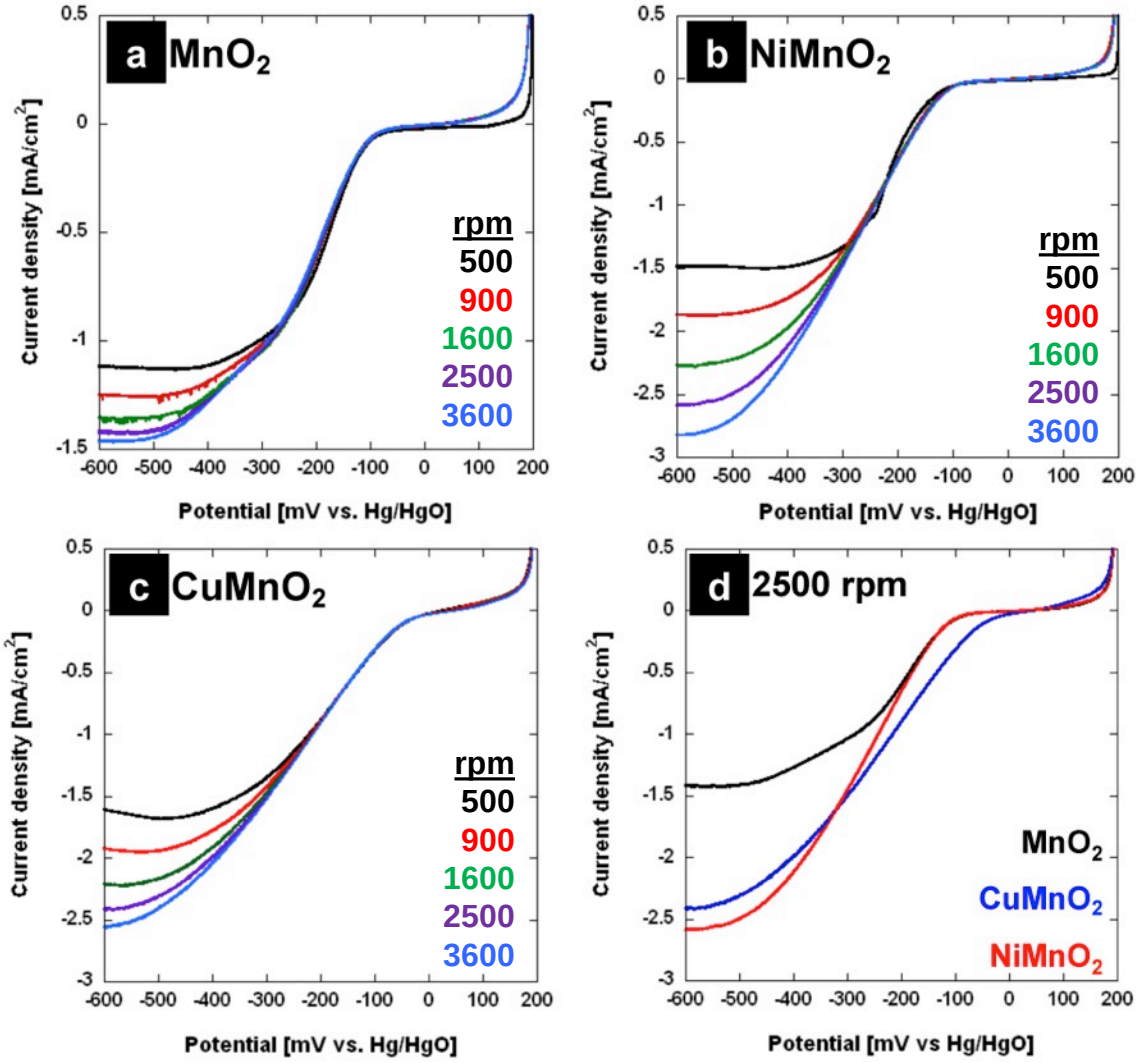

Nanowire Material	Average Onset Potential (mV)
α-MnO_2	-110
Cu-α-MnO_2	-75
Ni-α-MnO_2	-112

T. Lambert, D. Davis *et al.*, *Chem. Commun.*, **2012**, 48, pp 7931-7933.

Comparison of α-MnO_2 NW Catalysts

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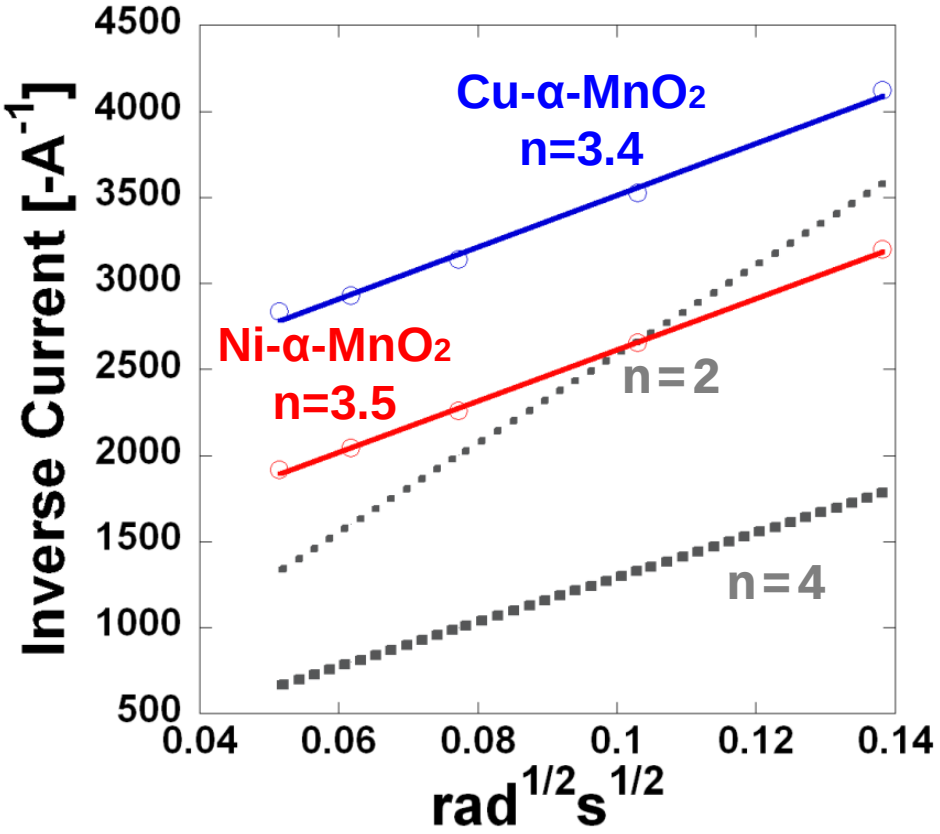
Koutecky-Levich Analysis



- Published n-value for MnO_2 = 3.1; our data consistent with this value (Cheng et. al., Chem. Mater. 2010, 22, 898-905)
- ORR n-values are improved with doping.
- Peroxide production is < 5% for all catalysts; this corresponds to a fast peroxide disproportionation reaction.
- Reaction rates also improved:
  - MnO_2 = 3.98 x 10^{-3} cm/s
  - $NiMnO_2$ = 1.53 x 10^{-2} cm/s
  - $CuMnO_2$ = 6.70 x 10^{-3} cm/s

Ni- and Cu-α-MnO_2 Nanowires

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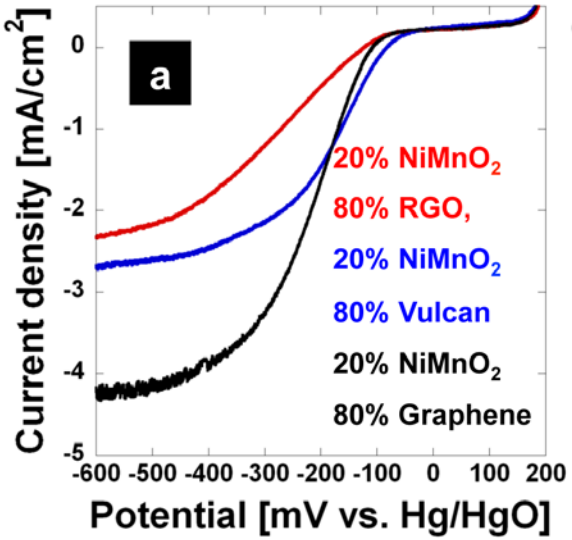
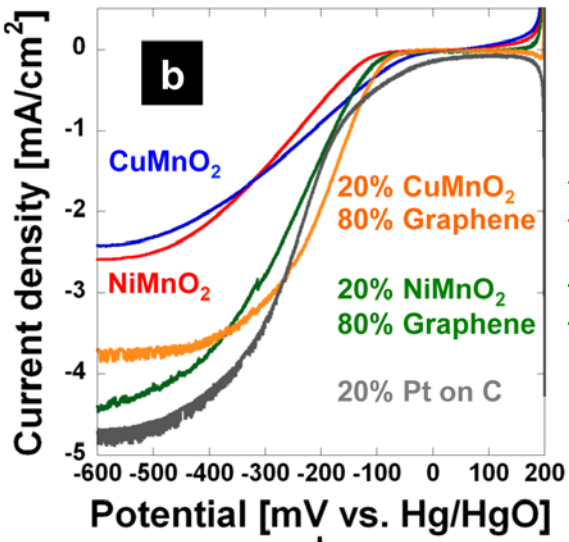


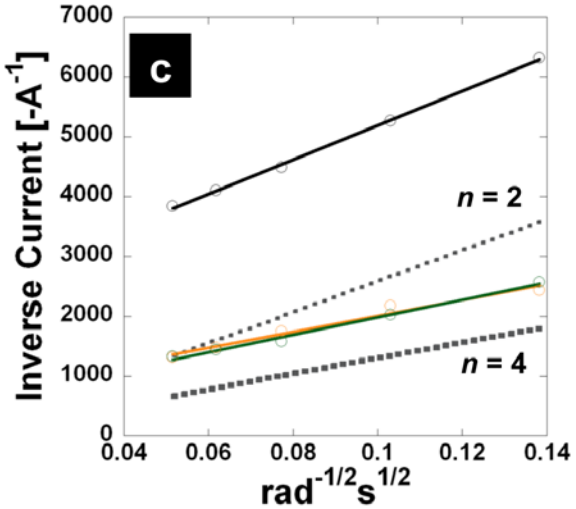


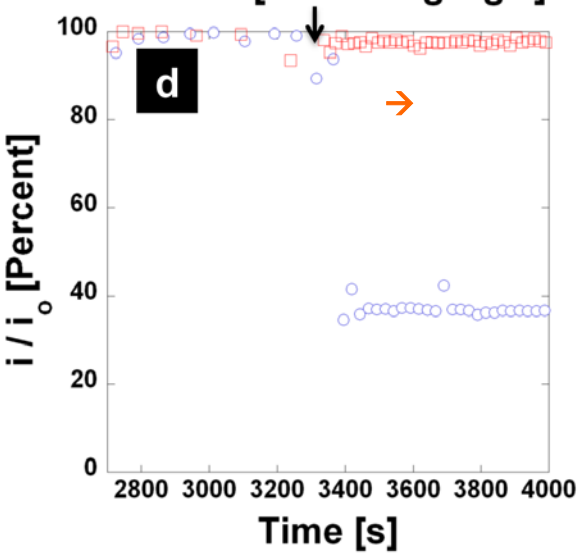
Graphene less conductive than Vulcan

→ 78% of current obtained by Pt/C
→ n = 3.9 ± 0.2 e$^-$

→ 91% of current obtained by Pt/C
→ 3.50 x 10^{-2} cm/s

vs. 3.24 x 10^{-2} cm/s for benchmark





MeOH Crossover Experiment *via* chronoamperometry

- **Probe to examine crossover effects**
- **Arrow indicates injection of 2 wt.% MeOH**
- **20% Pt/C suffers a ~60% ↓ in current.**
- **20% NiMnO$_2$/80% GLC ~5% ↓ in current.**

Good performance but what is the role of metal ion doping ?

Electrocatalytic Selectivity

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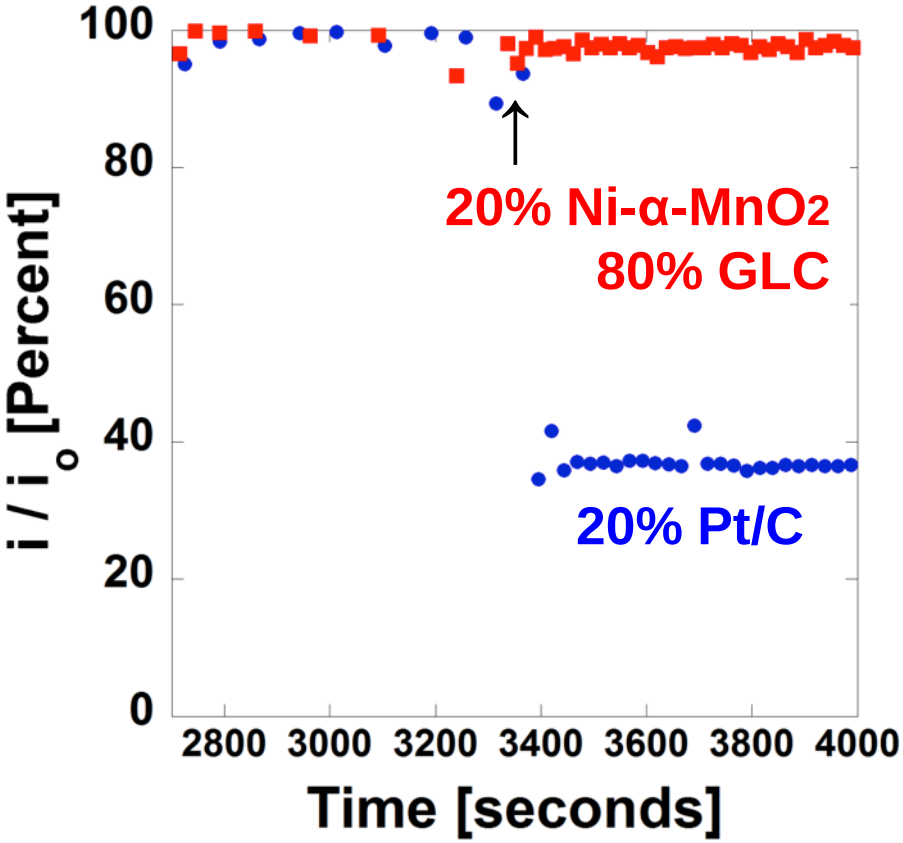
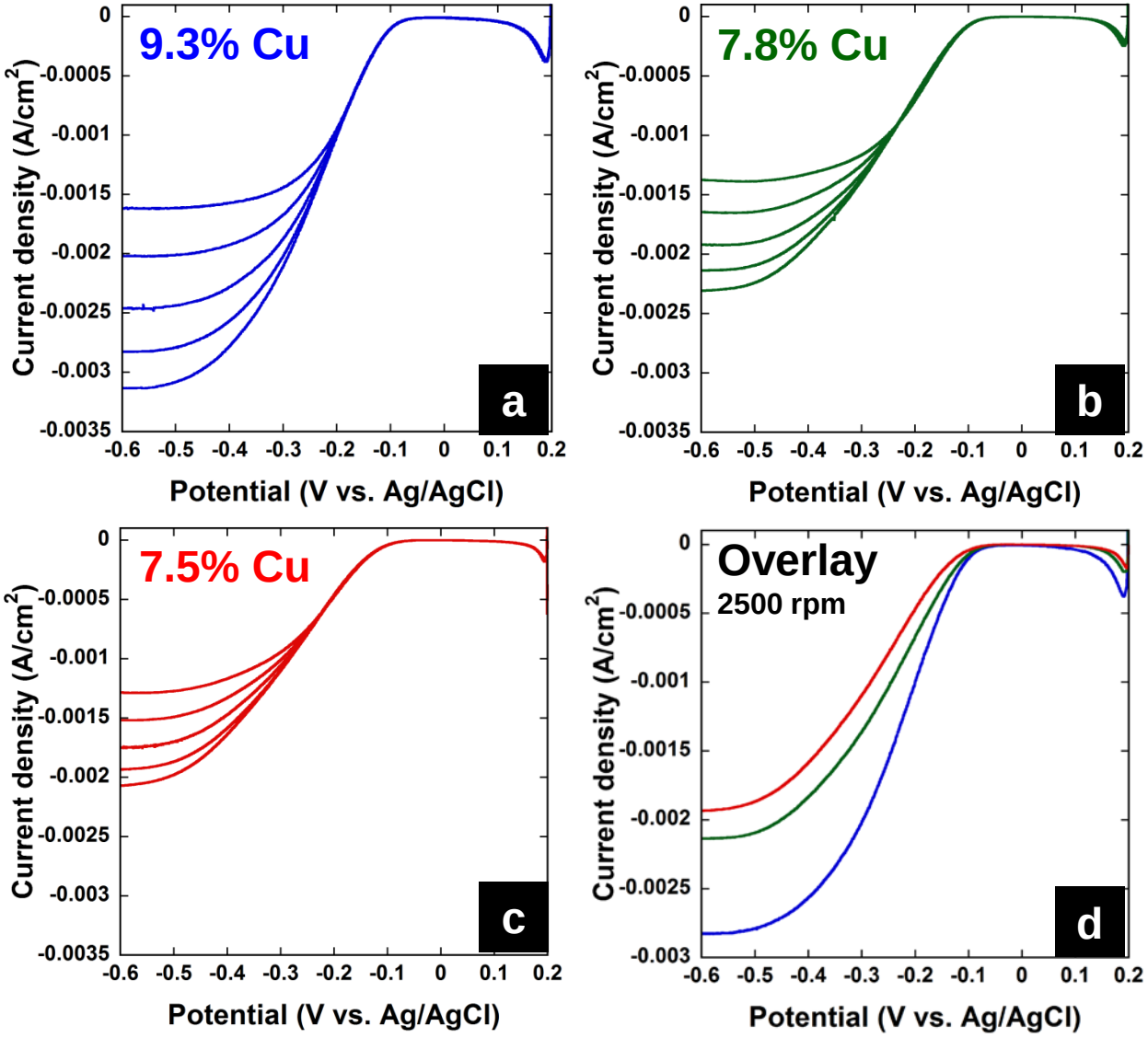
Chronoamperometric Percent Response



- Preliminary probe to examine crossover effects in alkaline methanol fuel cells
- Arrow indicates injection of 2 wt.% methanol
- 20% Pt/C suffers a ~60% decrease in current.
- 20% $NiMnO_2$/80% GLC only shows a ~5% decrease in current.

Electrochemical Analysis

Rotating Disk Electrode (RDE) Studies



What is role of metal ion (Cu)dopant ?

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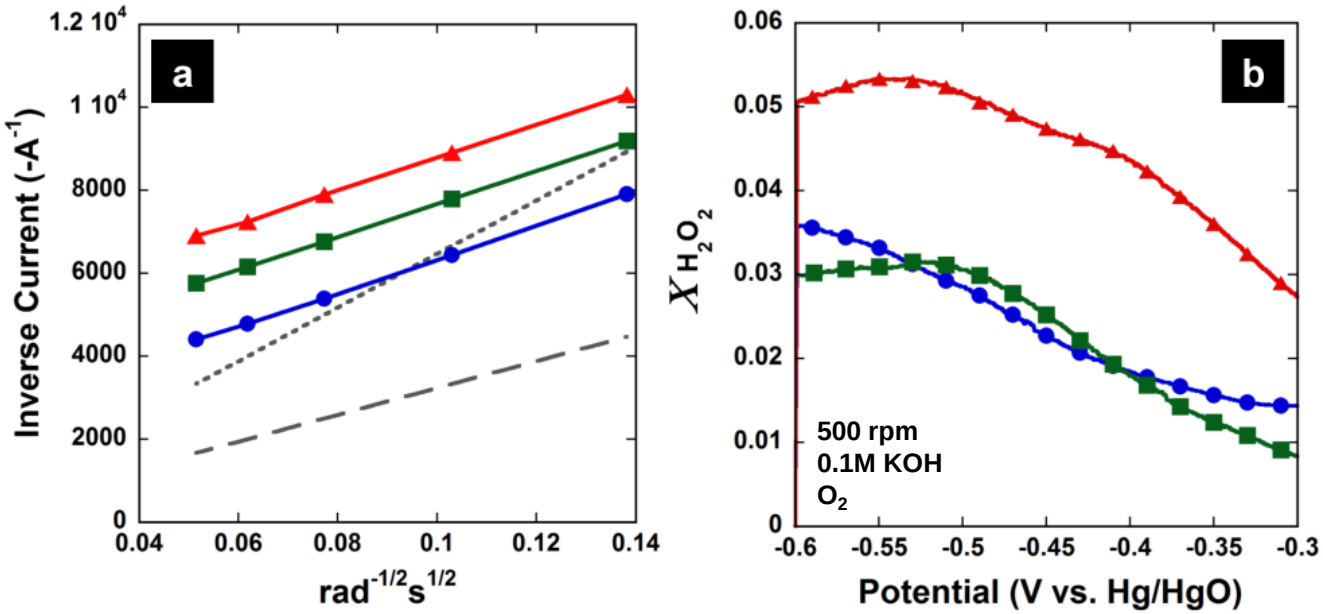
Koutecky-Levich Analysis *vs.* RRDE Studies

K-L *n* values 3.2-3.3 | **6% = *n* values ~ 3.8**

Mn:Cu
1:0.25
1:0.5
1:1



$X_{H2O2} = 2(I_R/N) / [(I_R/N)+(I_D)]$

$\%X_{H2O2} = X_{H2O2}$ x 100%

I_R is the ring current,
N is the collection efficiency
I_D is the disk current

Data suggests that up to 20% peroxide (RDE: n ~ 3.2) could be produced but majority of that undergoes catalytic decomposition prior to disassociation from the catalyst (RRDE: n~ 3.8).

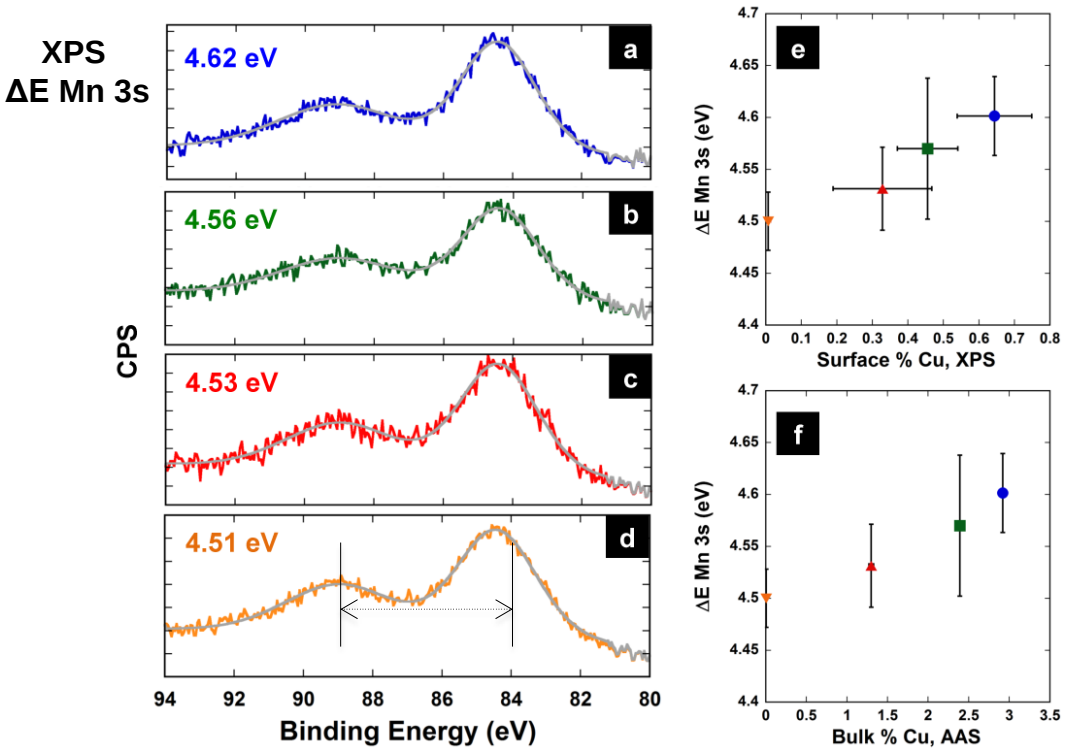
Catalytic Role of Mn^{3+}/Mn^{4+}

(1) $Mn^{4+}O^{2-}_{(s)} + H_2O_{(aq)} + e^- \rightarrow Mn^{3+}\text{-}OH^-_{(s)} + OH^-_{(aq)}$ *Electro-reduction*

(2) $Mn^{3+}\text{-}OH^-_{(s)} + O_2^-{}_{(g)\ adsorbed} + e^- \rightarrow Mn^{4+}\text{-}O\text{-}O^{2-}_{(s)} + OH^-_{(aq)}$ *Displacement (rate limiting step)*

(3) $Mn^{4+}\text{-}O\text{-}O^{2-}_{(s)} + H_2O_{(aq)} + e^- \rightarrow Mn^{3+}\text{-}O\text{-}OH^-_{(s)} + OH^-_{(aq)}$ *Surface peroxide*

(4) $Mn^{3+}\text{-}O\text{-}OH^-_{(s)} + e^- \rightarrow Mn^{4+}O^{2-}_{(s)} + OH^-_{(aq)}$ *Surface oxide reformation*



Mn^{3+}/Mn^{4+} couple mediates ORR

Doping can influence
- **electro-reduction**
- **peroxide decomposition**
- **conductivity**

Doping has been *claimed* to influence
- **stabilization of Mn^{3+} ions**

- **ΔE Mn 3s splitting correlates with Mn^{3+}/Mn^{4+}**
- **Increasing copper leads to increasing surface Mn^{3+}**
- **Less Cu observed at surface versus bulk**

$$O_2(g) + 2H_2O + 4e^- = 4OH^-(aq) \quad +0.401 \text{ vs SHE}$$