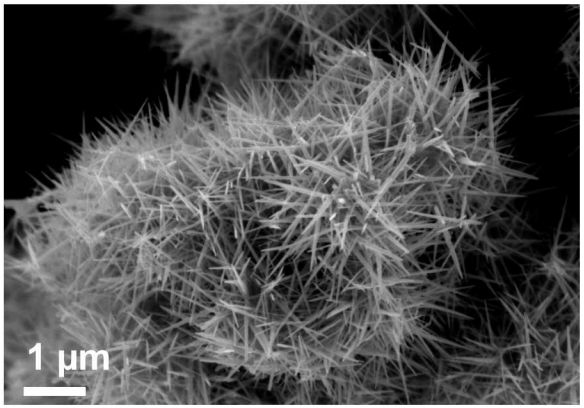
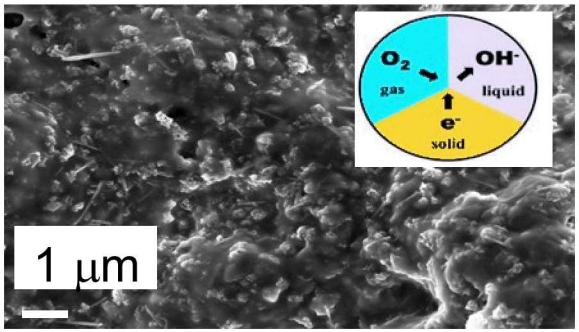
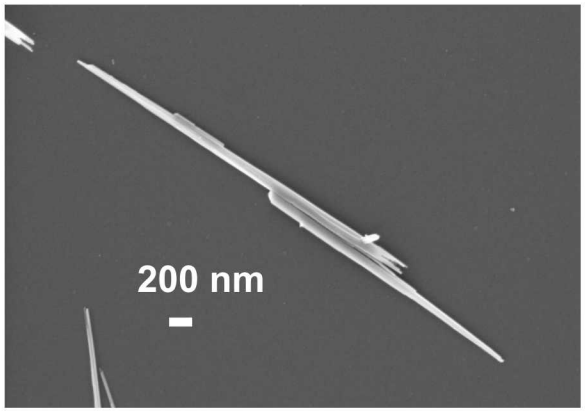
SAND2015-2916C







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

Cu- and Ni-doped α-MnO_2 Electrocatalysts for Reversible Oxygen Electrochemistry

2015 Spring ACS Presentation

March 26th, 2015: Denver, Colorado

Timothy N. Lambert, Danae J. Davis, Julian A. Vigil, Suzanne E. White and Brian Swartzentruber

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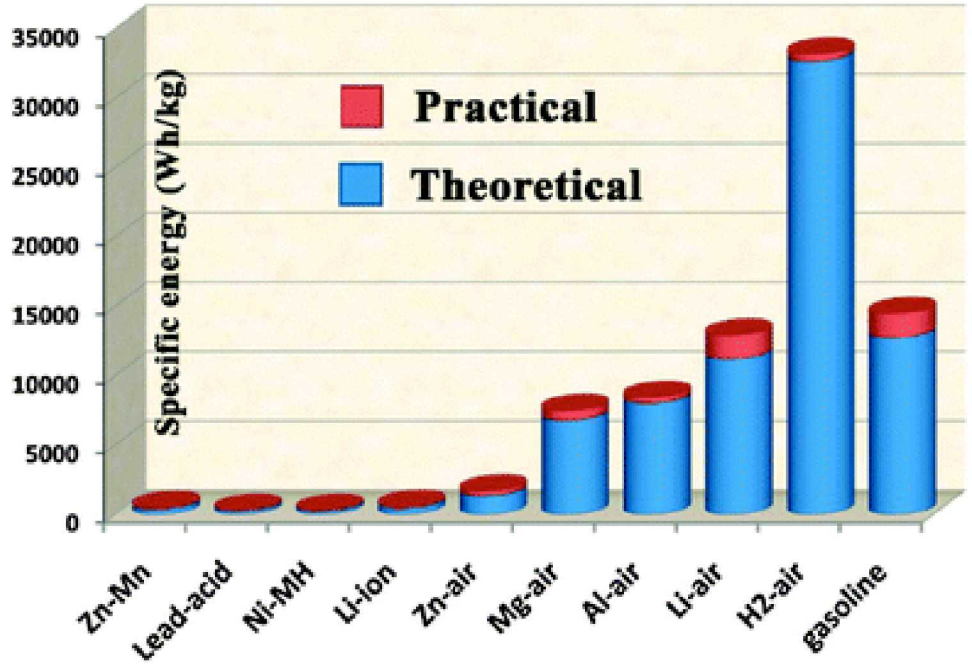
Importance of O_2 Electrochemistry

Electrical Energy Storage



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

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.

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. $VP + 6\ OH^- + 5/2\ O_2 \rightarrow VO_4^{3-} + PO_4^{3-} + 3\ H_2O$; $E^o = 1.47$ V

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

Importance of O_2 Electrochemistry

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

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

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

Alkaline Fuel Cells

Anodic half-reaction: $2\ H_2 + 4\ OH^- \rightarrow 4H_2O + 4e^-$

Cathodic half-reaction: $O_2 + 2\ H_2O + 4e^- \rightarrow 4\ OH^-$

Full cell reaction: $2\ H_2 + O_2 \rightarrow 2\ H_2O$

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

Bi-directional cathode could allow for anode activation

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

Our interest has been Alkaline Systems

Problem:

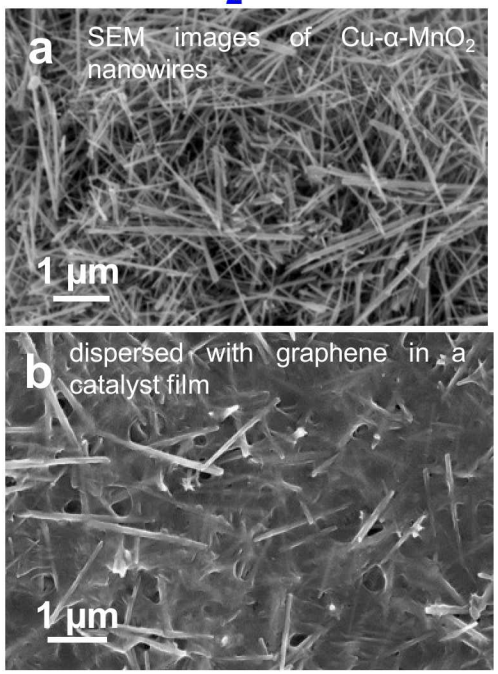
1.) Cathode: kinetics, high overpotentials, poor reversibility ~ 60% of energy losses due to cathode

2.) Leading Catalysts are expensive and rare metals/oxides

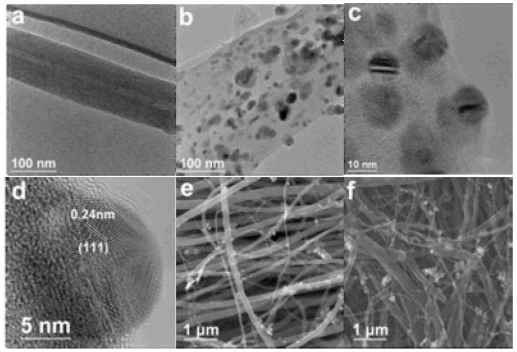
(e.g. Pt, Ir, IrO_x) – Also – poor stability and electrochemical selectivity.

Solution: Develop new non-Pt catalysts = durable, active, economically viable

Ni-α-MnO_2 & Cu-α-MnO_2 Nanowires



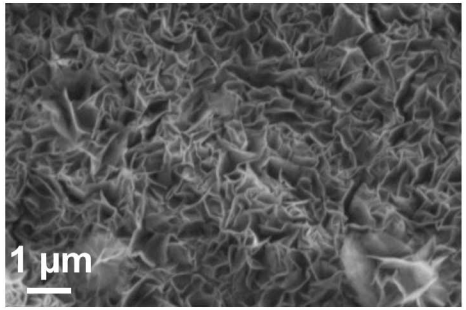
Ag-Graphene Nanoribbons Composite



TEM images of a) MWCNT, b) Ag-GNR; HRTEM images of c) Ag-GNR, d) Ag nanocrystal along one of its crystallographic planes; SEM images of e) MWCNTs, f) Ag-GNR.

D. J. Davis *et al. Electroanal.* **2013**, *1*, 164-170

Porous Co_3O_4 spinel films



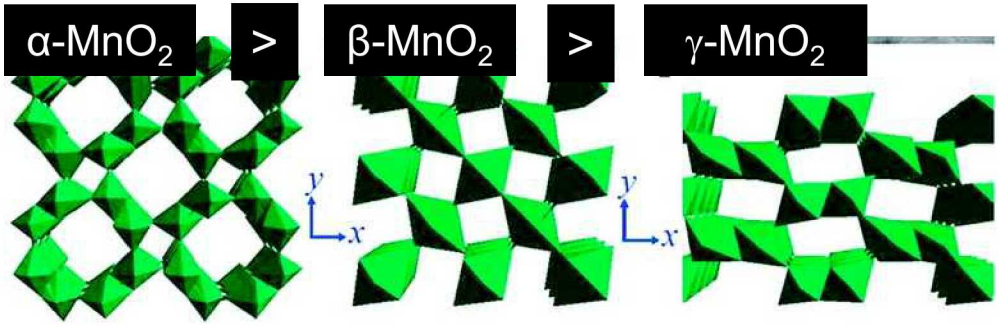
SEM image of electrochemically deposited cobalt oxide thin films

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

Manganese oxide Nanowires

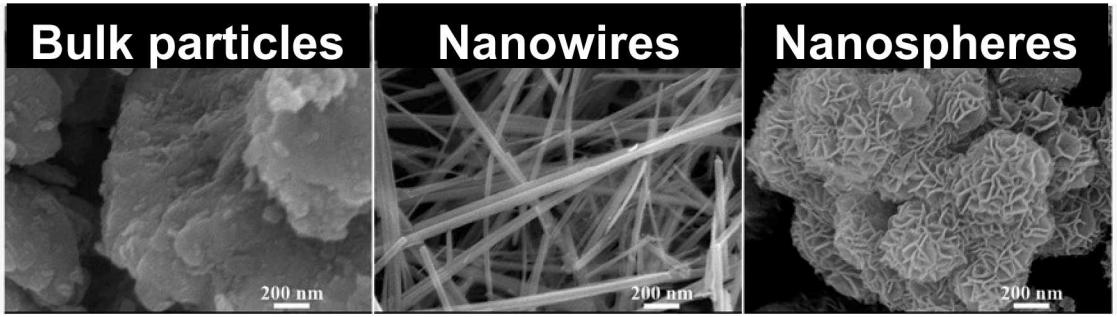
An effective catalyst must facilitate O_2 adsorption and HO_2^- decomposition

Phase



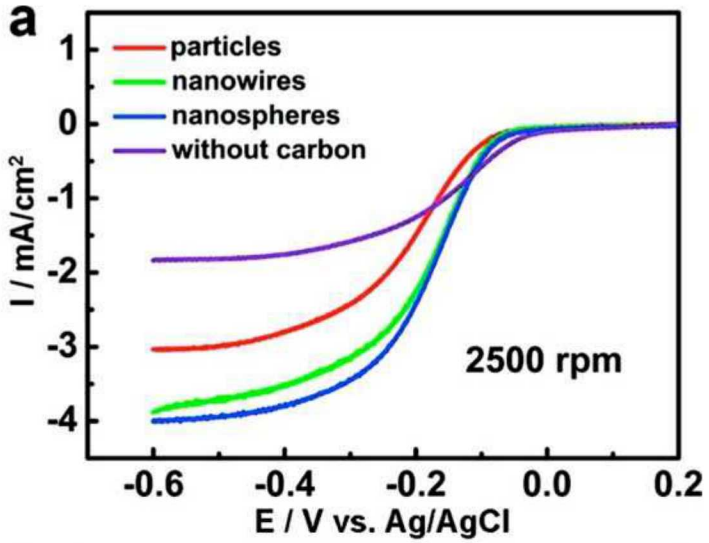
Size nm MnO_2 > μm MnO_2

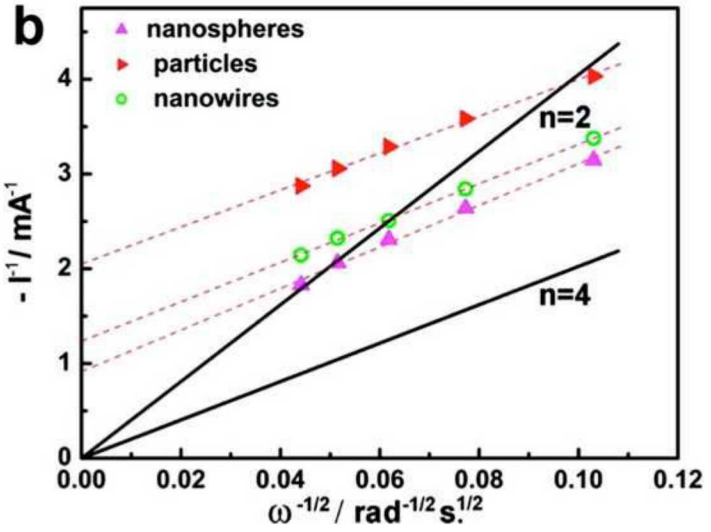
Morphology nanowires/spheres > nanoparticles



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

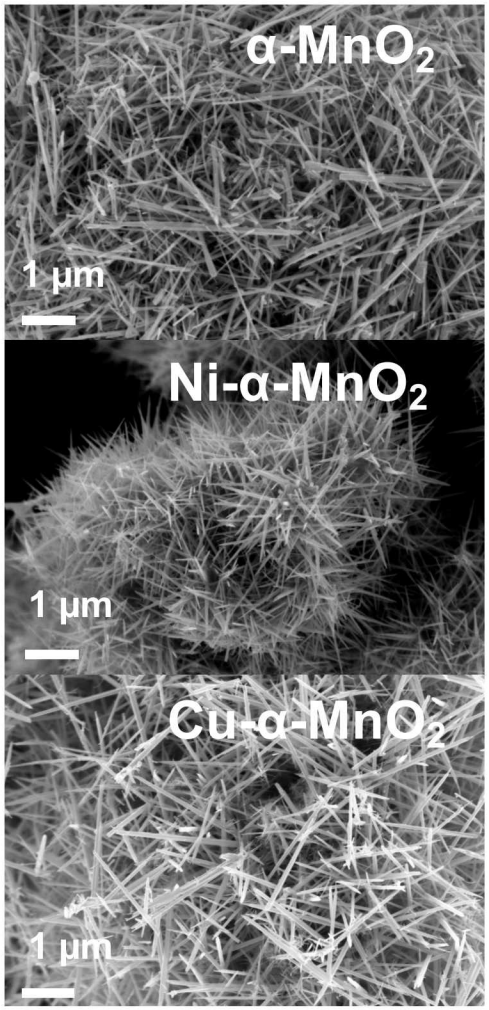
F. Cheng, *et al. Chem. Mater.* **2010**, *22*, 898–905

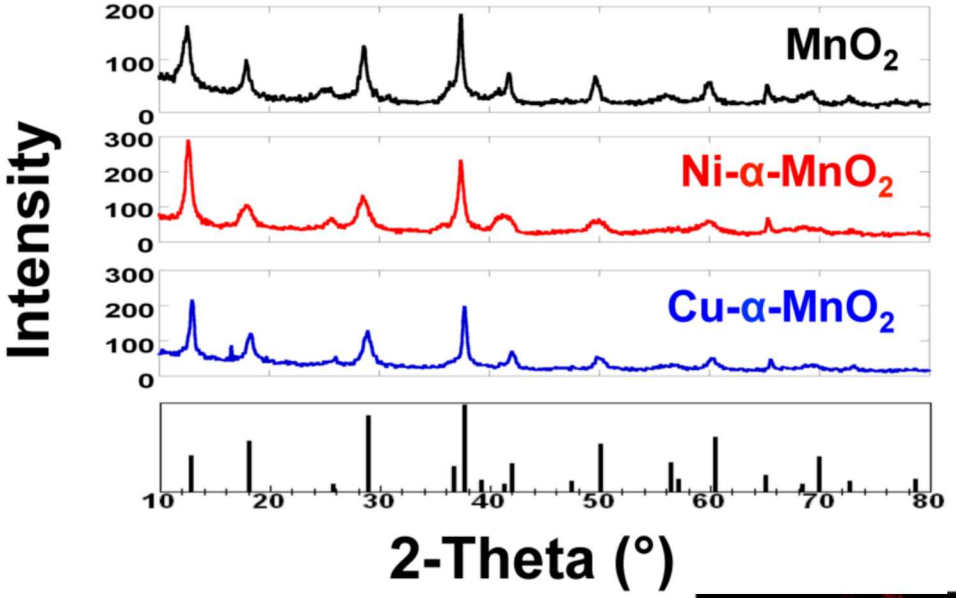


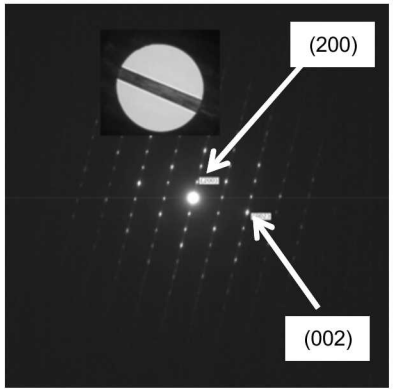


Ni- and Cu-α-MnO_2 Nanowires

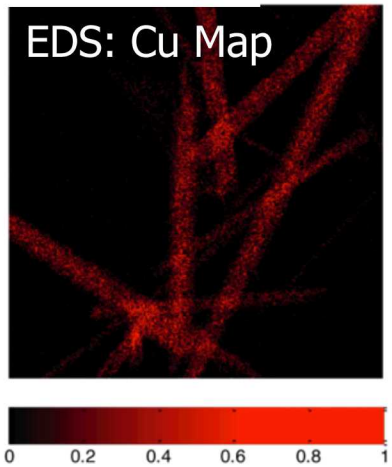
$^{II}MnSO_4 \cdot H_2O + (Ni/Cu\text{-}SO_4 \cdot H_2O) + {}^{VII}KMnO_4$ —Hydrothermal synthesis, 140° C, 12-120 h→ $^{IV}Ni\text{-}\alpha\text{-}MnO_2$ or $^{IV}Cu\text{-}\alpha\text{-}MnO_2$



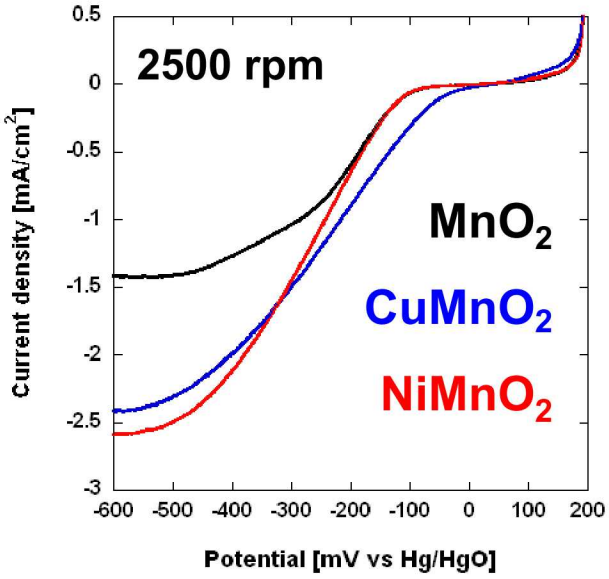




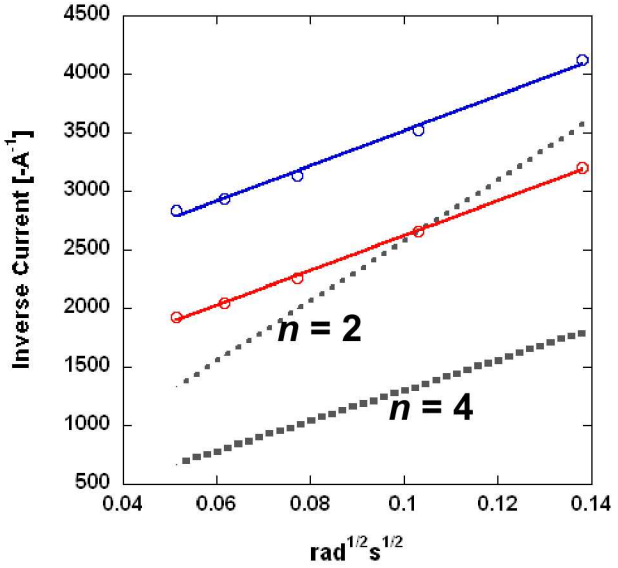
$Cu\text{-}MnO_2$



Ni- and Cu-α-MnO_2 Nanowires



- 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
  - $CuMnO_2$: 6.70 x 10^{-3} cm/s
  - $NiMnO_2$: 1.53 x 10^{-2} cm/s



Cu-α-MnO_2
n = 3.4

Ni-α-MnO_2
n = 3.5

MnO_2
n = 3.1

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

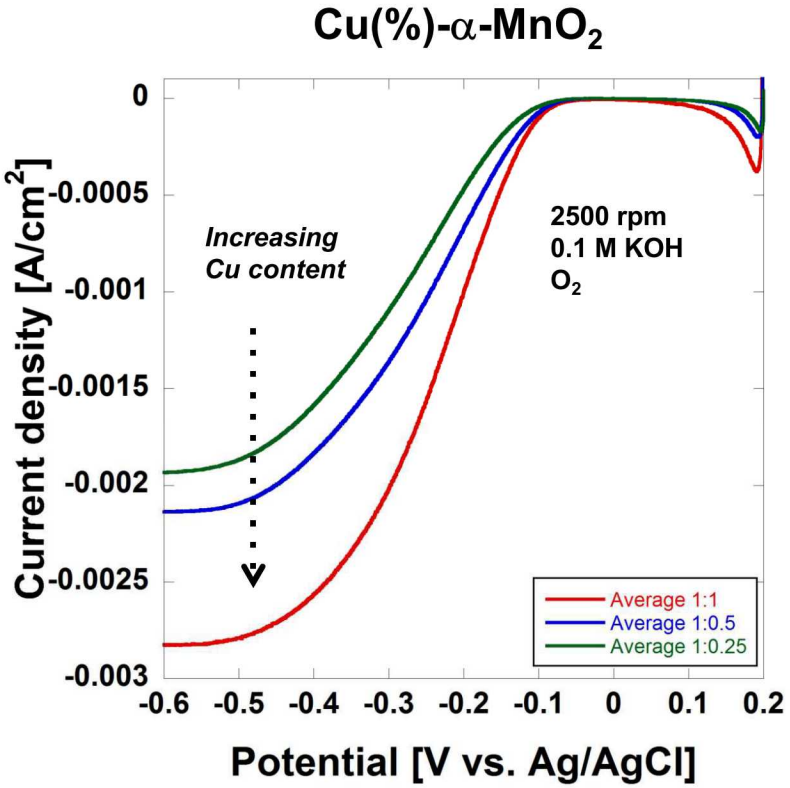
(ii) Indirect (peroxide) pathway:
$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$

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

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

What is role of metal ion (Cu)dopant ?

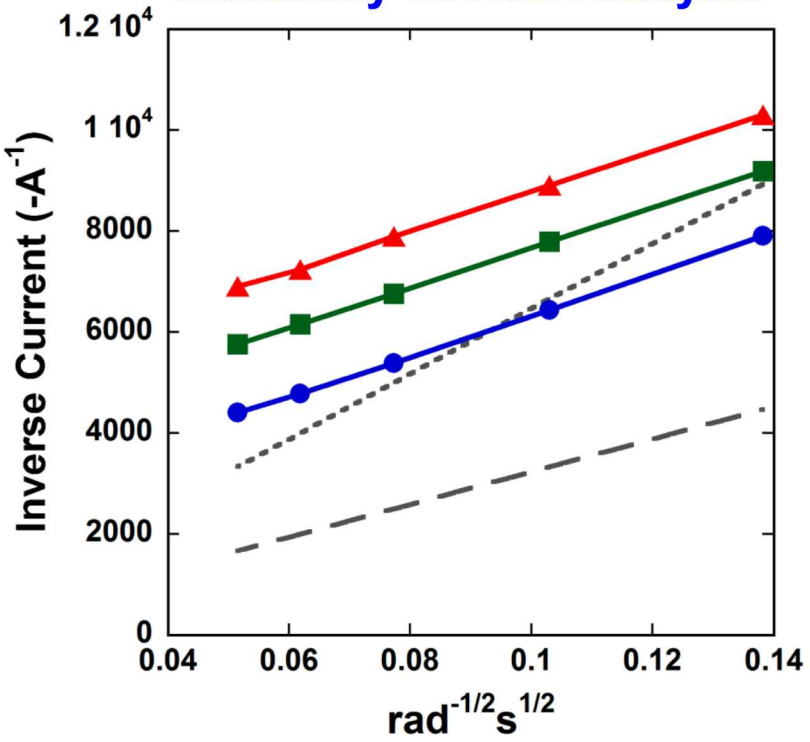
Series of Cu-α-MnO_2 NW electrocatalysts



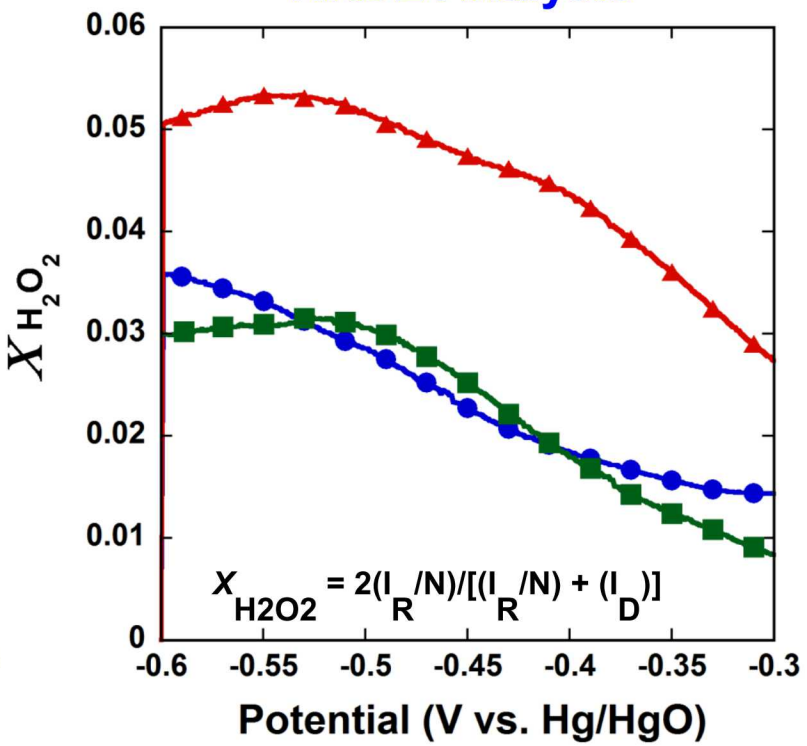
Ratio Mn:Cu	Onset (mV)	n (e-)	Current density (mA/cm^2)	Half-wave (mV)	Rate (cm/s)	Rct (Ω)
1:0.25	-107.7	3.28	-1.93	-312	0.0078	5744
1:0.5	-97.3	3.31	-2.14	-303	0.0097	4380
1:1	-100.3	3.20	-2.82	-292	0.019	3430

Cu-α-MnO_2 Nanowires

Koutecky-Levich Analysis



RRDE Analysis



Kinetic Rate Constants

Cu-1.3: 7.8 x 10^{-3} cm s^{-1}

Cu-2.4: 9.7 x 10^{-3} cm s^{-1}

Cu-2.9: 1.9 x 10^{-2} cm s^{-1}

***n* values ~ 3.2-3.3**

***n* values**

All < 6% implies

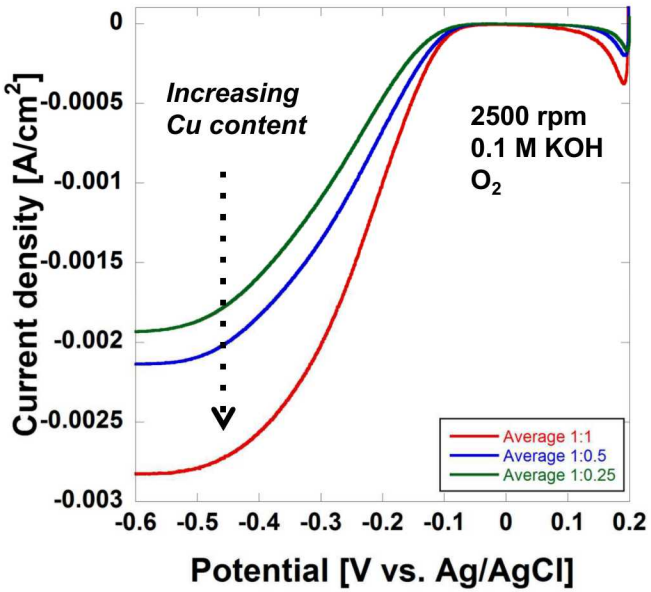
***n* values ≥ 3.8**

Apparent 4 e^- process

What is role of metal ion (Cu)dopant ?

Series of Cu-α-MnO_2 NW electrocatalysts

Cu(%)-α-MnO_2



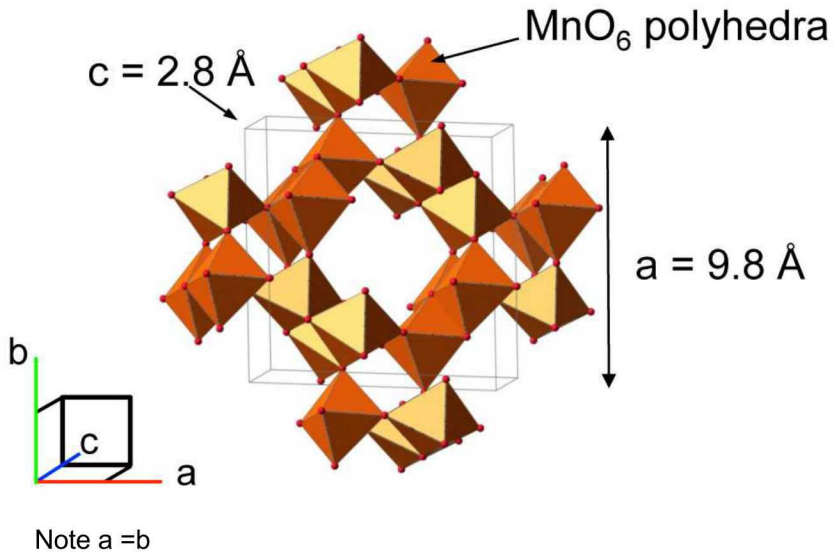
Geometric vs. Electronic Effects ?

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	1.3	59.1	9.4	0.14
1:0.5	2.39	80.7	9.2	0.19
1:1	2.92	83.8	11.6	0.24

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

Structural Effects of Cu ?

Tetragonal (*I*4/m) Structure



Analysis of XRD

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

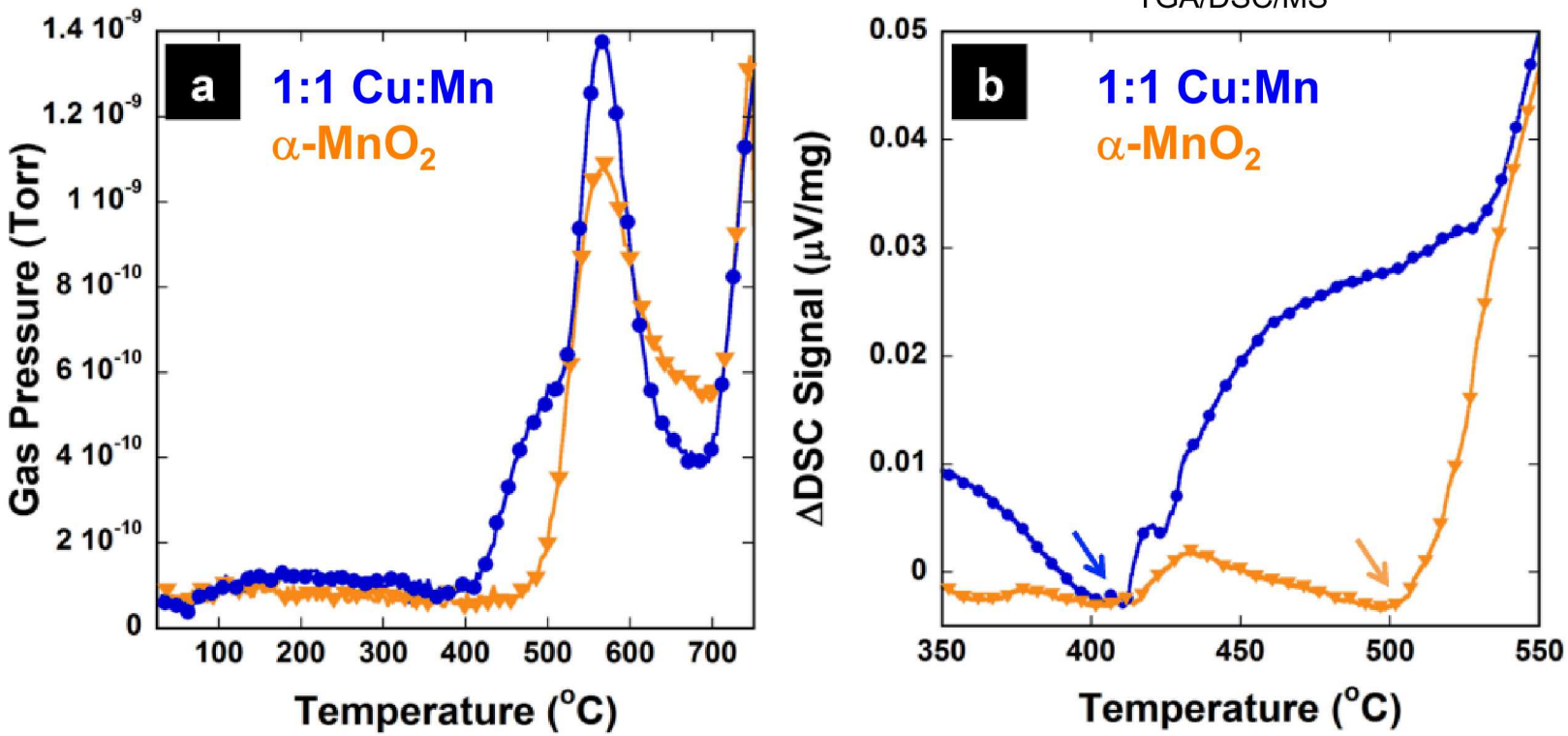
Lattice expands, becomes more covalent and there are more (catalytic) edge sites

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.

Structural Effects of Cu ?

O_2 evolution upon heating

TGA/DSC/MS



- O_2 release observed ~ 90 °C earlier for Cu-α-MnO_2 indicates a portion of more weakly bound O_2

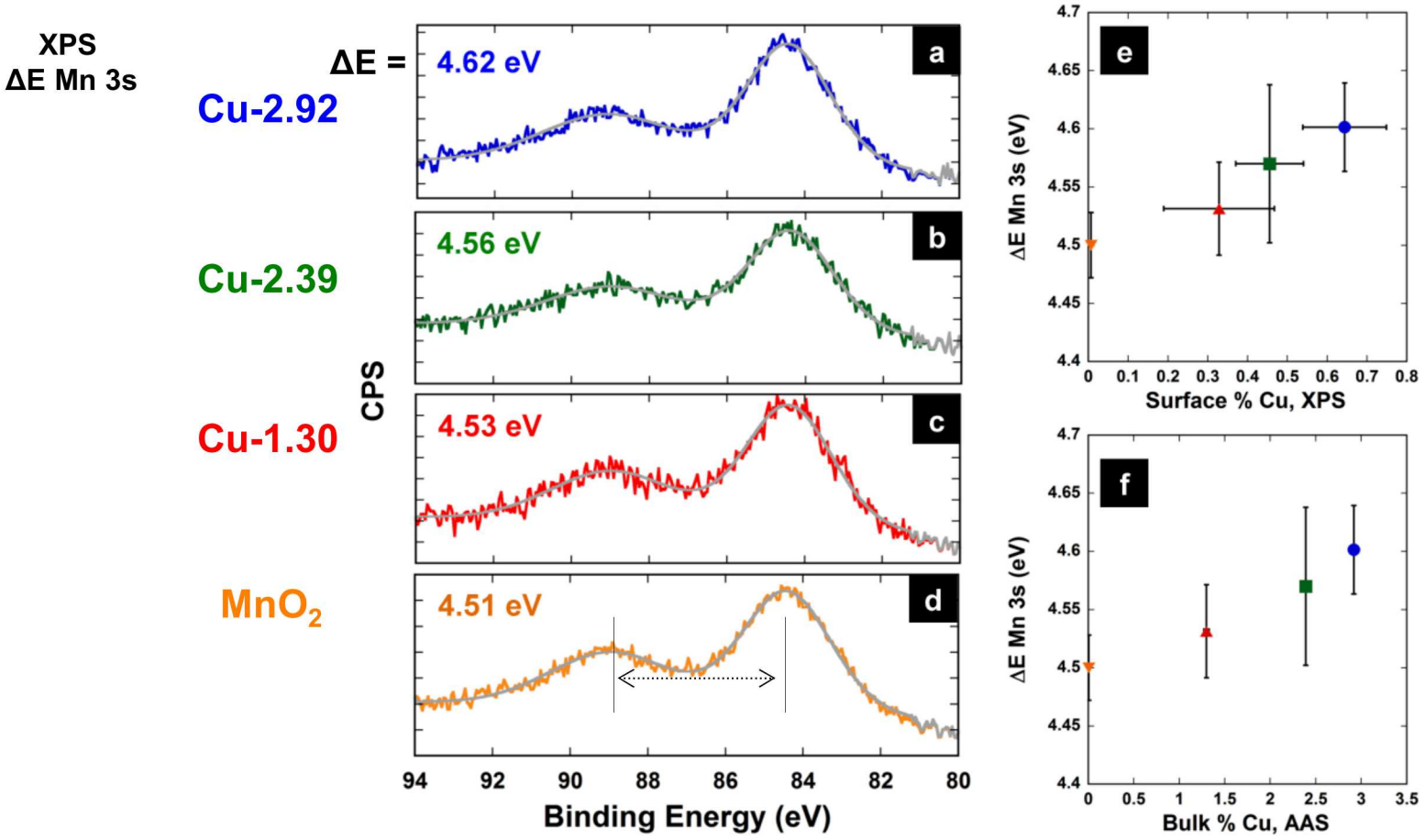
Higher number of crystalline edge defects

- 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

More loosely bound O

Electronic Effects of Cu ?

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

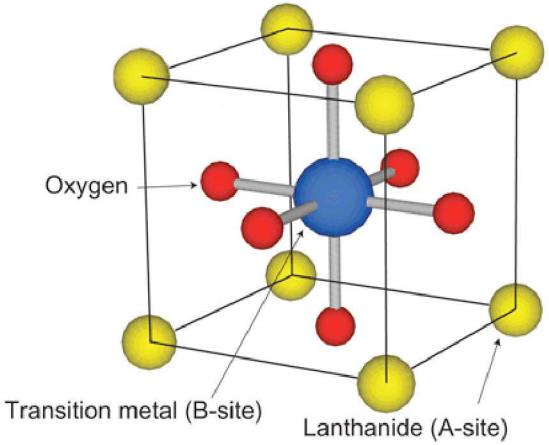


- **Increasing copper leads to increasing surface Mn^{3+}**
- **Less Cu observed at surface versus bulk**

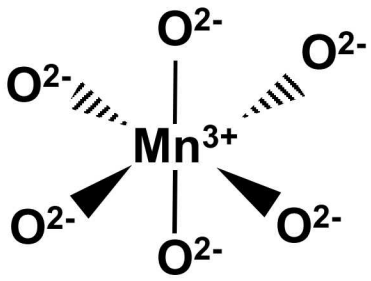
Electron Configuration of Mn^{3+}

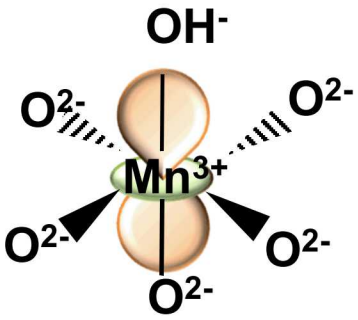
d^4* and *d^7 are most active metal ions in O_h B-site of perovskite oxide catalysts
➔ relevant to our Mn^{3+} here.

d4 = High Spin in Octahedral coordination



Mn^{3+}

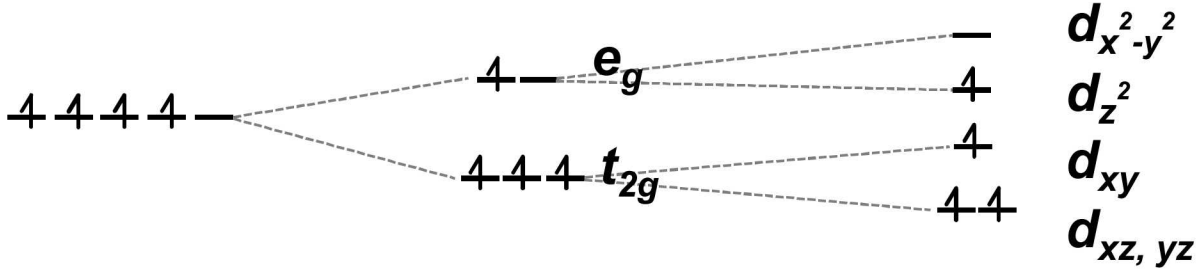


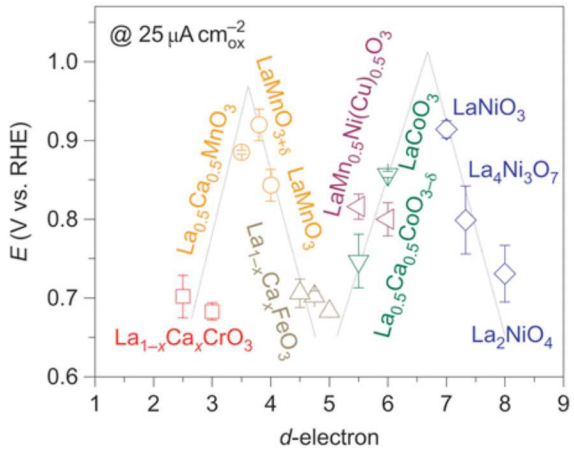


d^4 : *d*-manifold

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

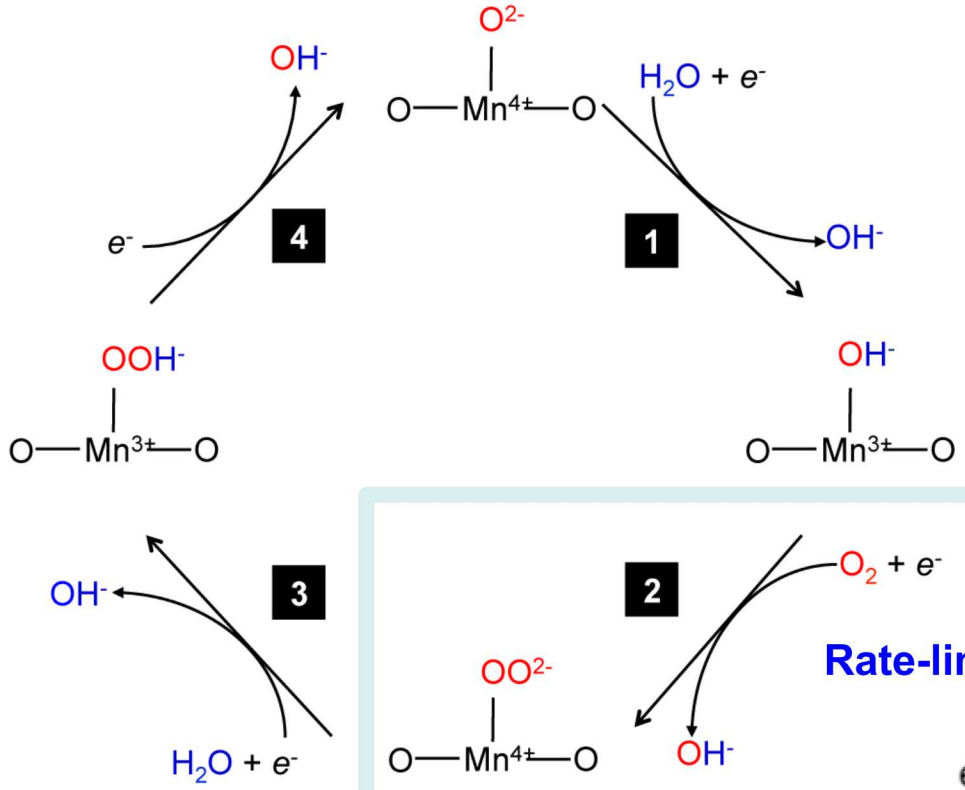
d-manifold in tetragonal symmetry *(high spin)*





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

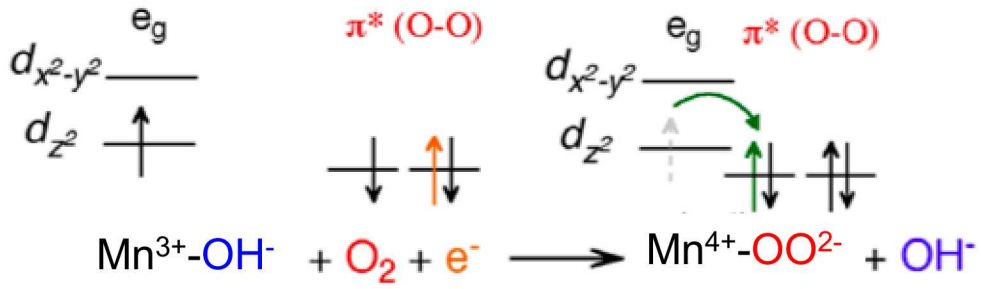
The role of Mn^{3+}/Mn^{4+} Couple



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

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

Rate-limiting step



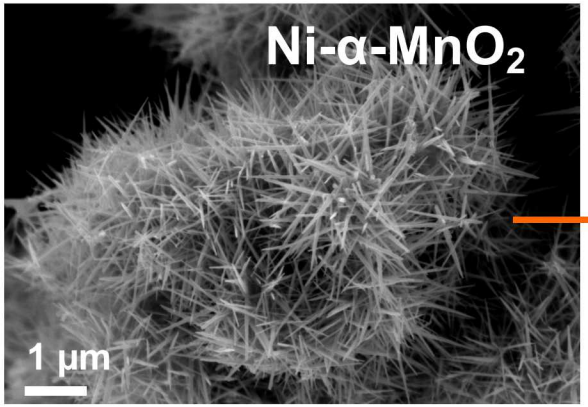
*Adapted from: J. Suntivich *et al.* Nature Chemistry **2011** *3*, 546-550.

Conductivity effects of M^{n+} ?

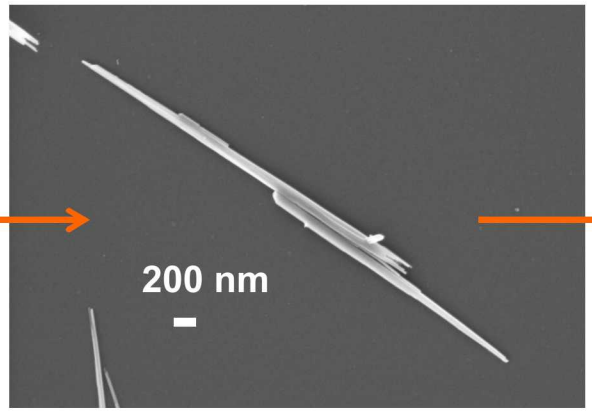
Charge transfer resistance values suggest increased conductivity

Copper	***Nickel***
Cu-1.3: 5744 ± 1925 Ω	****Ni-2.0**: 7919 Ω
Cu-2.4: 4380 ± 796 Ω	**Ni-4.4**: 4840 Ω
Cu-2.9: 3430 ± 1136 Ω	

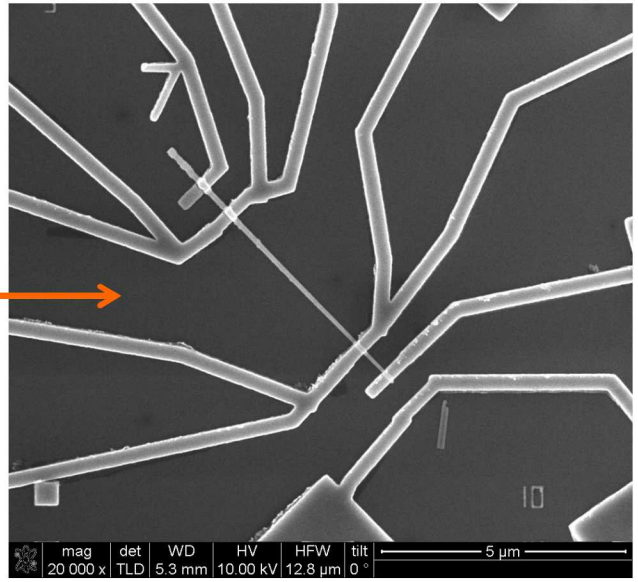
As Prepared



Dispersed NWs



Electrical Contacts

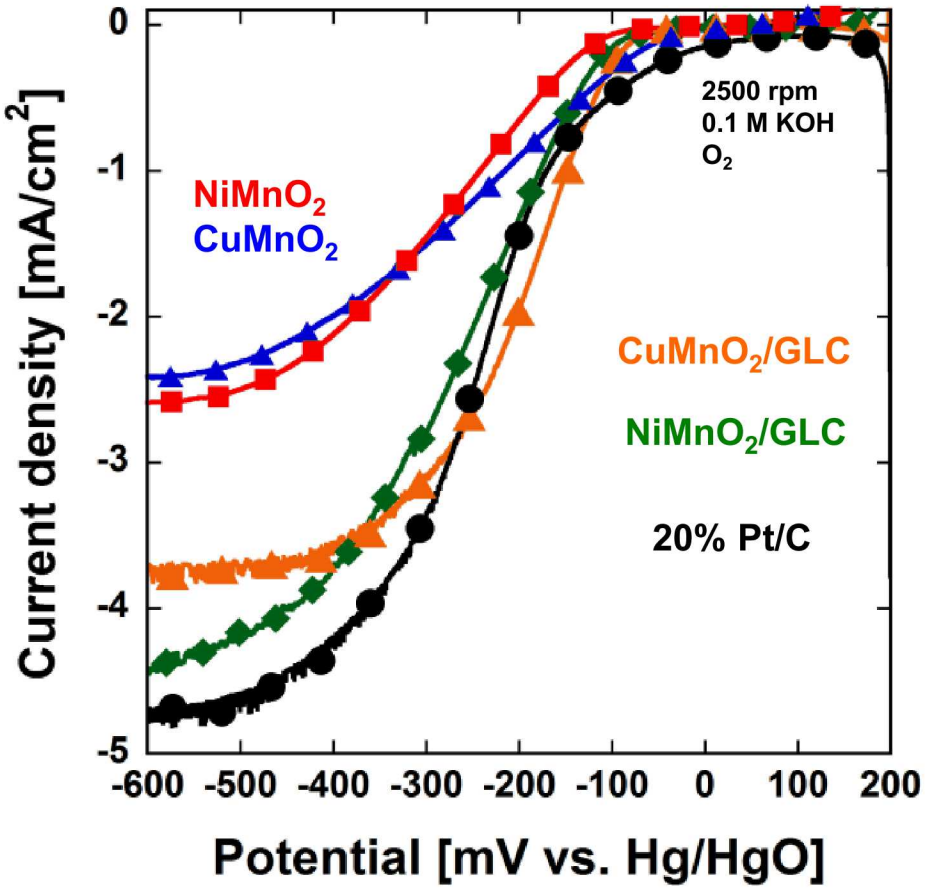


CY15 CINT User Proposal:
w/Brian Swartzentruber and Collin Delker

Temperature dependent 4-point conductivity measurements

** as determined from EDS

Graphene Ni- and Cu-α-MnO_2 Blends



Cu-MnO_2: 78% of current obtained by Pt/C, *n* = 3.9

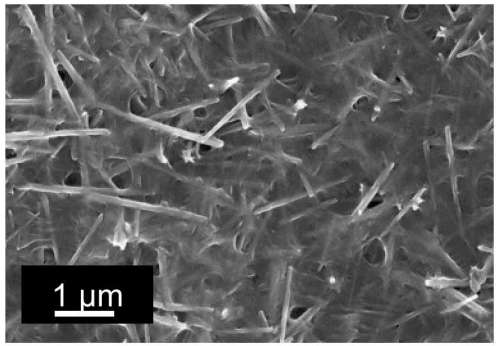
Ni-MnO_2: 91% of current obtained by Pt/C, rate = 3.50 x 10^{-2} cm/s

Pt/C rate = 3.24 x 10^{-2} cm/s

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

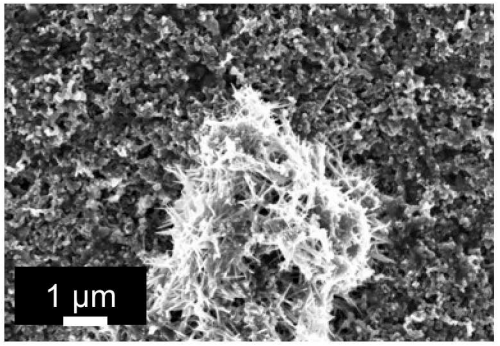
For GLC (Prof. JM Tour@ Rice) synthesis see:
Z. Jin *et al. J. Am. Chem. Soc.* **2010**, 132, 15246–15251.

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

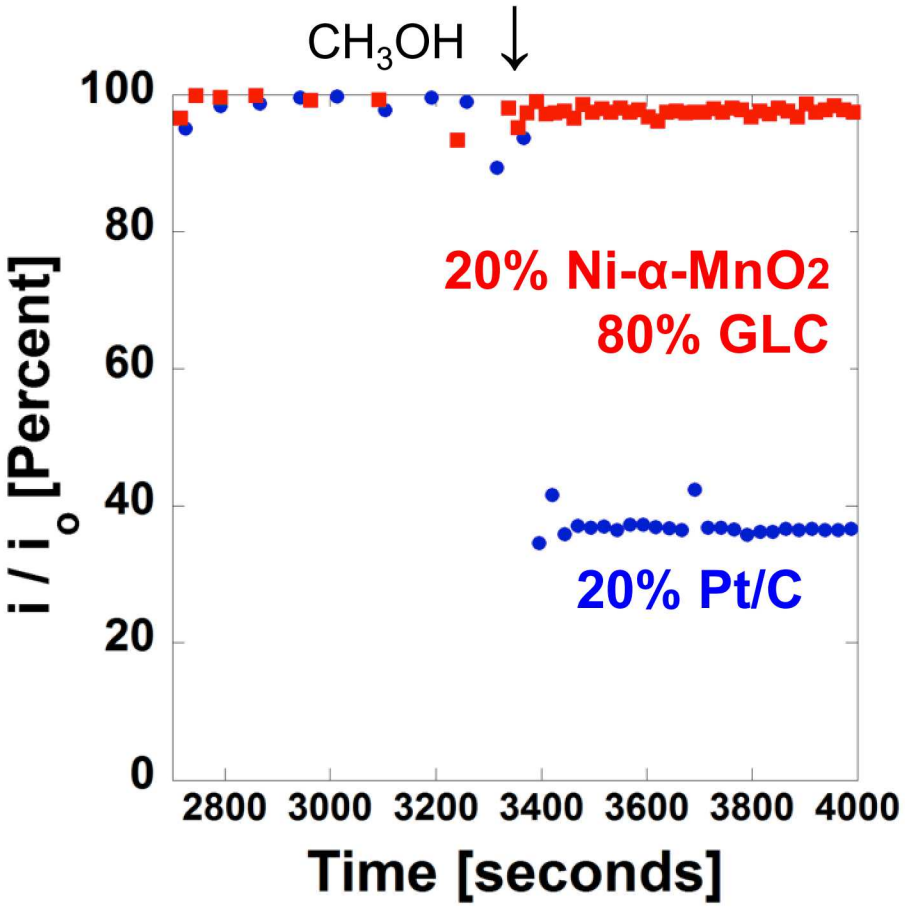
Cu-α-MnO_2 NWs / Vulcan XC-72/ Nafion



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

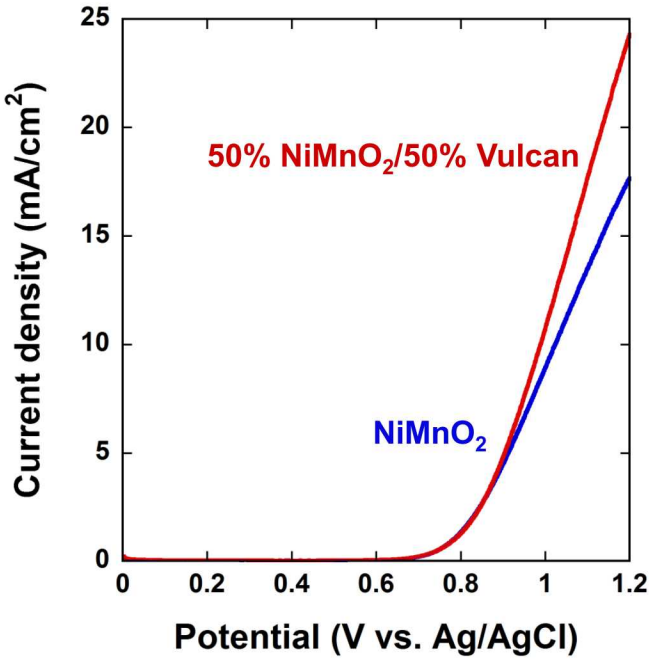
Electrocatalytic Selectivity

Chronoamperometric Percent Response



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

Bifunctional Electrodes for O_2



α-$NiMnO_2$
(Not Optimized)

Sample	E@ ½ wave	E@ 10 mA cm^{-2}	Δ(E_{OER}-E_{ORR})
20% Ir/C	0.57	1.85	1.28
20% Pt/C	0.75	2.13	1.38
20% Ir/C[1]	0.69	1.61	0.92
20% Pt/C[1]	0.86	2.02	1.16
Mn_2O_3[1]	0.75	1.77	1.02
α-MnO_2-SF[2]	0.78	1.72	0.94
Ni/α-MnO2-SF[2]	0.76	1.74	0.98
MnO_x[3]	0.7	1.8	1.1
Ni-α-MnO_2 1:0.5	0.71	1.99	1.15
Ni-α-MnO_2/Vulcan	0.76	1.91	1.32

Manganese Oxide, Jaramillo, *J. Am. Chem. Soc.* **2010**, *132*, 13612–13614.
Bifunctional MnO_2, Meng, *J. Am. Chem. Soc.* **2014**, *136*, 11452
MnOx bifunctional catalyst, Su, *PCCP*, **2012**, *14*, 14010

Ni- and Cu-α-MnO_2 Electrocatalysts

Sandia National Laboratories

Summary

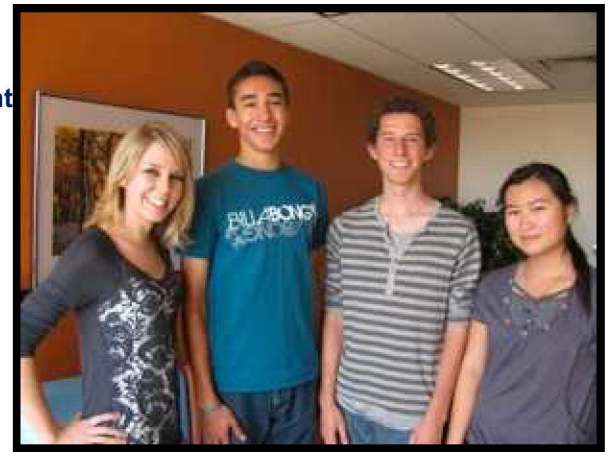
- The -dopant species, when added to α-MnO_2, improves the electrochemical performance (half wave, current, kinetics) as a catalyst for ORR in alkaline media.
- Ni/Cu is "inside the wire"
- Ni and Cu lead to higher Mn^{3+}/Mn^{4+} ratio *at the surface*
- Mn^{3+}/Mn^{4+} plays role in mediating ORR
- 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 for Cu-α-MnO_2 is poor (?) but Ni-α-MnO_2 is promising

- Conductivity ?
  - Single wire conductivity measurements ongoing

Acknowledgements

- Sandia National Laboratories (LDRD), CINT, Department of Energy
- SNL STAR Program
- Lambert Group

Pictured Left to Right:
Danae Davis
UNM Graduate Student
Julian Vigil
Sandia High School
Landon Davis
UNM Undergraduate
Kimberly Wong
UNM Undergraduate



Alexis Thuli
High School Student

Suzanne White
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Madalyn Hungate
High School Student

- Additional SNL/CINT collaborators:

Collin Delker, Steven Limmer,
Mark Rodriguez, Mike Brumbach,
Eric Coker, Paul Kotula

- Rice University collaborators (Graphene materials):

Professor James M. Tour's Group

Thank you

Literature Pathways

Coexisting Reaction Schemes

Sandia National Laboratories

Direct four electron pathway:

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

$MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^-$

$2\ MnOOH + O_2 \leftrightarrow 2\ (MnOOH\cdots O)$

Oxygen adsorbs onto two neighboring sites.

$(MnOOH\cdots O) + e^- \leftrightarrow MnO_2 + OH^-$

Indirect (peroxide) pathway:

$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^-$

$MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^-$

$MnOOH + O_2 \leftrightarrow MnOOH\cdots O_2$

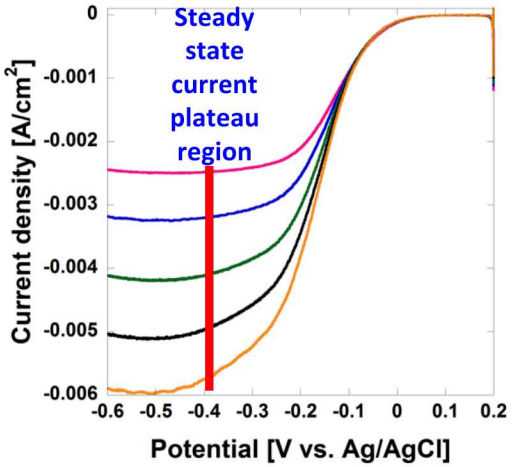
Oxygen is adsorbed onto a single Mn site.

$MnOOH\cdots O_2 + e^- \leftrightarrow MnO_2 + HO_2^-$

Adapted from: F. Cheng *et al. Chem. Mater.* **2010**, *22 (3)*, 898-905.

Analyzing the Catalytic Performance

Linear Scanning Voltammogram (LSV)

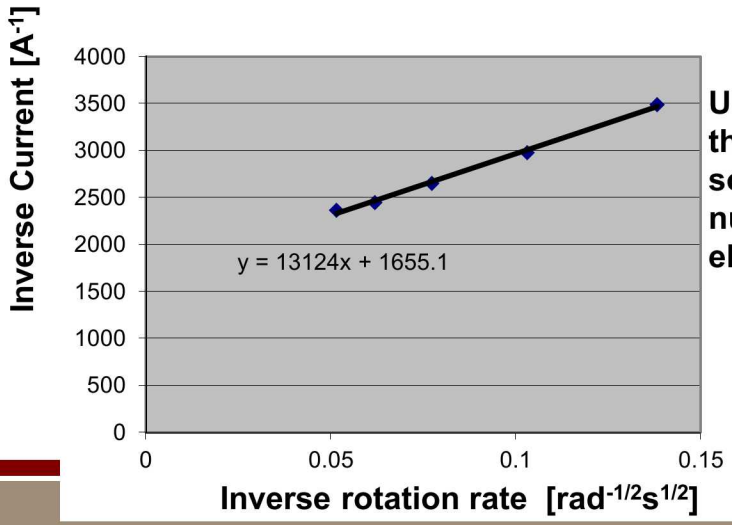


Using current density values at a constant potential for each rotation speed, construct a Koutecky-Levich plot.

Koutecky-Levich Equation

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

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



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

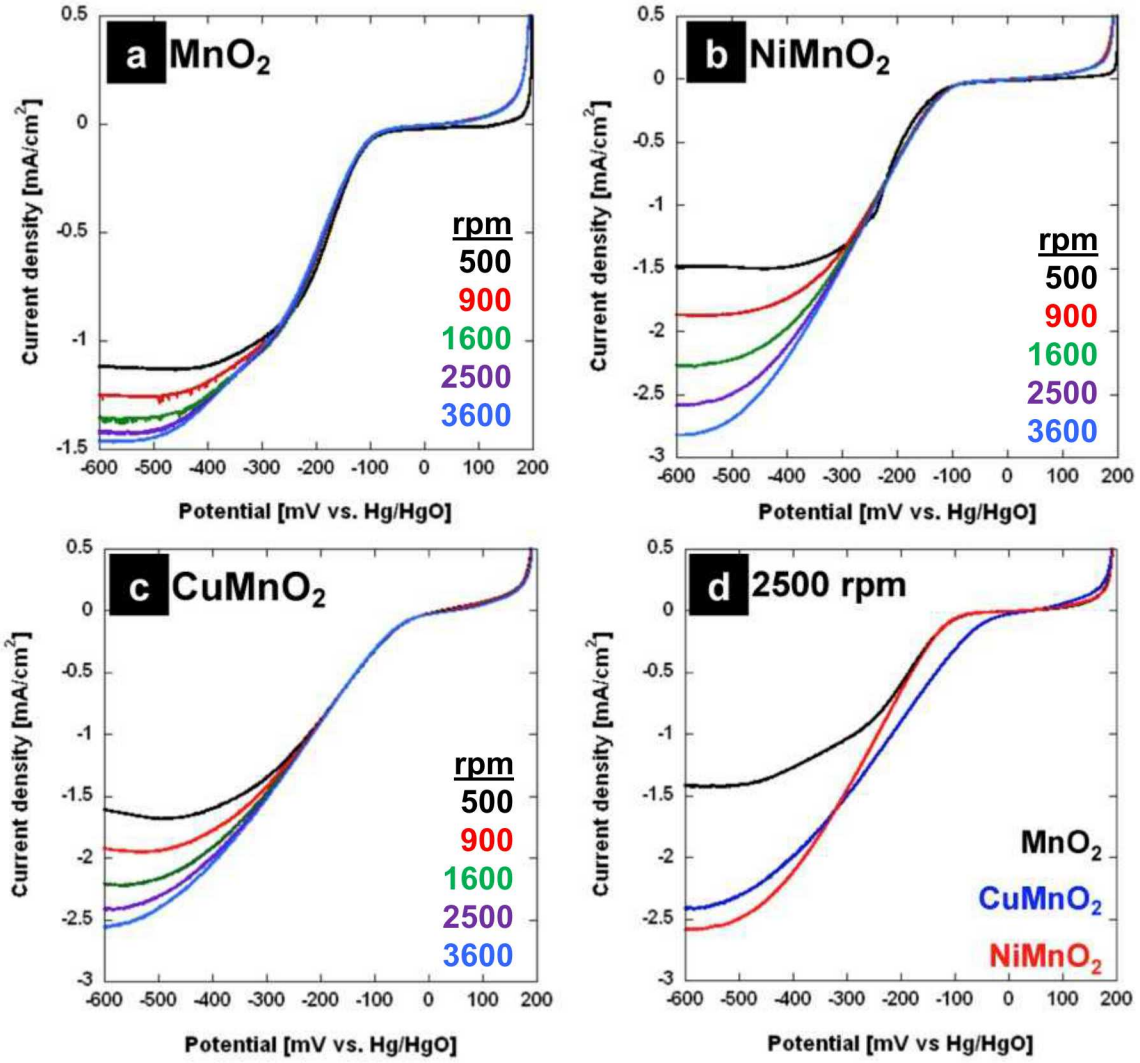
C° = saturated concentration of O_2 in 0.1M KOH

D_{O2}= diffusion coefficient of oxygen

ν = kinetic viscosity of electrolyte solution

ω = rotation rate

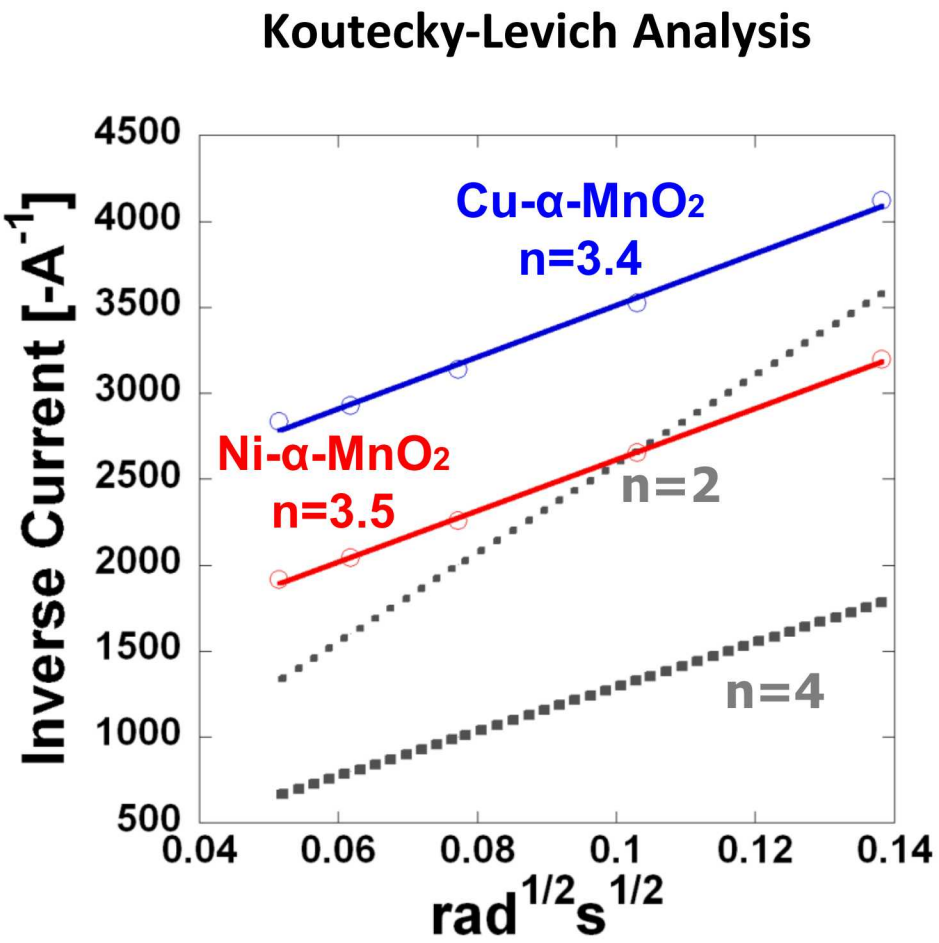
Comparison of α-MnO_2 NW Catalysts



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.

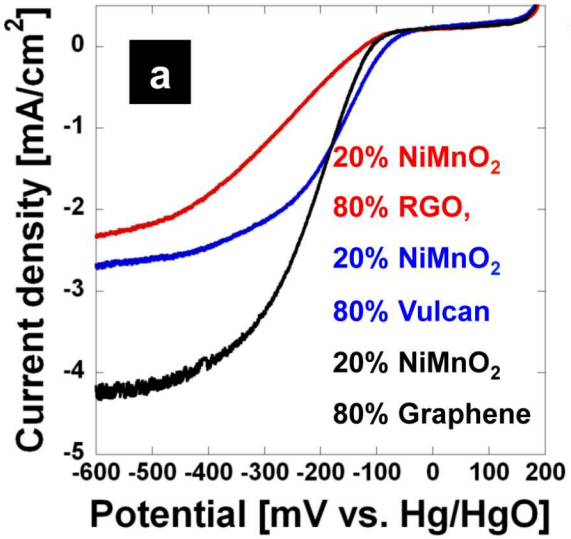
Comparison of α-MnO_2 NW Catalysts

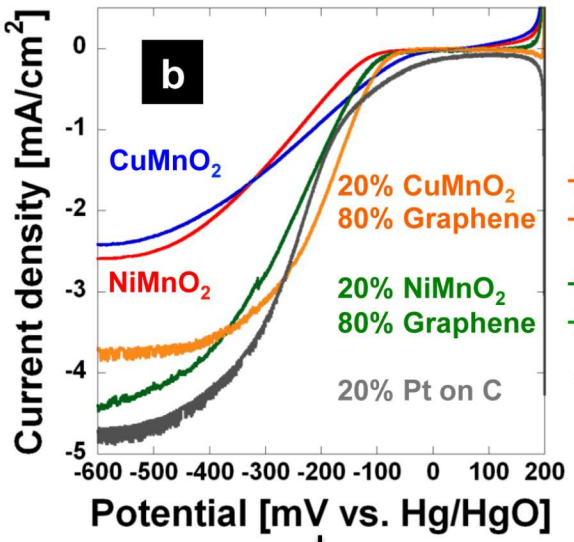


- Published n-value for MnO_2 = 3.1; our data consistent with this value (Cheng et. al., Chem. Mater. 2010, 22, 898-905)
- ORR n-values are improved with doping.
- Peroxide production is < 5% for all catalysts; this corresponds to a fast peroxide disproportionation reaction.
- Reaction rates also improved:
  - 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

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

Ni- and Cu-α-MnO_2 Nanowires



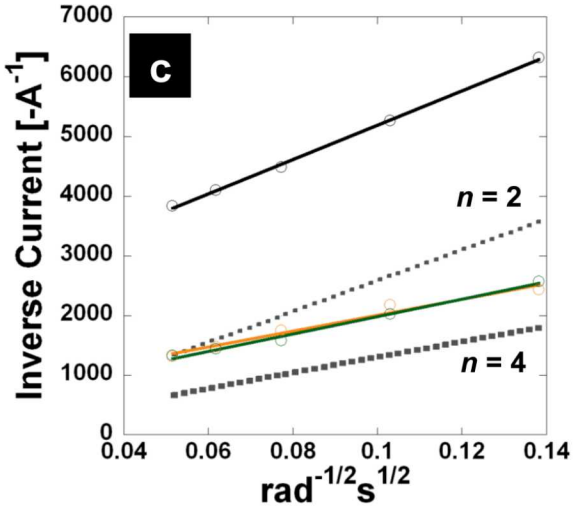


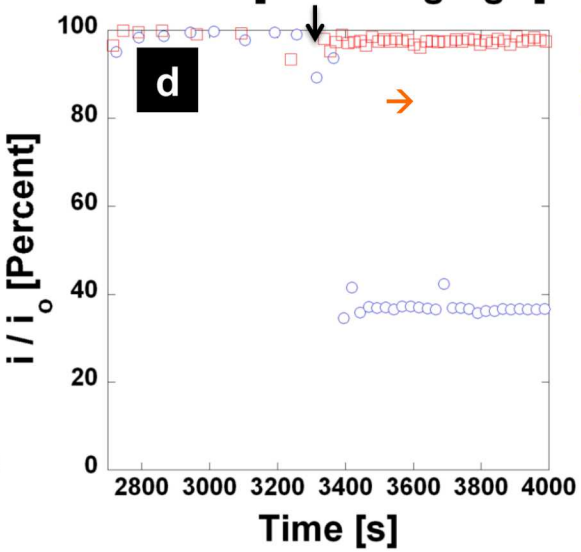
Graphene less conductive than Vulcan

→ 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





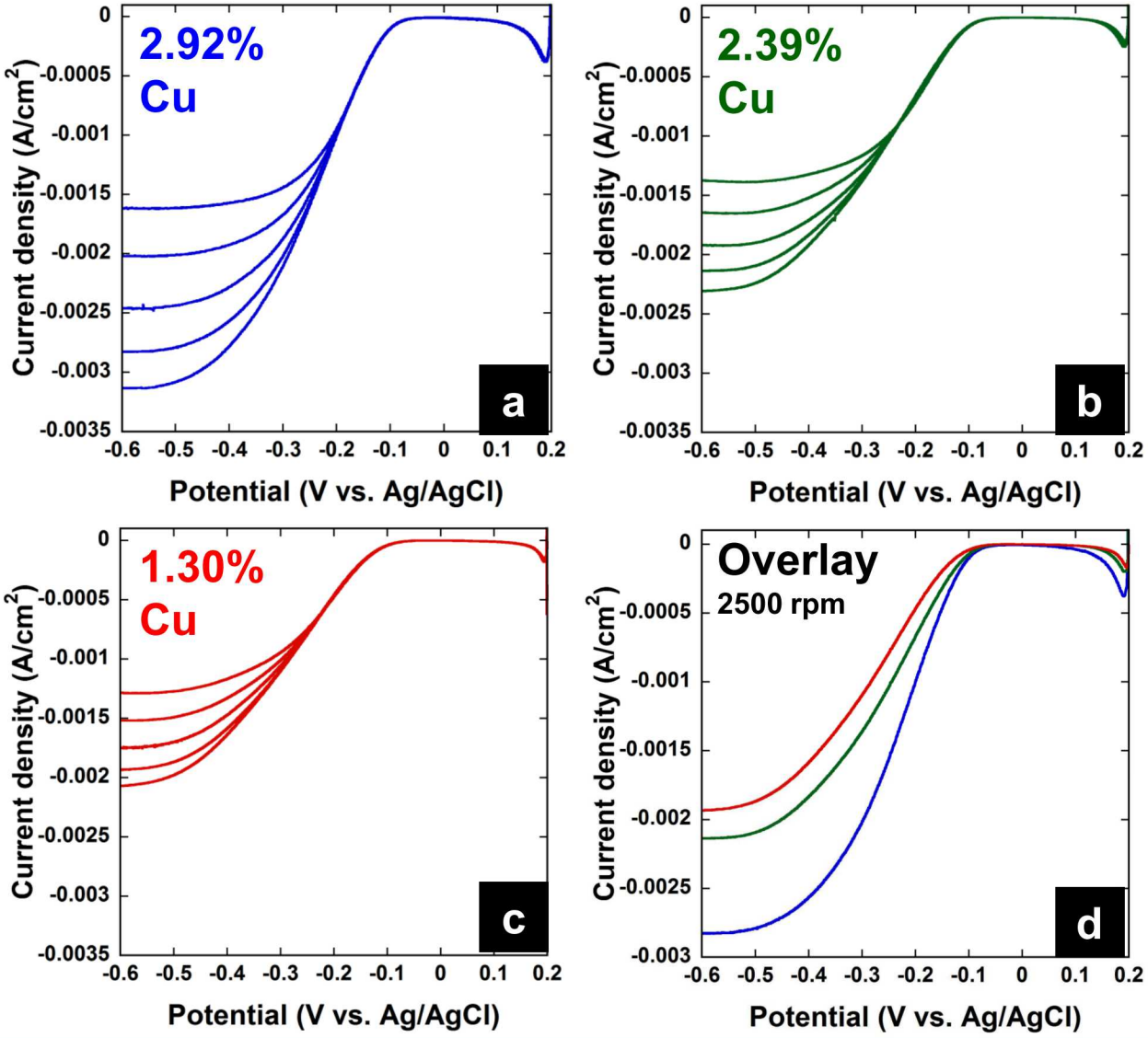
MeOH Crossover Experiment *via* chronoamperometry

- **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 ?

Electrochemical Analysis

Rotating Disk Electrode (RDE) Studies



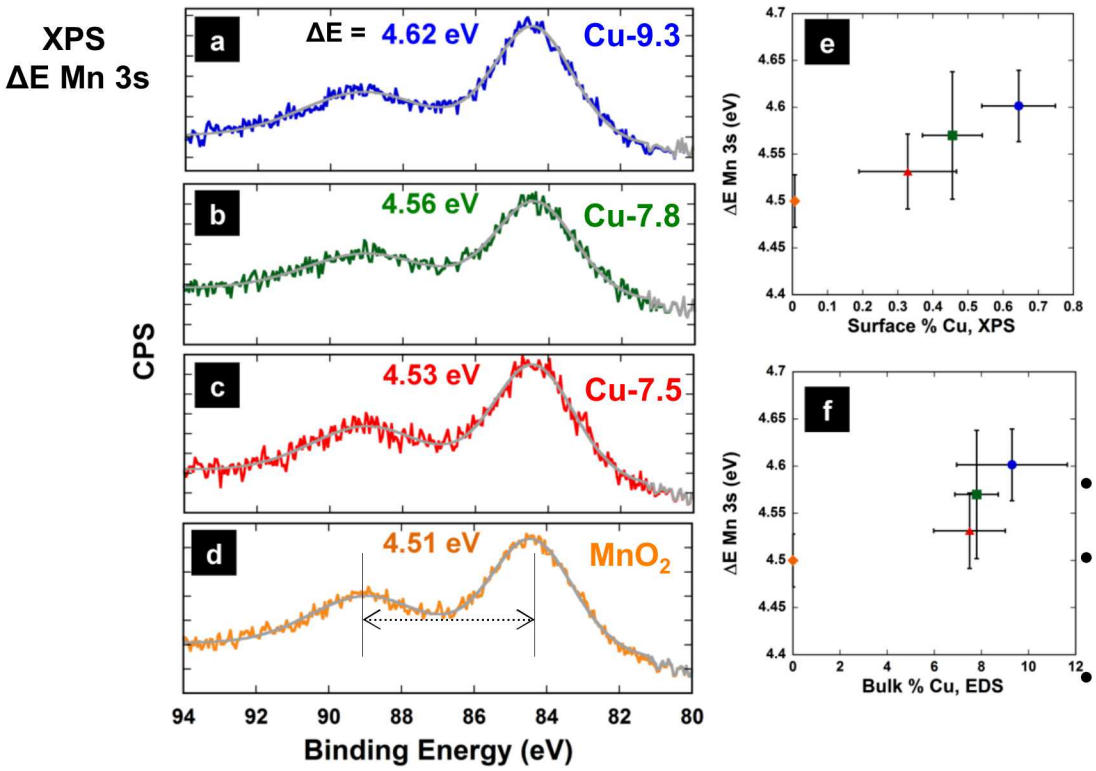
Catalytic Role of Mn^{3+}/Mn^{4+}

(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**

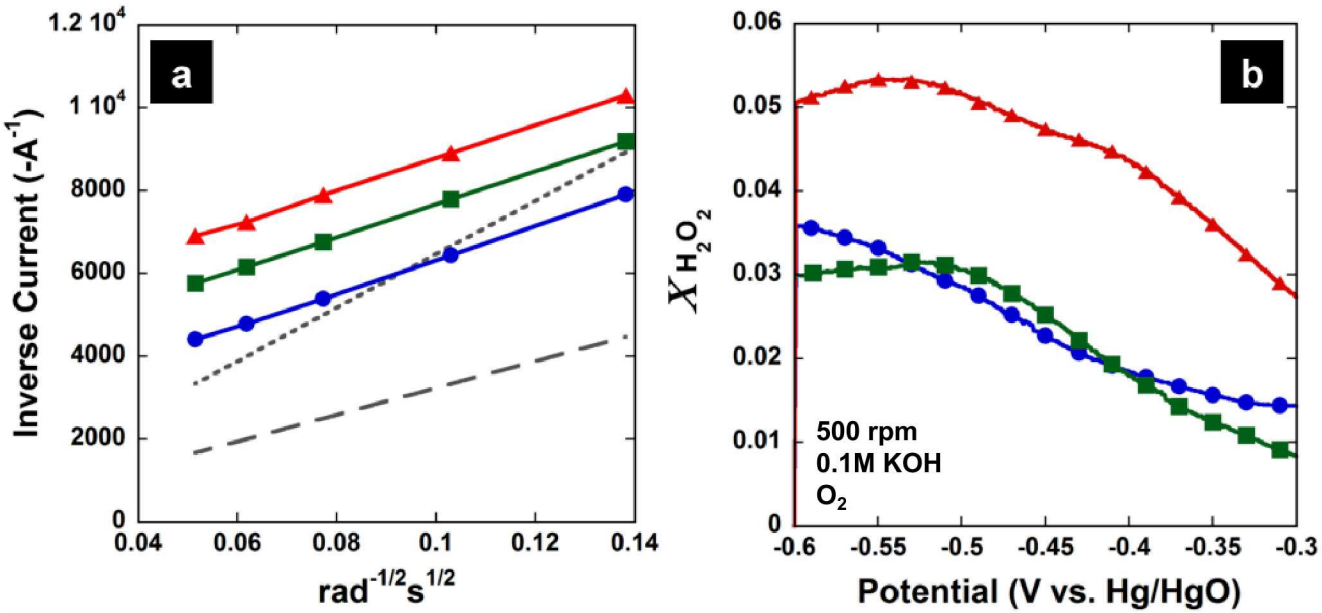
$$O_2(g) + 2H_2O + 4e^- = 4OH^-(aq) \quad +0.401 \text{ vs SHE}$$

What is role of metal ion (Cu)dopant ?

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



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

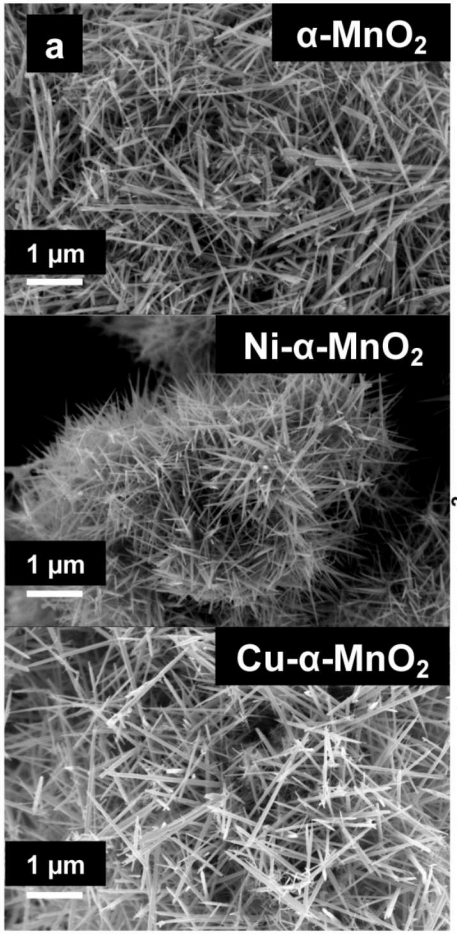
$$\%X_{H2O2} = X_{H2O2} \times 100\%$$

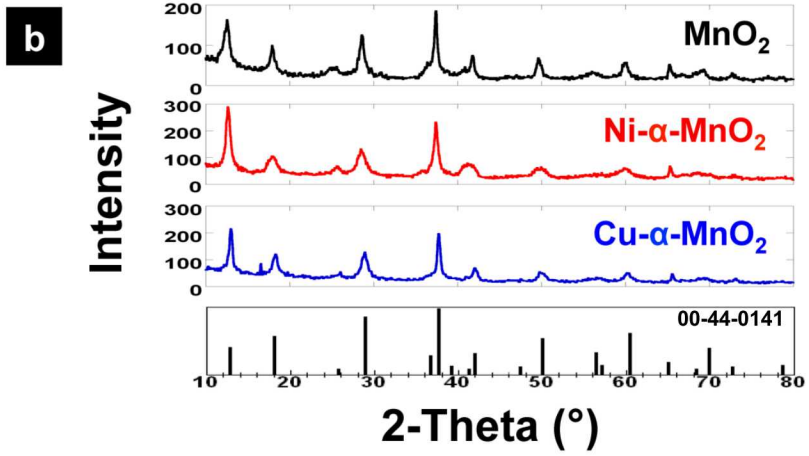
I_R is the ring current,
N is the collection efficiency
I_D is the disk current

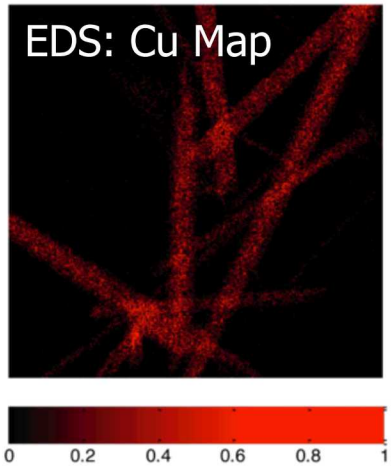
Data suggests that up to 20% peroxide (RDE: n ~ 3.2) could be produced but majority of that undergoes catalytic decomposition prior to disassociation from the catalyst (RRDE: n~ 3.8).

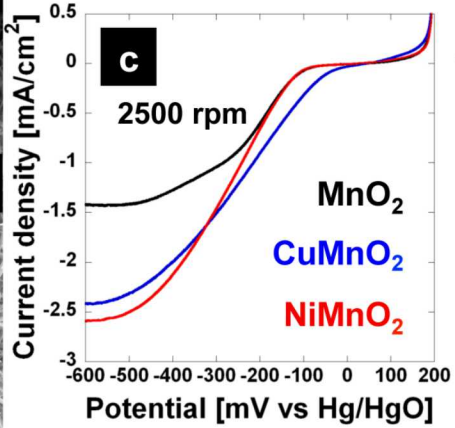
Ni- and Cu-α-MnO_2 Nanowires

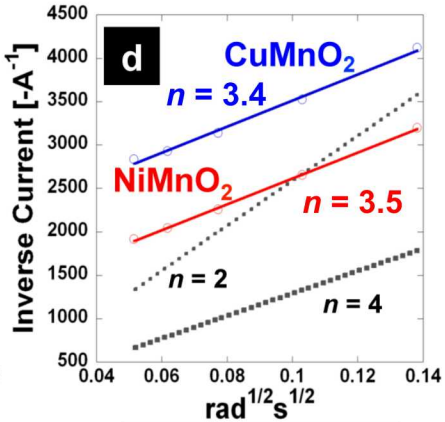
$^{II}MnSO_4 \cdot H_2O + (Ni/Cu\text{-}SO_4 \cdot H_2O) + {}^{VII}KMnO_4$ —Hydrothermal synthesis, 140° C, 12-120 h→ $^{IV}Ni\text{-}\alpha\text{-}MnO_2$ or $^{IV}Cu\text{-}\alpha\text{-}MnO_2$



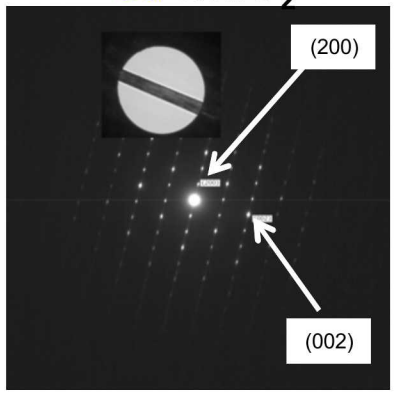








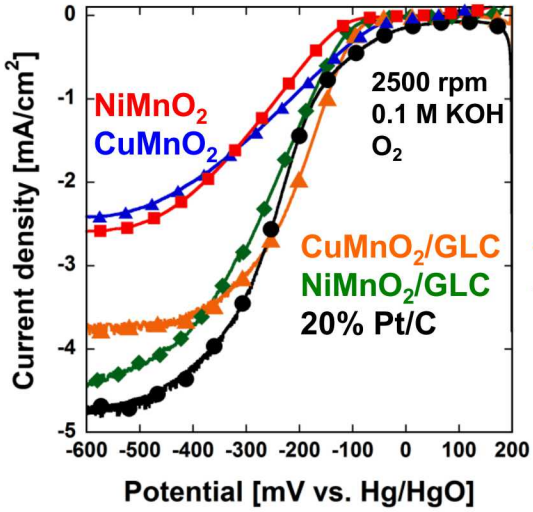
α-MnO_2: n = 3.1



For highly active α-MnO_2 see: F. Cheng et al. *Chem. Mater.* **2010**, *22*, 898-905.

Highly active Graphene 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.

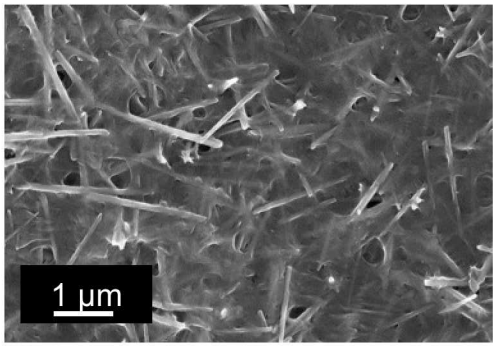
(i) Direct four electron pathway:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

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

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

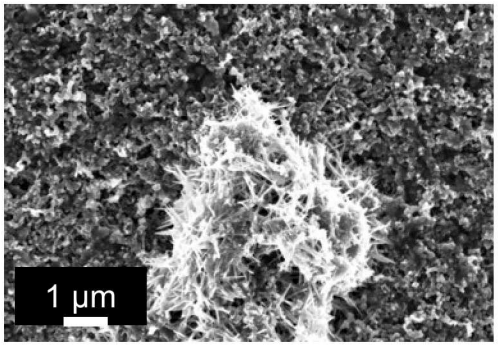
or (b) the catalytic peroxide decomposition:
$HO_2^- \rightarrow ½\ O_2 + OH^-$

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

Importance of O_2 Electrochemistry

A. 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. $VP + 6\ OH^- + 5/2\ O_2 \rightarrow VO_4^{3-} + PO_4^{3-} + 3\ H_2O$; $E^o = 1.47$ 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)*, 6835-6840

C. Alkaline Fuel Cells (Bi-directional beneficial)

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

Bi-directional cathode could allow for anode activation

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

D. 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

Water Electrolysis

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