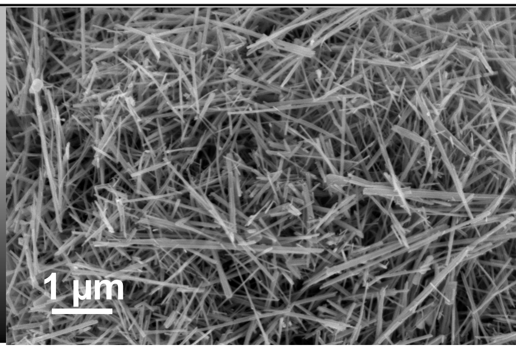
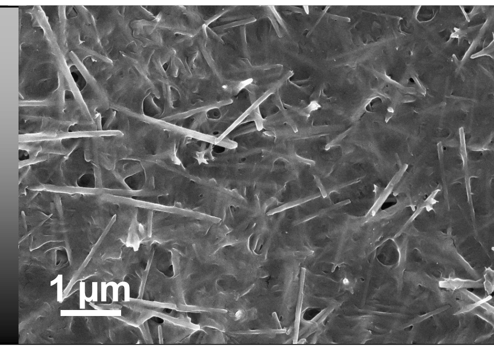
SAND2013-8682C

Exceptional service in the national interest

Sandia National Laboratories



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



Elucidating the Role of Cu-dopants in α-MnO_2 Catalysts for the Oxygen Reduction Reaction in Alkaline Media

Danae J. Davis, Julian A. Vigil, and Timothy N. Lambert

Rio Grande Symposium on Advanced Materials, October 2013

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. SAND NO. 2011-XXXXP

The Importance of Efficient Oxygen Reduction

- Devices such as fuel cells and metal-air batteries require electrocatalysts for the **oxygen reduction reaction (ORR)**, as this reaction plays a **critical role in the performance** of the system.

- ORR electrocatalysts are found at the air cathode of electrochemical systems.
  - Durable
  - Highly active
  - Economically viable to enable widespread utilization

The Pathways of ORR

(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:

$HO_2^- \rightarrow \frac{1}{2}\ O_2 + OH^-$

The Pathways of ORR

Sandia National Laboratories

(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

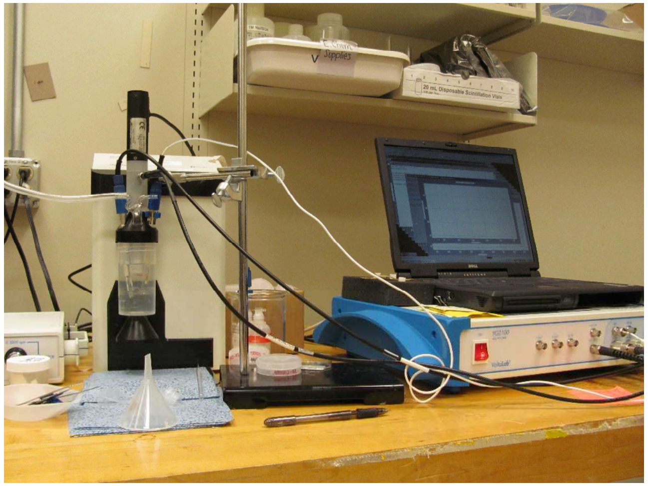
(a) the further reduction of peroxide:

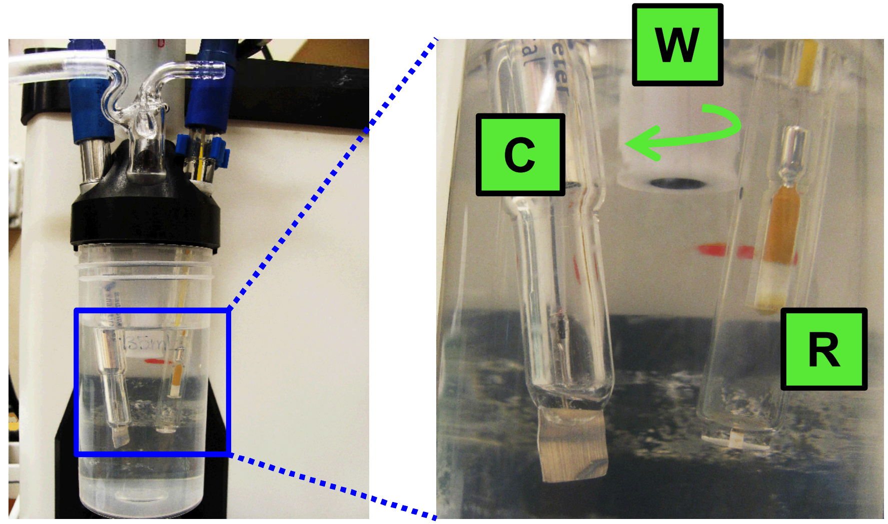
$$HO_2^- + H_2O + 2e^- \rightarrow 3\ OH^-$$

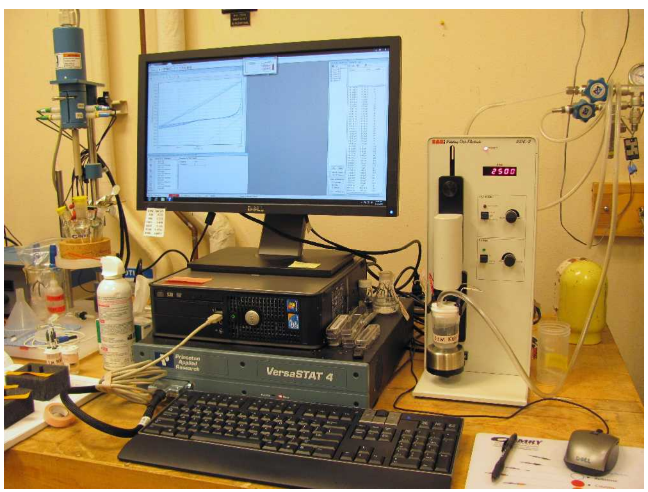
or (b) the catalytic peroxide decomposition:

$$HO_2^- \rightarrow \tfrac{1}{2}\ O_2 + OH^-$$

Analyzing the Catalytic Performance





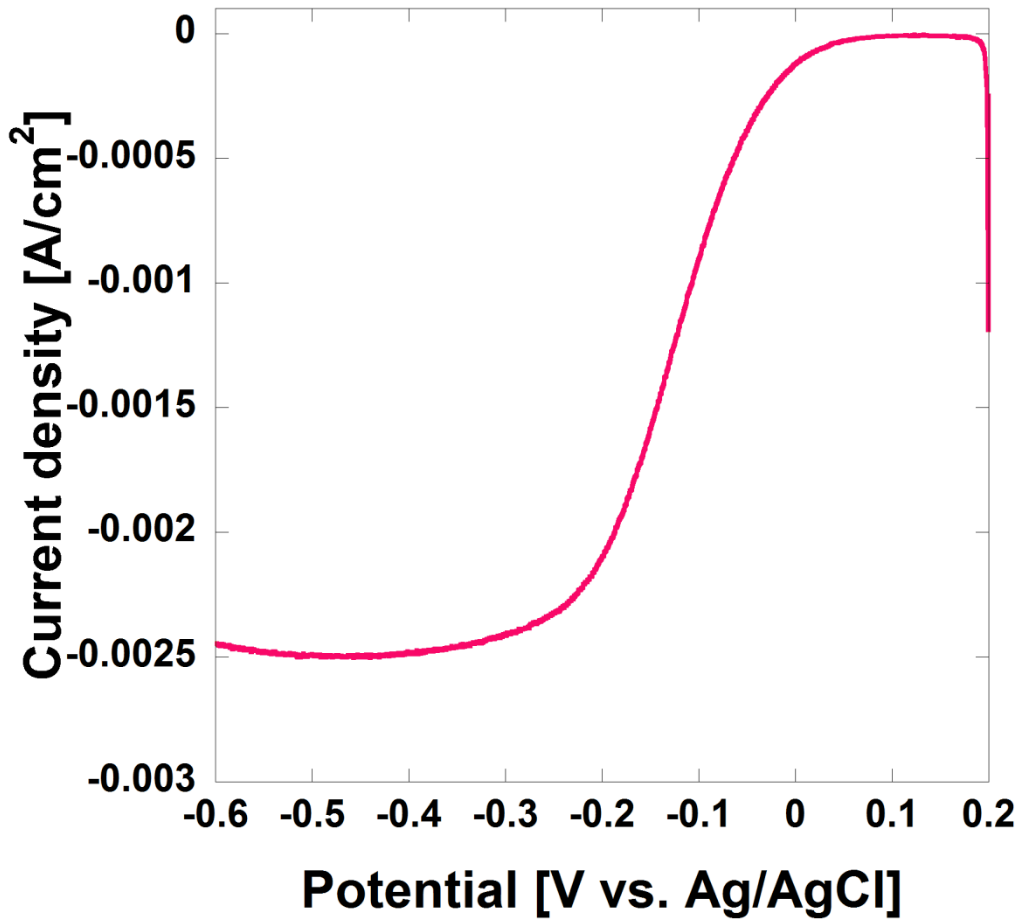


In the **three electrode cell**:

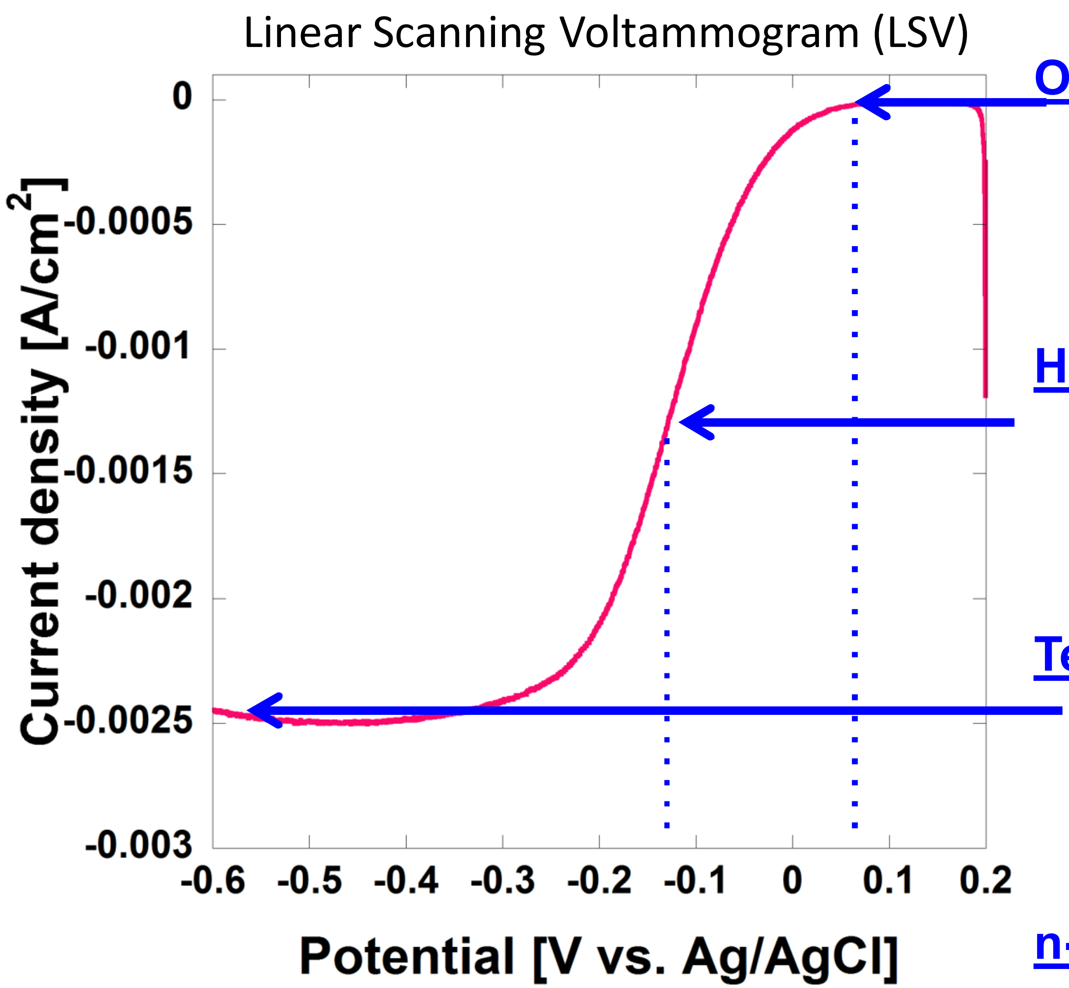
- **W**orking Electrode
  - Glassy carbon coated in catalyst ink: Nanowires + IPA + Nafion
  - Motor enables rotation at discrete rates: 500, 900, 1600, 2500,3600 rpm
- **C**ounter Electrode: Pt°
- **R**eference Electrode: Hg/HgO or Ag/AgCl
- **O_2** purged 0.1 KOH as electrolyte

Analyzing the Catalytic Performance

Linear Scanning Voltammogram (LSV)



Analyzing the Catalytic Performance



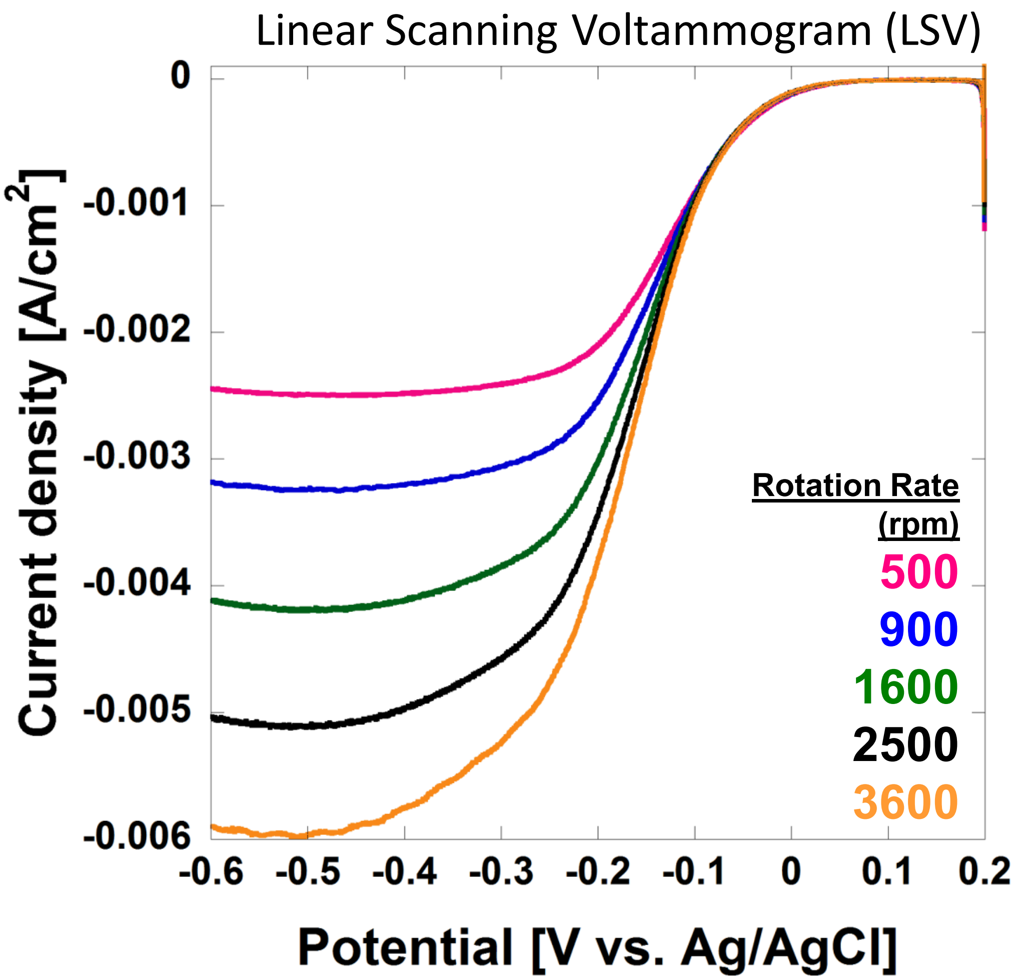
Onset Potential ($E_{i=0}$)

Half-Wave Potential ($E_{1/2}$)

Terminal Current Density

n-value (e^-)

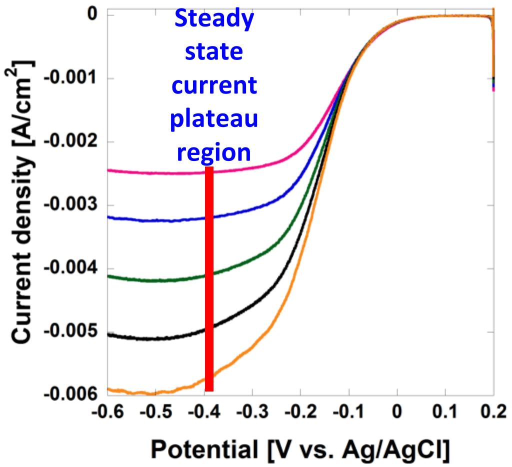
Analyzing the Catalytic Performance



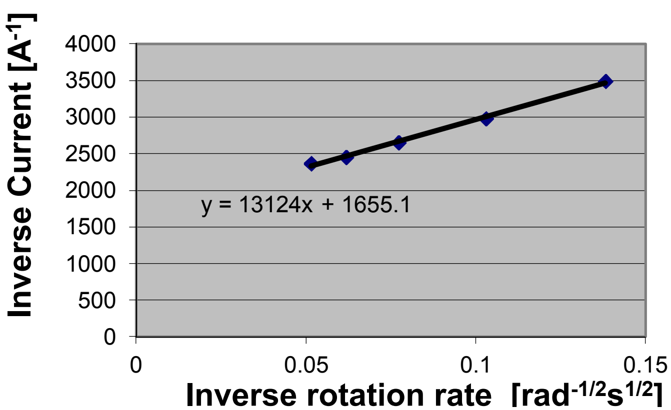
- By changing the rate at which the working electrode is rotating, the flux of O_2 to the catalyst surface can be changed.
- Electrode rotation permits the kinetically controlled process of ORR to be studied.

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.



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

Koutecky-Levich Equation

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

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

***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

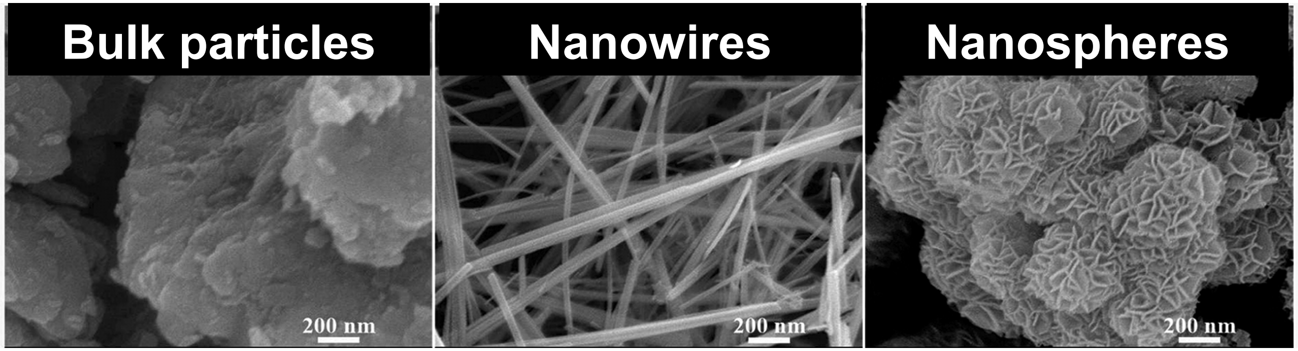
C° = saturated concentration of O_2 in 0.1M KOH

D_{O2}= diffusion coefficient of oxygen

v = kinetic viscosity of electrolyte solution

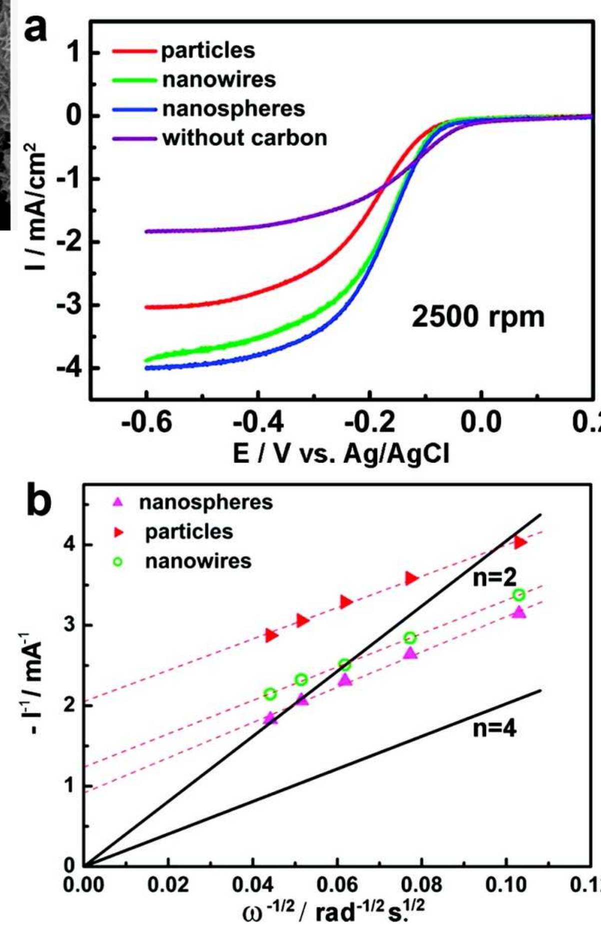
ω = rotation rate

Recent Studies



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

- Manganese oxides (MnO_x) as potential catalysts
  - Active and abundant
  - Low cost
- **α-MnO_2** > β-MnO_2 > ϒ-MnO_2
- **nanostructures** > microstructures
  - Porosity of nanostructures facilitates the diffusion, adsorption, and transport of O_2.
  - Higher surface area permits more active sites for interaction between O_2 catalyst.
- **nanowires (n=3.8)** > nanospheres (n=3.7)



F. Cheng, J. Chen *et al.*, *Chem. Mater.*, **2010**, *22* (3), pp 898-905.

Recent Studies

Coexisting Reaction Schemes

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

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

$MnOOH + O_2 \leftrightarrow MnOOH\cdots O_2$

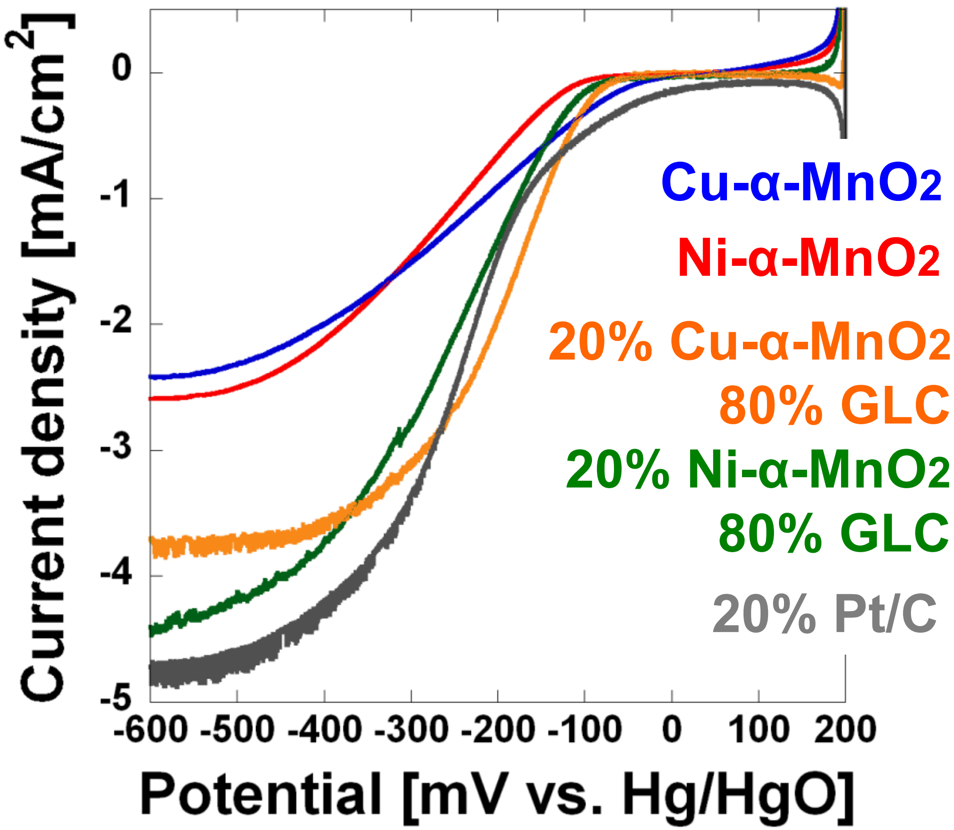
Oxygen is adsorbed onto a single Mn site.

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

F. Cheng, J. Chen *et al.*, *Chem. Mater.*, **2010**, *22* (3), pp 898-905.

Recent Studies

Linear Scanning Voltammograms



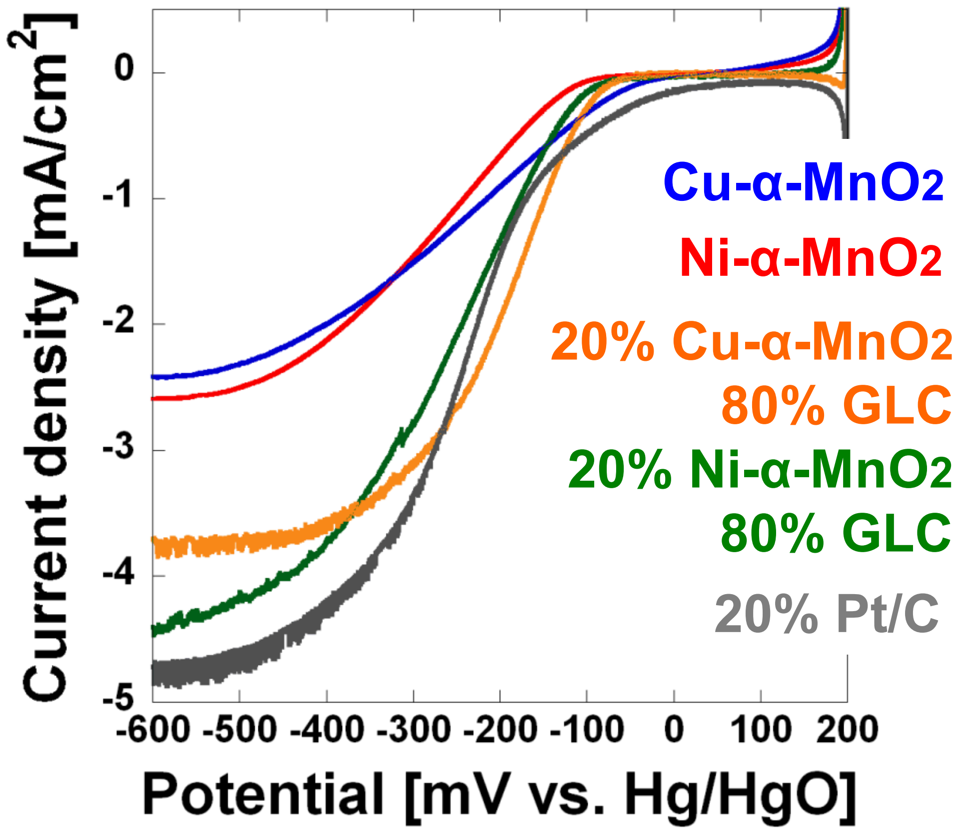
→ **78%** of current obtained by Pt/C

→ **91%** of current obtained by Pt/C

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

Recent Studies

Linear Scanning Voltammograms



→ $n = 3.9 \pm 0.2\ e^-$

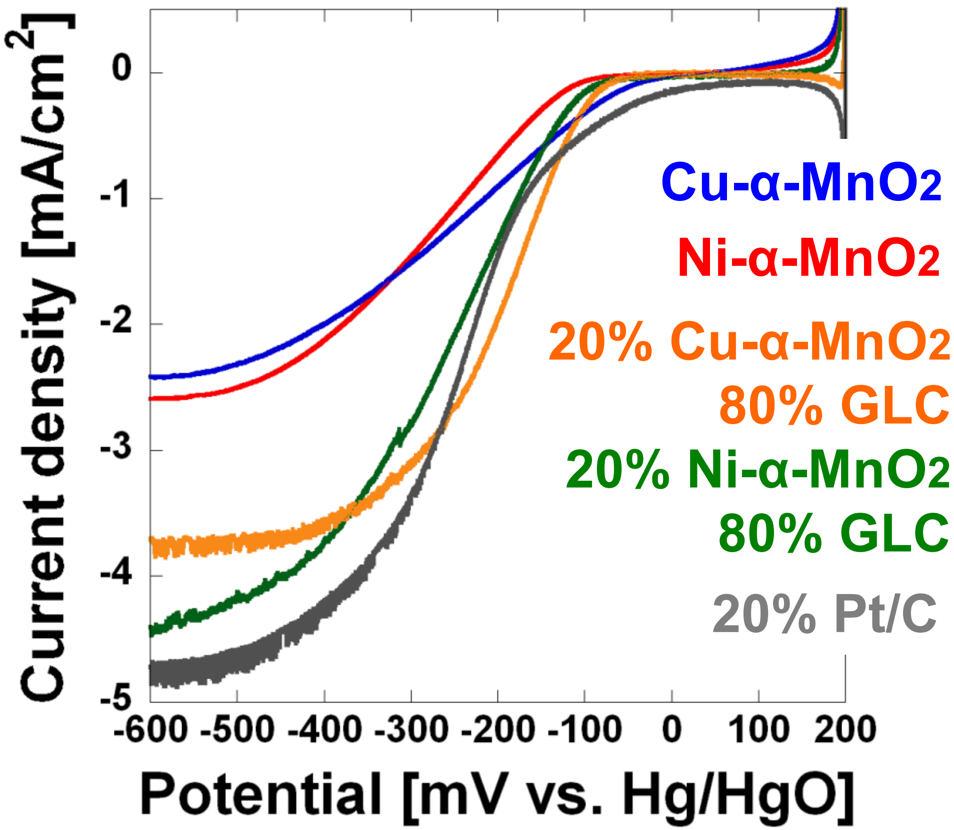
→ 3.50×10^{-2} cm/s

vs. 3.24×10^{-2} cm/s for benchmark 20% Pt/C

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

Recent Studies

Linear Scanning Voltammograms



→ **<u>Outperforms</u> Pt/C in the potential range of -127mV to -267mV**

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

Reaction Scheme

Can catalytic activity be better understood and possibly controlled by changing the molar ratio between Mn and Cu?

Cu-doped α-MnO_2 :

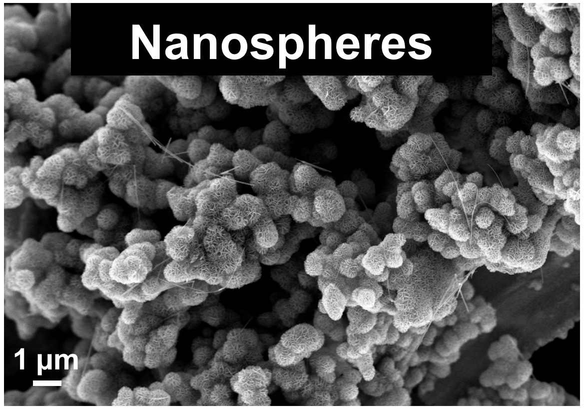
$$MnSO_4{\bullet}H_2O + Cu(NO_3)_2{\bullet}3H_2O + KMnO_4 \xrightarrow[\text{140 °C, 120 hours}]{\text{Hydrothermal Synthesis}} \text{“}K\text{-}Cu_XMn_{1\text{-}X}O_2\text{”}$$

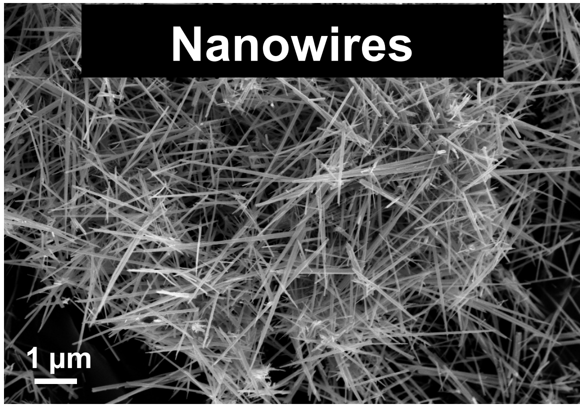
Three reactions with varied amounts of Cu precursor:

Synthesized at 1:1 ratio (Mn:Cu)

Synthesized at 1:0.5 ratio (Mn:Cu)

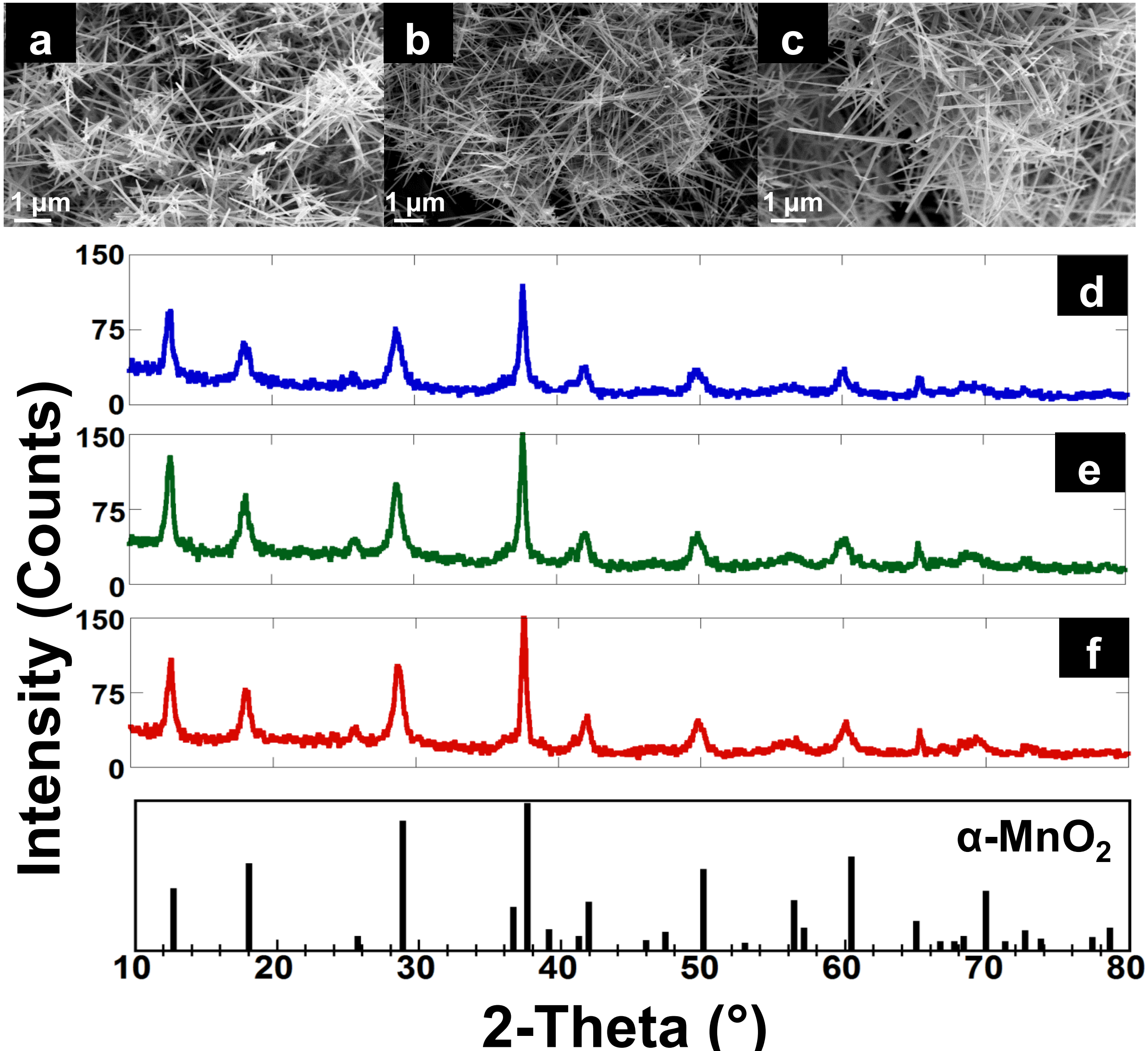
Synthesized at 1:0.25 ratio (Mn:Cu)





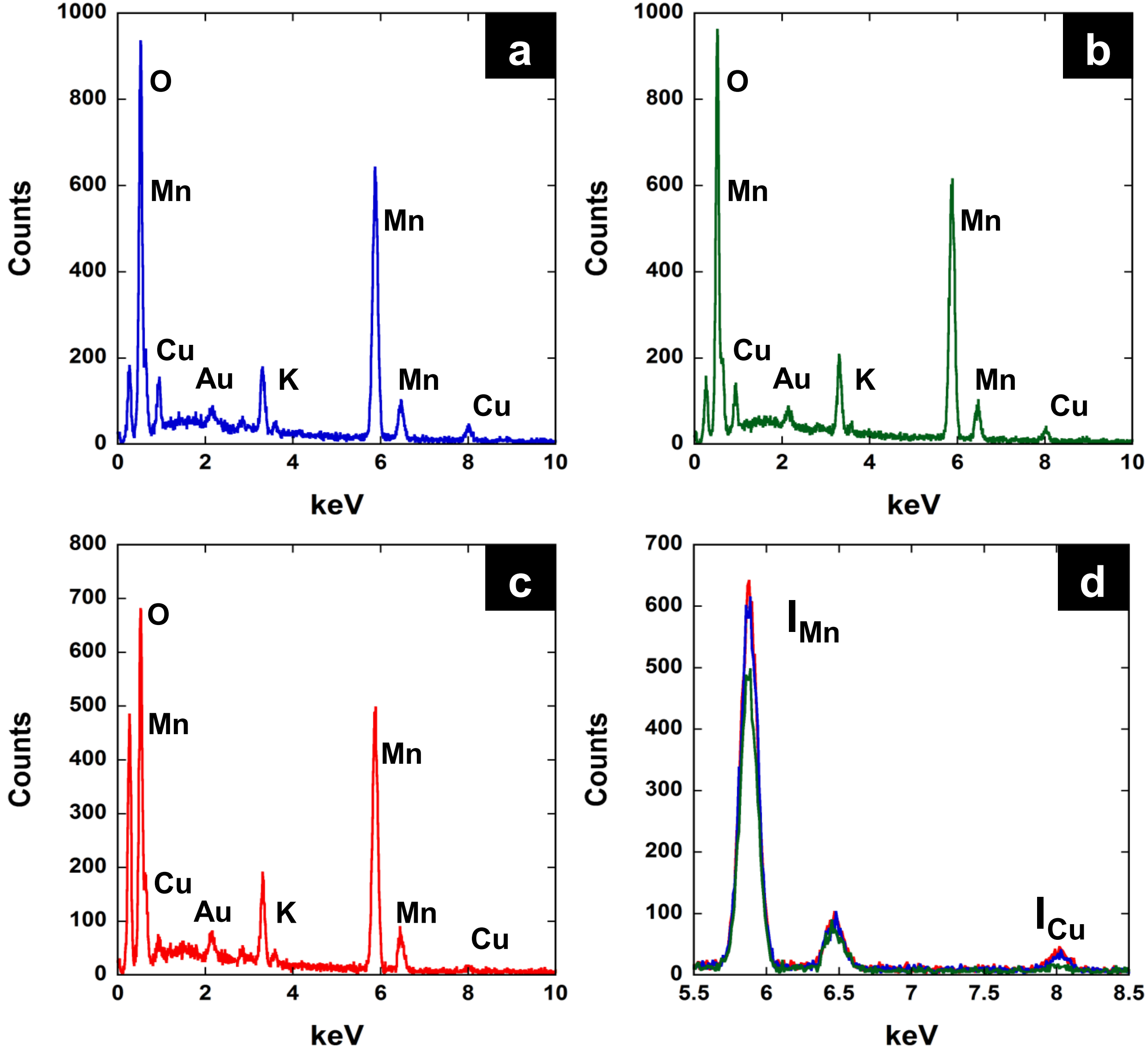
Characterization:

SEM and XRD



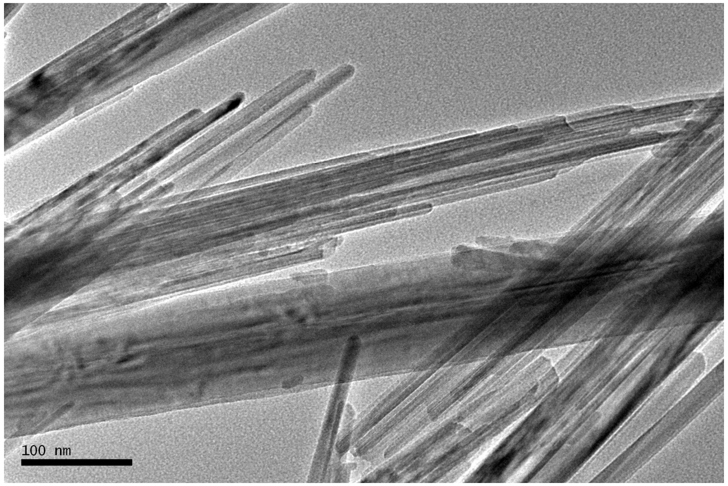
Characterization:

EDS



Characterization

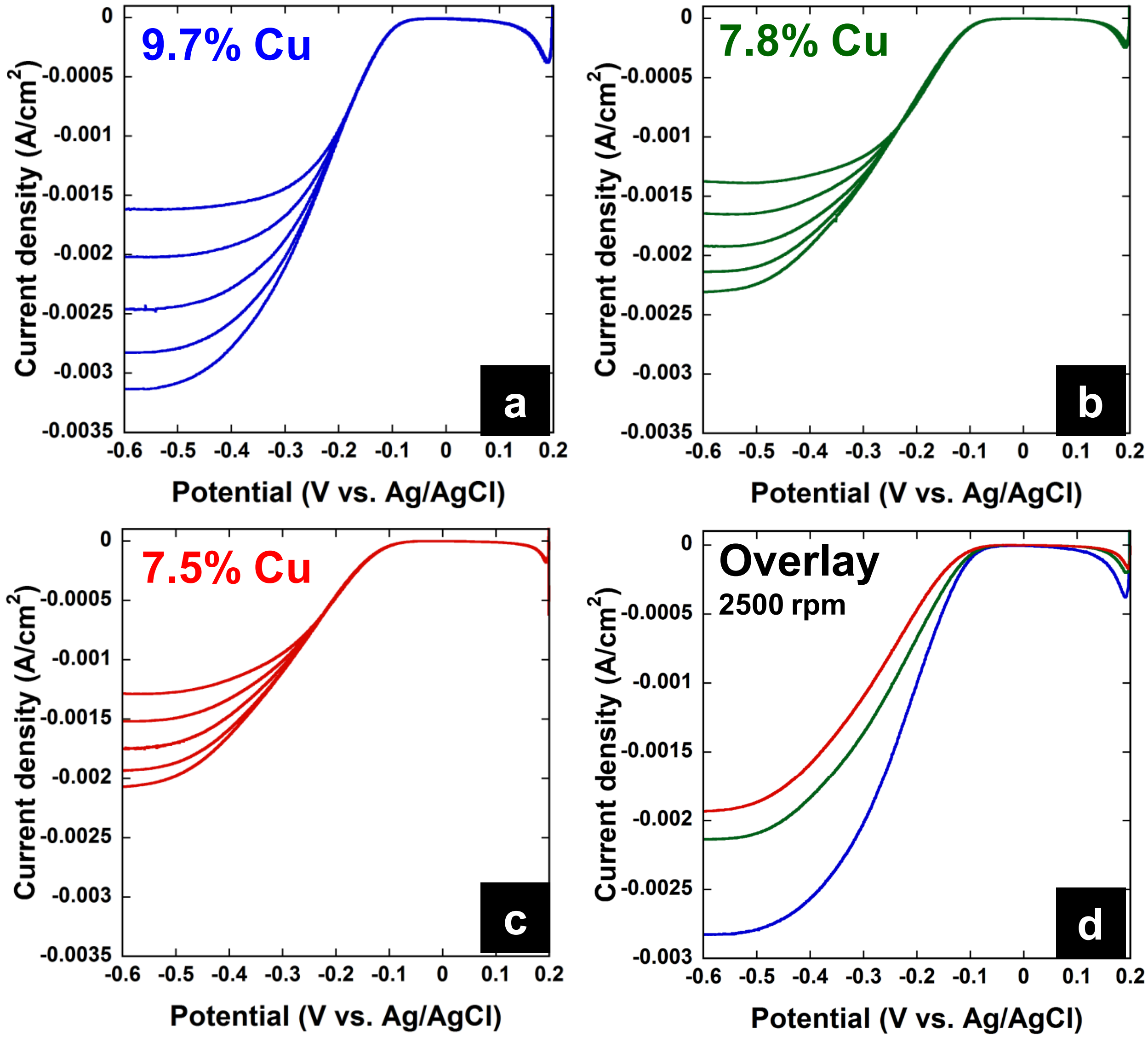
TEM and EDS



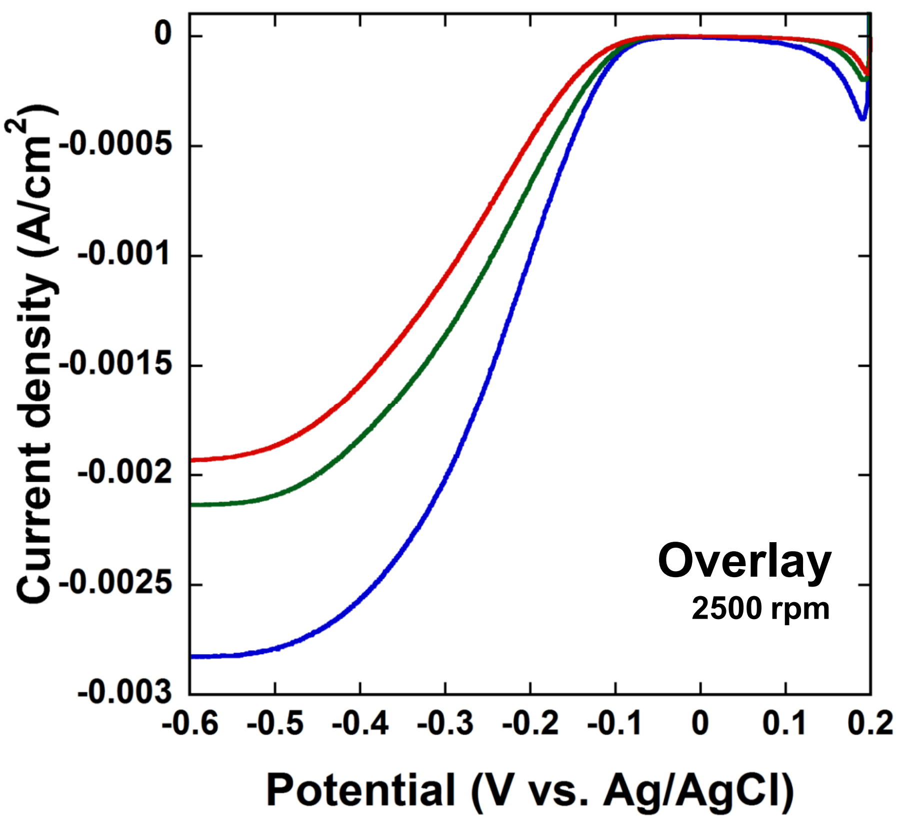
Reactant Ratio (Mn:Cu)	% Cu	% Mn	% O	% K
1:1	9.31	38.97	49.43	2.92
1:0.5	7.78	39.74	49.17	3.31
1:0.25	7.55	41.03	49.53	1.90

Electrochemical Analysis

Rotating Disk Electrode (RDE) Studies

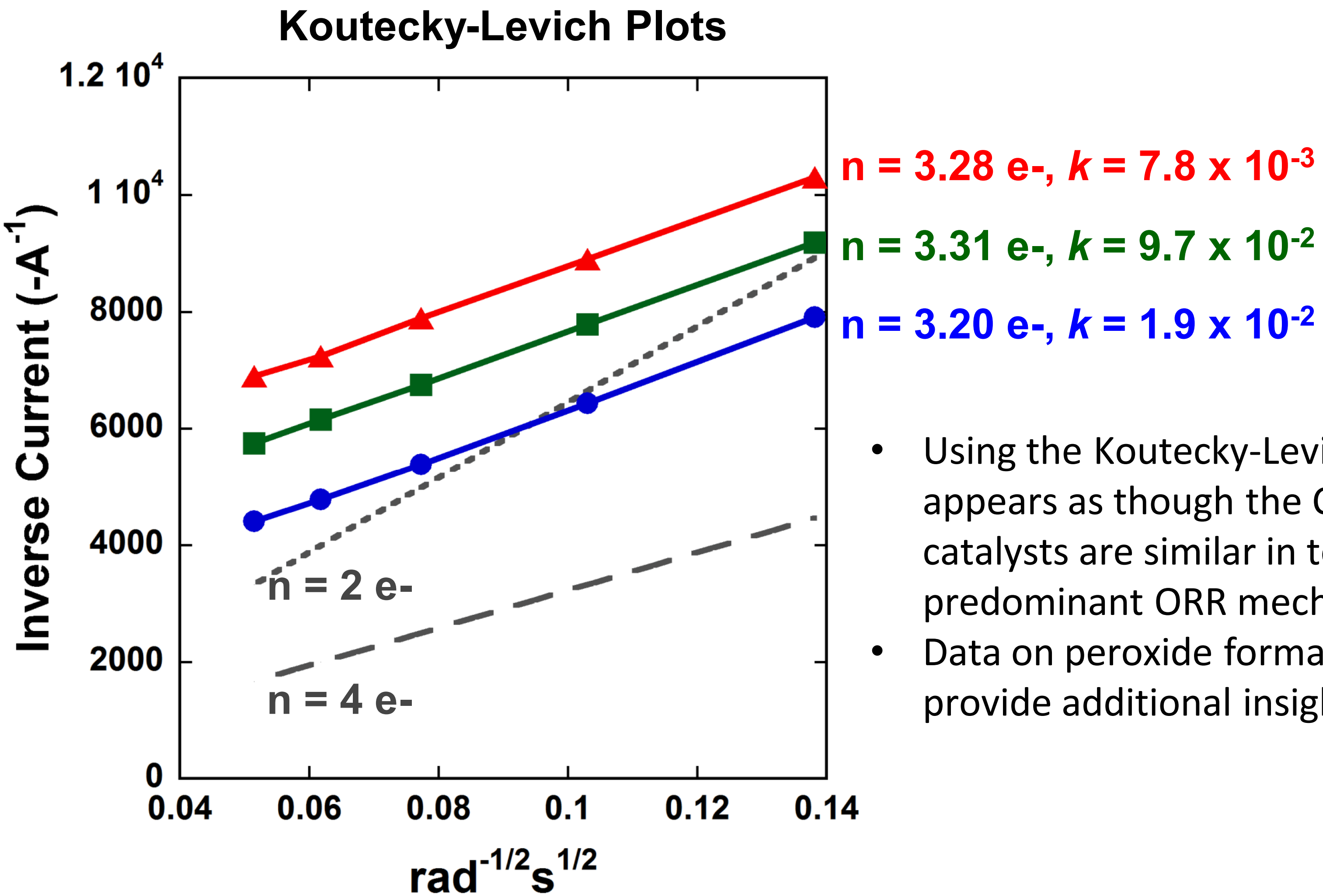


Electrochemical Analysis



Ratio Mn:Cu	Onset (mV)	Half-wave (mV)	Current density (mA/cm^2)	Rct (Ω)
1:1	-100.3	-291.6	-2.82	3430.33
1:0.5	-97.3	-303	-2.14	4379.67
1:0.25	-107.7	-312	-1.93	5743.67

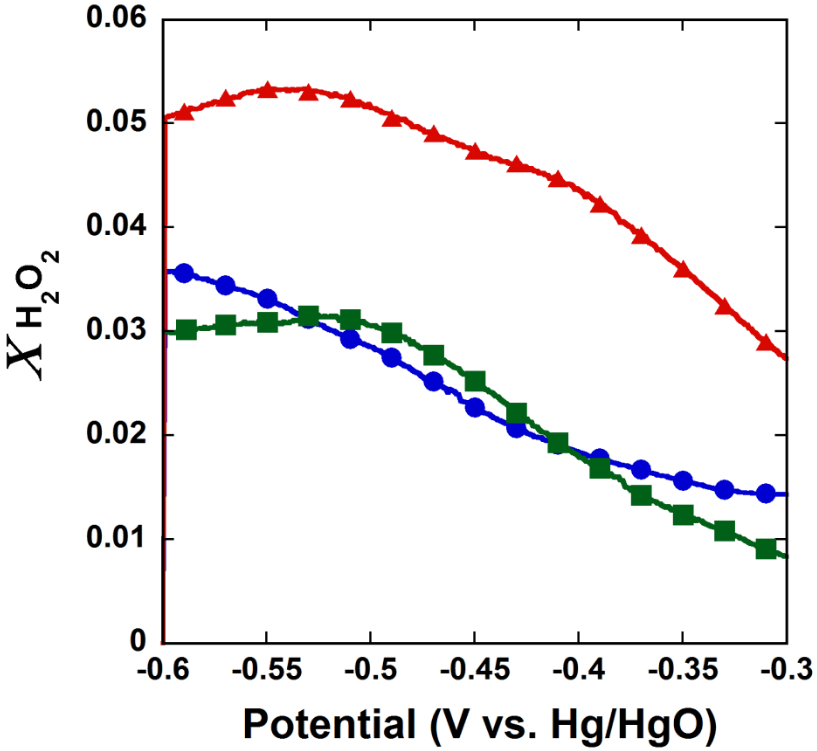
Reduction Mechanism and Rate

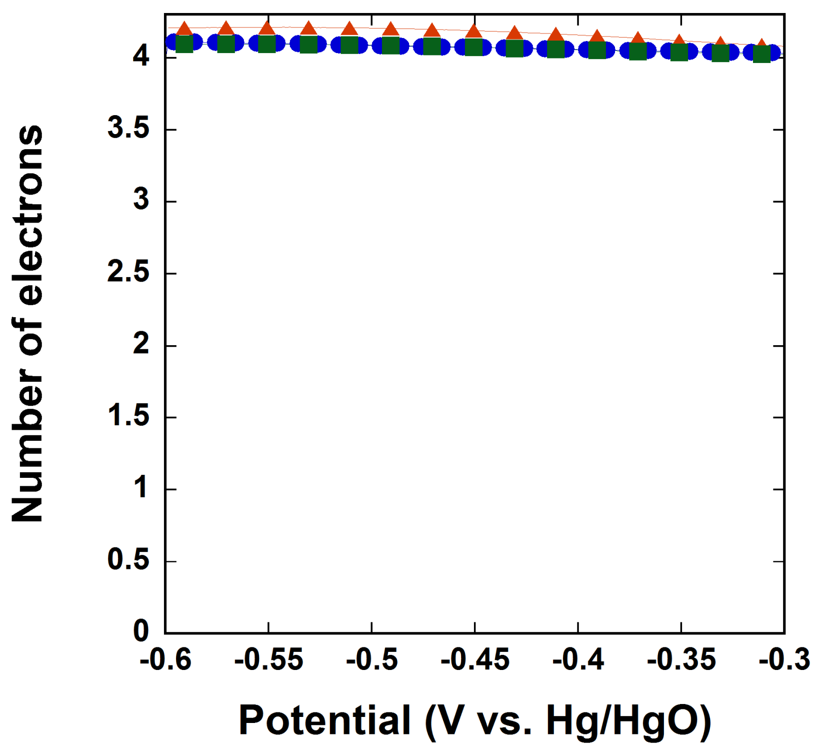


- Using the Koutecky-Levich method, it appears as though the Cu-α-MnO_2 catalysts are similar in terms of the predominant ORR mechanism.
- Data on peroxide formation can provide additional insight.

Electrochemical Analysis

Rotating Ring Disk Electrode (RRDE) Studies

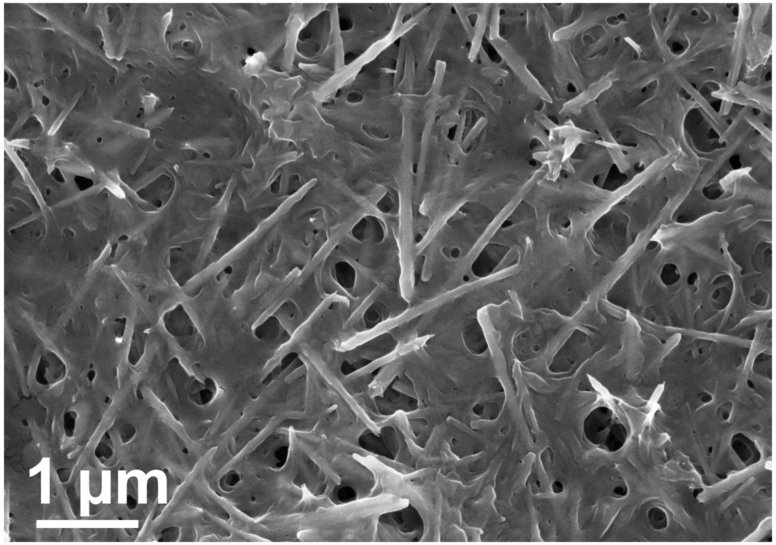




- Observed trends in peroxide formation from half-wave potential to terminal potential show slight variation.
- While peroxide is being formed at low percentages, it is being rapidly reduced, resulting in an apparent 4 e^- process.

Elucidating the Role of Cu

- Improvements made by doping the α-MnO_2 with Cu:
  - Current density
  - Half-wave potential
  - n-value (> α-MnO_2 alone)
  - Kinetic rate constant
  - Peroxide formation
- The Cu-dopant has a critical role in the performance of the catalyst.
  - Surface Area
  - Lattice Expansion
  - Oxidation State of Mn



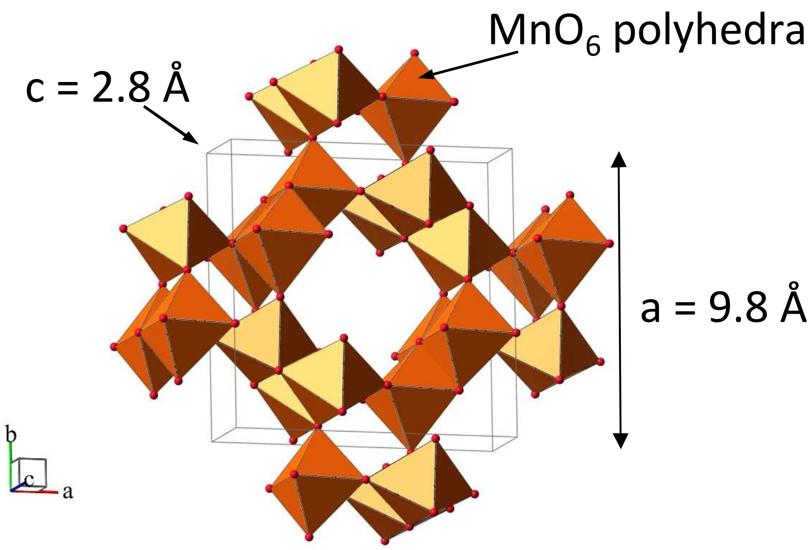
Surface Area Analysis

	Reactant Ratio (Mn:Cu)	BET Surface Area (m^2/g)	Pore Size (nm)	Pore Volume (cm^3/g)
Cu-α-MnO_2	1:1	81.5	5.9	0.24
	1:0.5	78.5	4.7	0.18
	1:0.25	59.1	4.7	0.14

Measurements obtained by Eric Coker (SNL).

Lattice Refinements

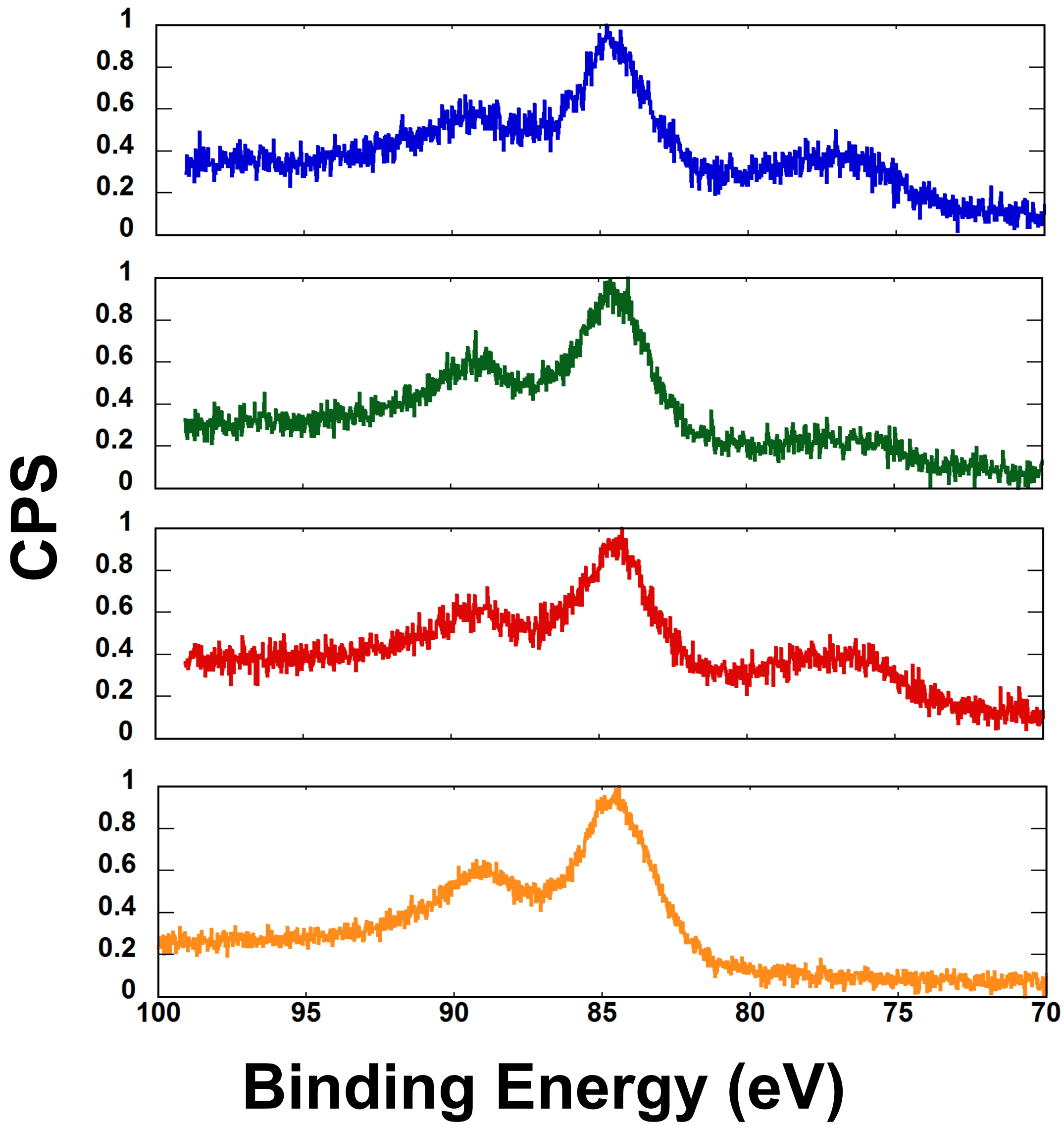
Sample	a (Å)	c (Å)	Volume ($Å^3$)
JCPDF 00-044-0141	9.785	2.863	274.1
α-MnO_2	9.836 (3)	2.858 (1)	276.45
Cu-α-MnO_2 7.545% Cu	9.838 (3)	2.859 (1)	276.74
Cu-α-MnO_2 7.785% Cu	9.84(1)	2.857(2)	276.5
Cu-α-MnO_2 9.311% Cu	9.866 (5)	2.857 (1)	278.12



Measurements and graphic by Mark Rodriguez (SNL).

Tetragonal (I4/m) structure
After Rossouw, et al., *Materials Research Bulletin* (1992) 27, 221-230

X-Ray Photoelectron Spectroscopy



Analysis performed by Michael Brumbach (SNL).

Summary and Conclusions

- The Cu-dopant species, when added to α-MnO_2, improves the electrochemical performance as a catalyst for ORR in alkaline media.
- There is not a single property that independently determines the catalytic behavior of these materials. There are numerous factors that work in conjunction with each other to influence the performance.
  - Cu content (both at the surface, and throughout the wire)
  - Surface area
  - Expansion of crystalline lattice
  - Oxidation State of Mn

Future Work

- Determine if catalysis be further improved by heating Cu-α-MnO_2
  - Heating has been demonstrated to induce oxygen vacancies in the structure.
  - Vacancy sites…
- Obtain conductivity measurements on single nanowires.
  - Low surface content of Cu indicates that the majority of the dopant is residing inside of the wire.
  - Conductivity is likely influenced by Cu content throughout the wire.
- Blend Cu-α-MnO_2 with conductive carbon to further augment performance.

Acknowledgements

Eric Coker, SNL

Michael Brumbach, SNL

Mark Rodriguez, SNL

Ying-Bing Jiang, UNM

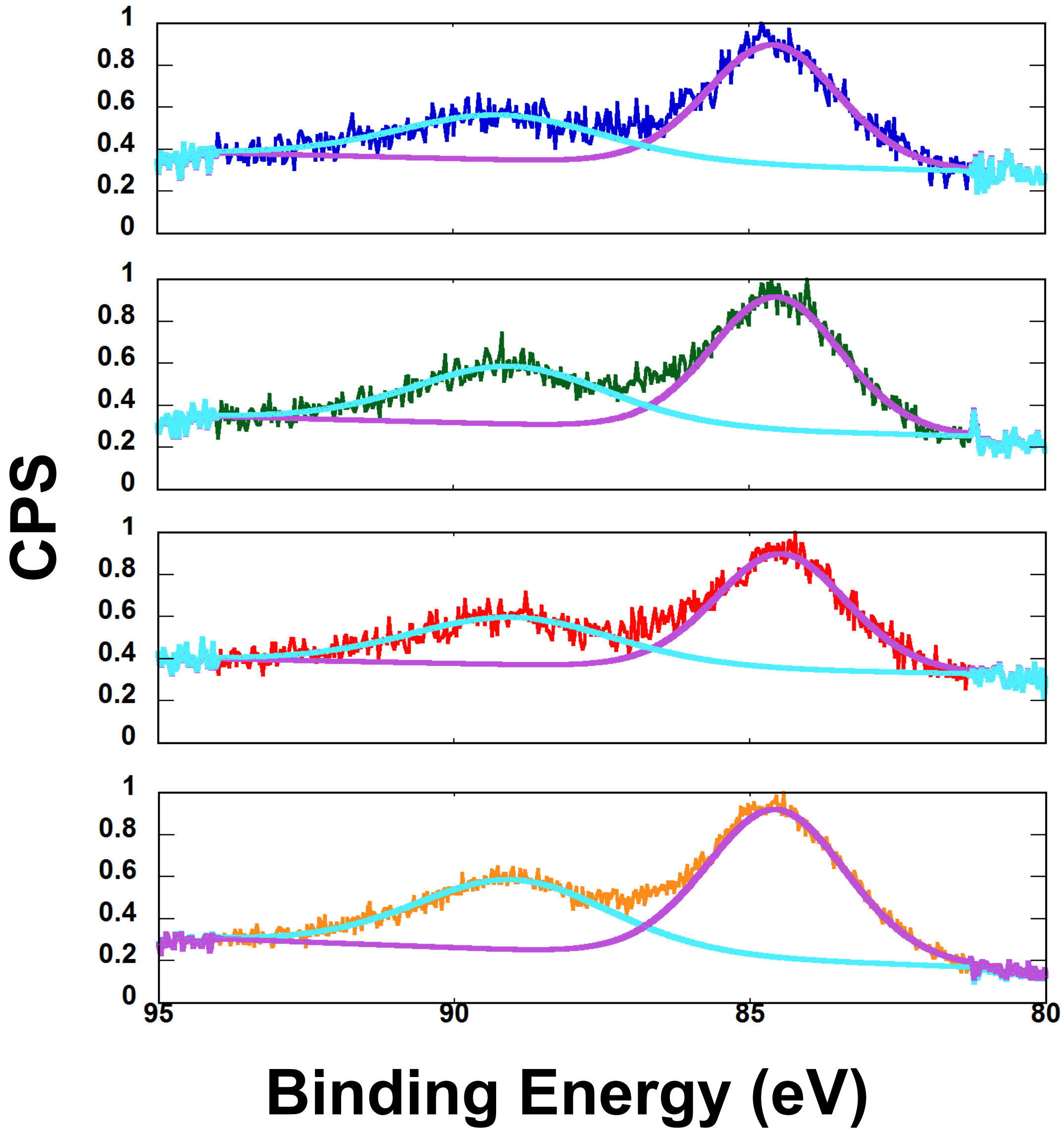
Bonnie McKenzie, SNL

Richard Kemp, SNL & UNM

Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed-Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Questions?

X-Ray Photoelectron Spectroscopy



Analysis performed by Michael Brumbach (SNL).