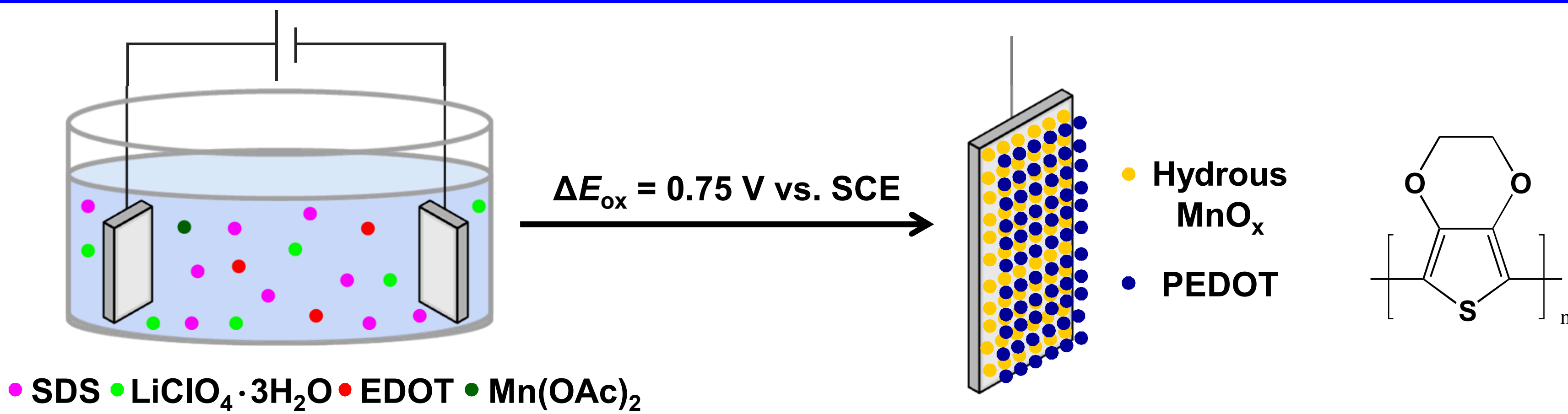
$$O_2 + 2H_2O + 4e^- = 4OH^-$$



Electrodeposited MnOx/PEDOT Thin Films as Catalysts for the Oxygen Reduction Reaction

2016 Spring ACS Presentation

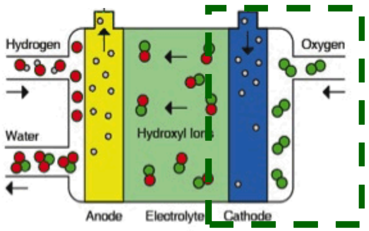
March 17th, 2015: San Diego, California

Timothy N. Lambert, Julian A. Vigil, and Kaitlyn Eldred

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.

Electrocatalysis in energy devices



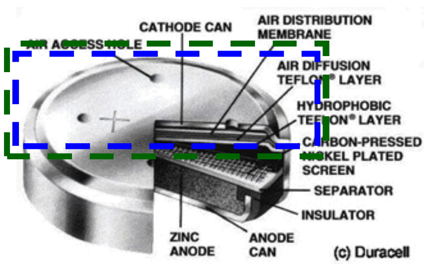
Fuel cell schematic

Alkaline fuel cell:

Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ — Oxygen Reduction Reaction (ORR)

Overall: $2H_2 + O_2 \longrightarrow 2H_2O$



Zn-air battery schematic

Secondary metal-air battery (e.g. Zn-air):

Discharge

Anode: $2Zn_{(s)} \longrightarrow 2Zn^{2+} + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ — ORR

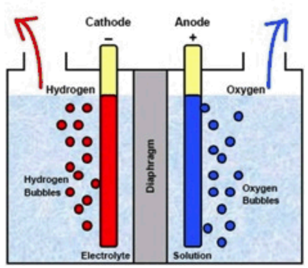
Overall: $2Zn_{(s)} + O_2 + 2H_2O \rightarrow 2Zn^{2+} + 4OH^-$

Charge

Anode: $2Zn^{2+} + 4e^- \longrightarrow 2Zn_{(s)}$

Cathode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ — Oxygen Evolution Reaction (OER)

Overall: $2Zn^{2+} + 4OH^- \rightarrow 2Zn_{(s)} + O_2 + 2H_2O$



Electrolyzer schematic

Alkaline Electrolyzer:

Anode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$ — OER

Cathode: $4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$ — Hydrogen Evolution Reaction (HER)

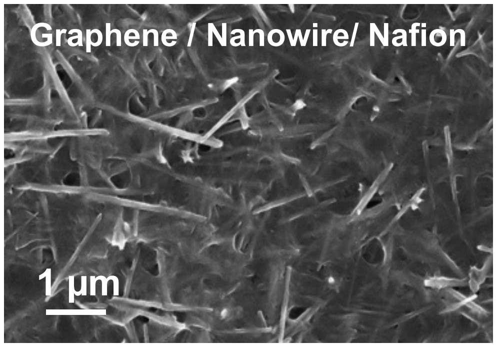
Overall: $4H_2O \longrightarrow 2H_2 + O_2$

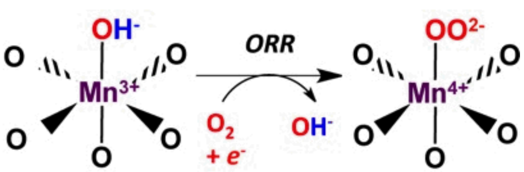
Catalysts: environmentally benign, earth-abundant, and overall potentially cost effective

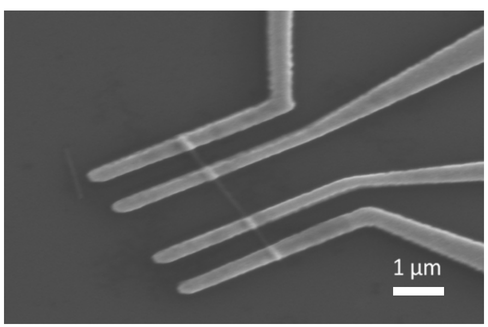
Nanoscale Electrocatalysts

Approach: Develop new nanoscale non-PGM electrocatalysts

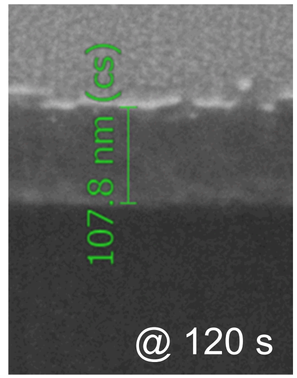
Graphene/Ni-α-MnO_2 Cu-α-MnO_2 Nanowires



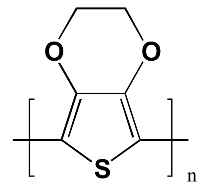


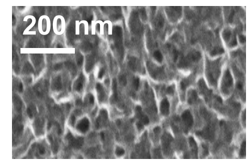


MnOx/PEDOT Thin Films

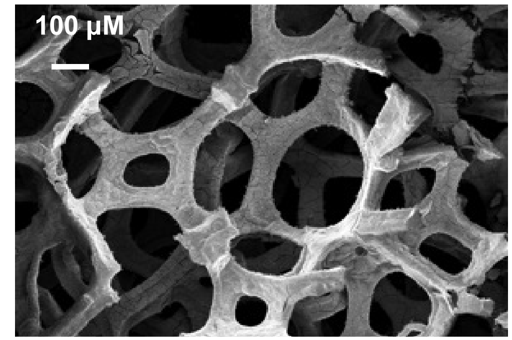


PEDOT

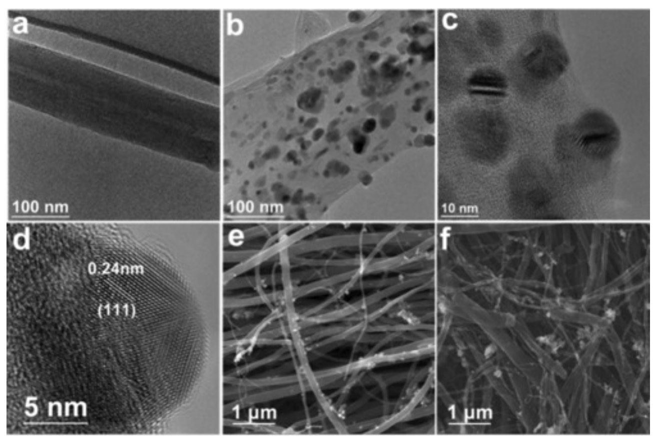




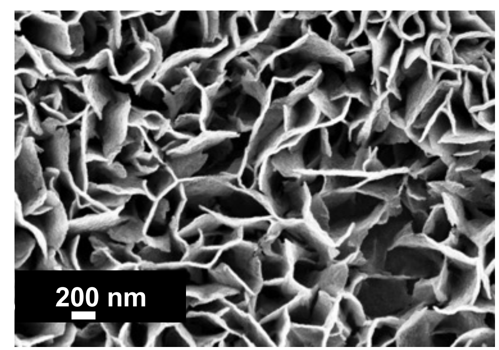
$Ni_xCo_{3-x}O_4$ Thin Films



Graphene Nanoribbon/Ag



CoP Thin Films



(ORR/OER): *ACS Appl. Mater. Interfaces* **2016**, *in prep., ACS Appl. Mater. Interfaces* **2015**, *Chem. Commun.* **2015**, *J. Phys. Chem. C* **2014**, *Electroanal.* **2013**, *ACS Nano* **2012**, *Chem. Commun.* **2012**: ***(HER/OER):*** *J. Mater. Chem. A* **2016** *submitted*, RSC Adv. **2015**

Oxygen Reduction Reaction

Direct 4 e^- reduction $n = 4$

$$O_{2\,(g)} + 2H_2O_{\,(l)} + 4e^- \rightarrow 4OH^-_{\,(aq)}$$

2 e^- reduction to form peroxide $n = 2$

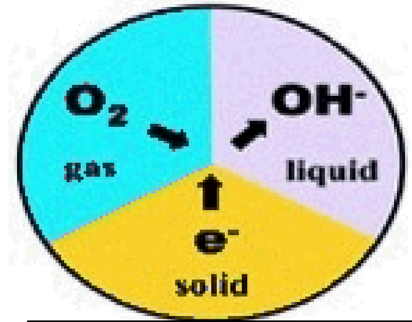
$$O_{2\,(g)} + H_2O_{\,(l)} + 2e^- \rightarrow HO_2^-{}_{(aq)} + OH^-_{\,(aq)}$$

Indirect 2 + 2 = 4 e^-

$$HO_2^-{}_{(aq)} + H_2O_{\,(l)} + 2e^- \rightarrow 3OH^-_{\,(aq)}$$

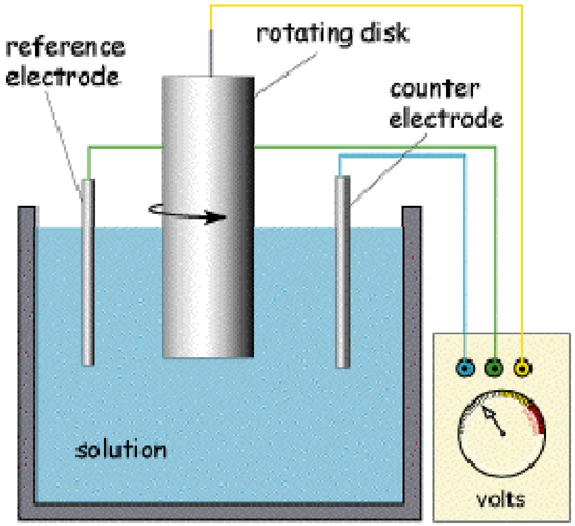
Disproportionation

$$2HO_2^-{}_{(aq)} \rightarrow 2OH^-_{\,(aq)} + O_{2\,(g)}$$



Electrocatalyst

RDE/RRDE methodology



Oxygen Reduction Reaction

Sandia National Laboratories

Formation of surface hydroxide

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

Displacement of surface hydroxide

$$Mn^{3+}\text{–}OH^-{}_{(s)} + O_{2\ (g)adsorbed} + e^- \rightarrow Mn^{4+}\text{–}O\text{–}O^{2-}{}_{(s)} + OH^-{}_{(aq)}$$

Formation of surface peroxide

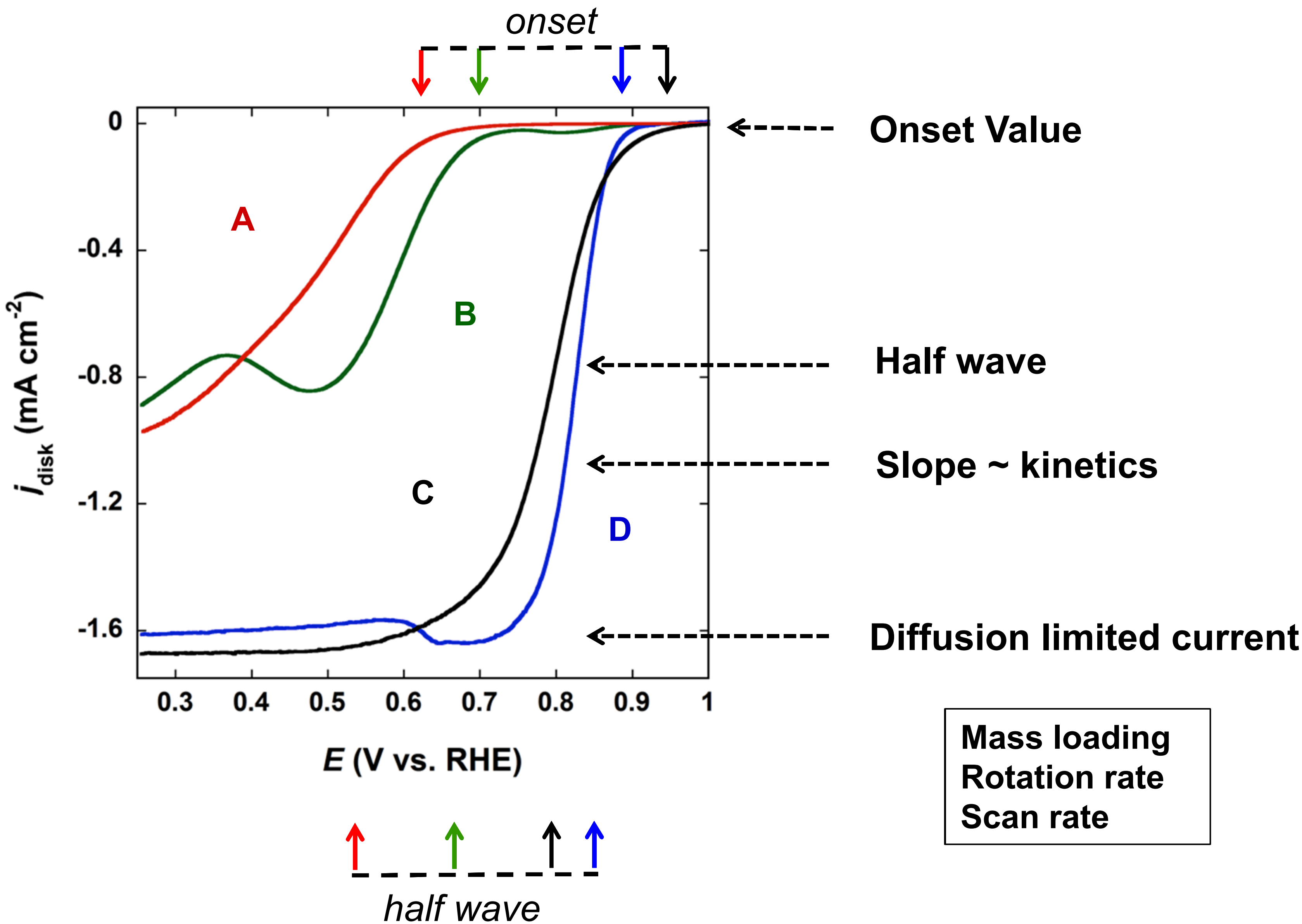
$$Mn^{4+}\text{–}O\text{–}O^{2-}{}_{(s)} + H_2O_{(aq)} + e^- \rightarrow Mn^{3+}\text{–}O\text{–}OH^-{}_{(s)} + OH^-{}_{(aq)}$$

Formation of surface oxide

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

Mn(III)/Mn(IV)

RDE Electrode Data



Mass loading
Rotation rate
Scan rate

What factors are important for MnOx?

- Size:
- Morphology:
- Phase: (α-MnO_2 vs. β-MnO_2 vs. γ-MnO_2)
- Valency: Mn(III)/Mn(IV) ratio
- Conductivity: (Doping, Hybridize with NPs, Carbon, semi-conducting polymers)

= Composite Catalysts

D. J. Davis *et al. J. Phys. Chem. C.* **2014**, *118*, 17342-17350.

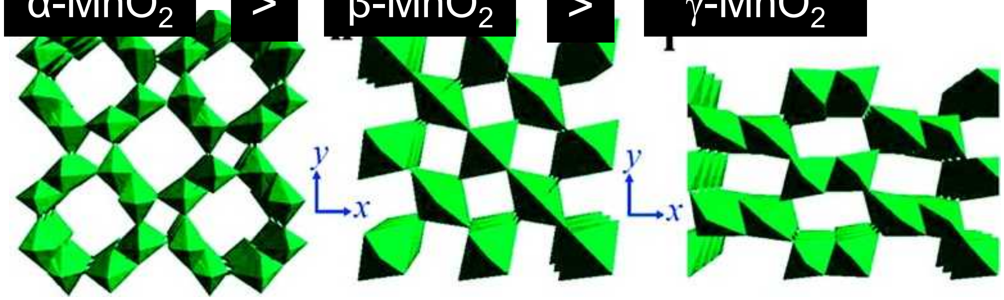
Manganese oxide Nanowires

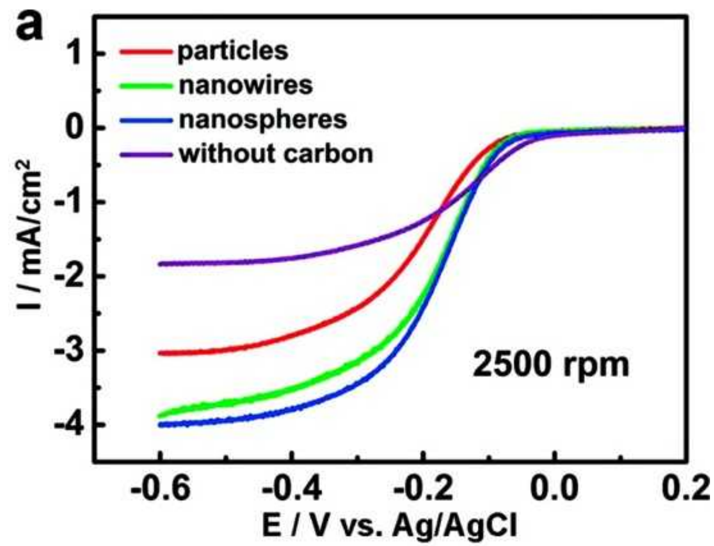
Sandia National Laboratories

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

Phase:

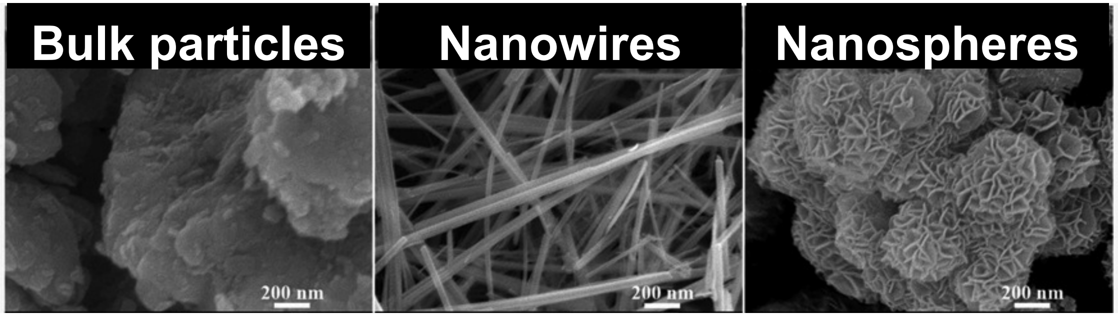
α-MnO_2 > β-MnO_2 > γ-MnO_2



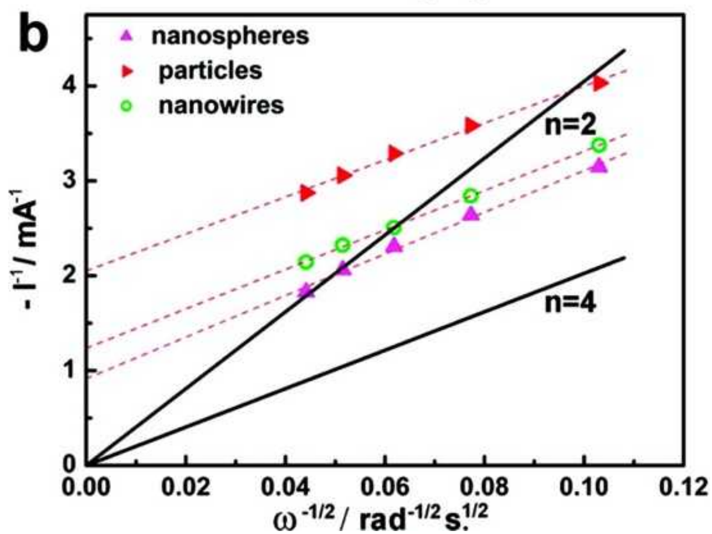


Size: **nm MnO_2 > μm MnO_2**

Morphology: nanowires/spheres > nanoparticles



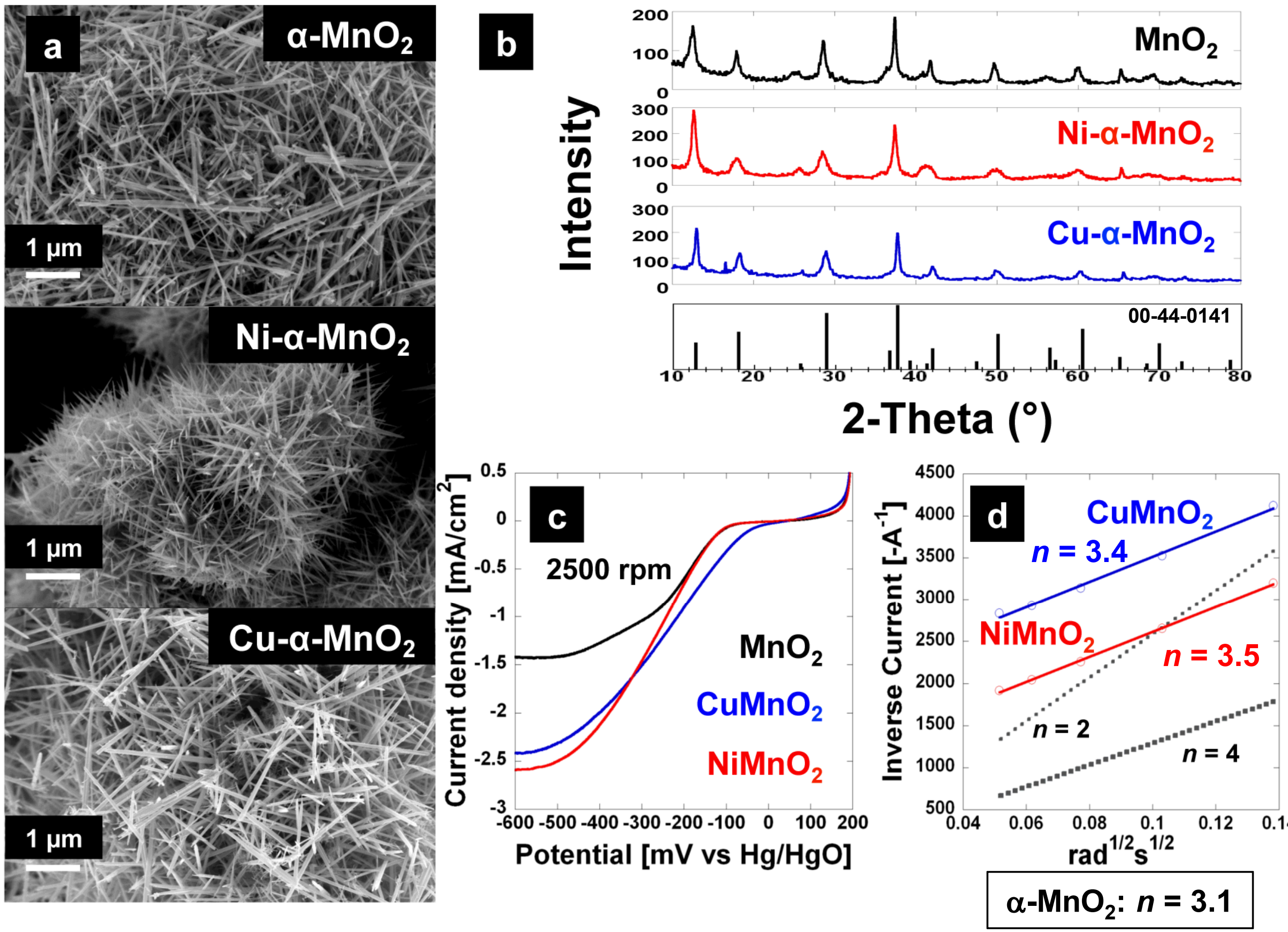
Bulk particles	Nanowires	Nanospheres
7.9 m^2/g	32.9 m^2/g	40.1 m^2/g

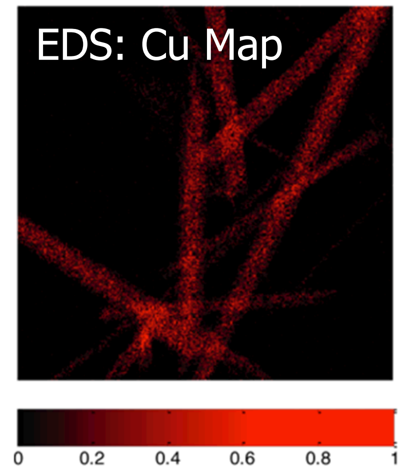


F. Cheng, *et al. Chem. Mater.* **2010**, 22, 898–905

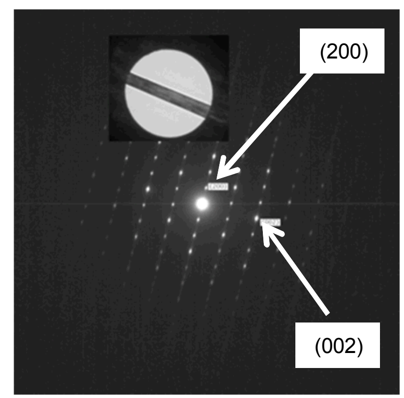
Ni- and Cu-α-MnO_2 Nanowires

$$\overset{II}{Mn}SO_4 \cdot H_2O + (\text{Ni}/\text{Cu}\text{-}SO_4 \cdot H_2O) + K\overset{VII}{Mn}O_4 \xrightarrow[140^\circ\text{ C, 12-120 h}]{\text{Hydrothermal synthesis}} \text{Ni-α-}\overset{IV}{Mn}O_2 \text{ or Cu-α-}\overset{IV}{Mn}O_2$$





Cu-MnO_2

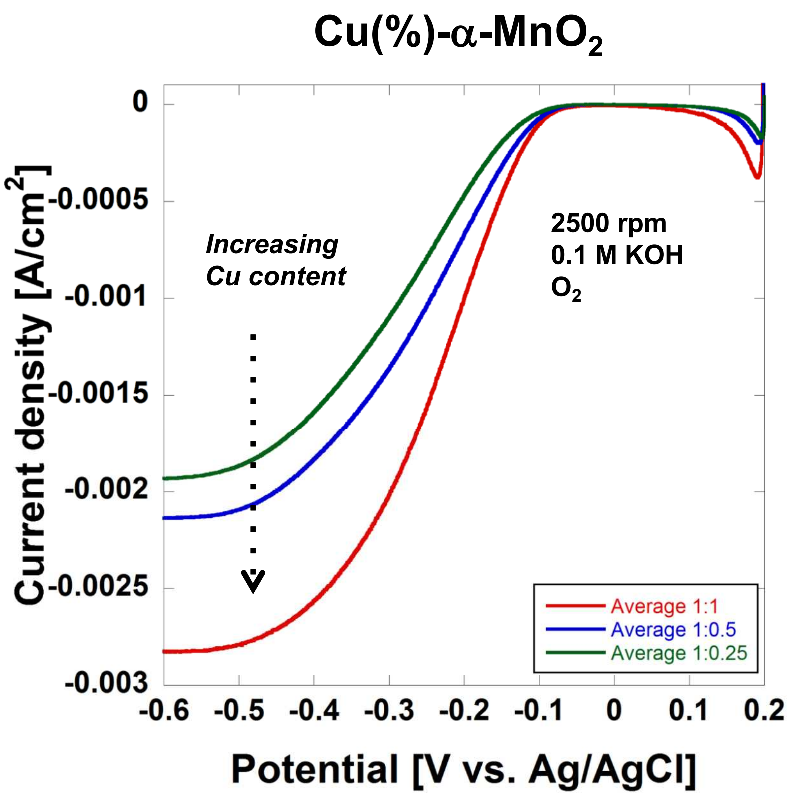


For highly active α-MnO_2 see: F. Cheng et al. *Chem. Mater.* **2010**, *22*, 898-905.

What is role of metal ion (Cu)dopant ?

Sandia National Laboratories

Series of Cu-α-MnO_2 NW electrocatalysts



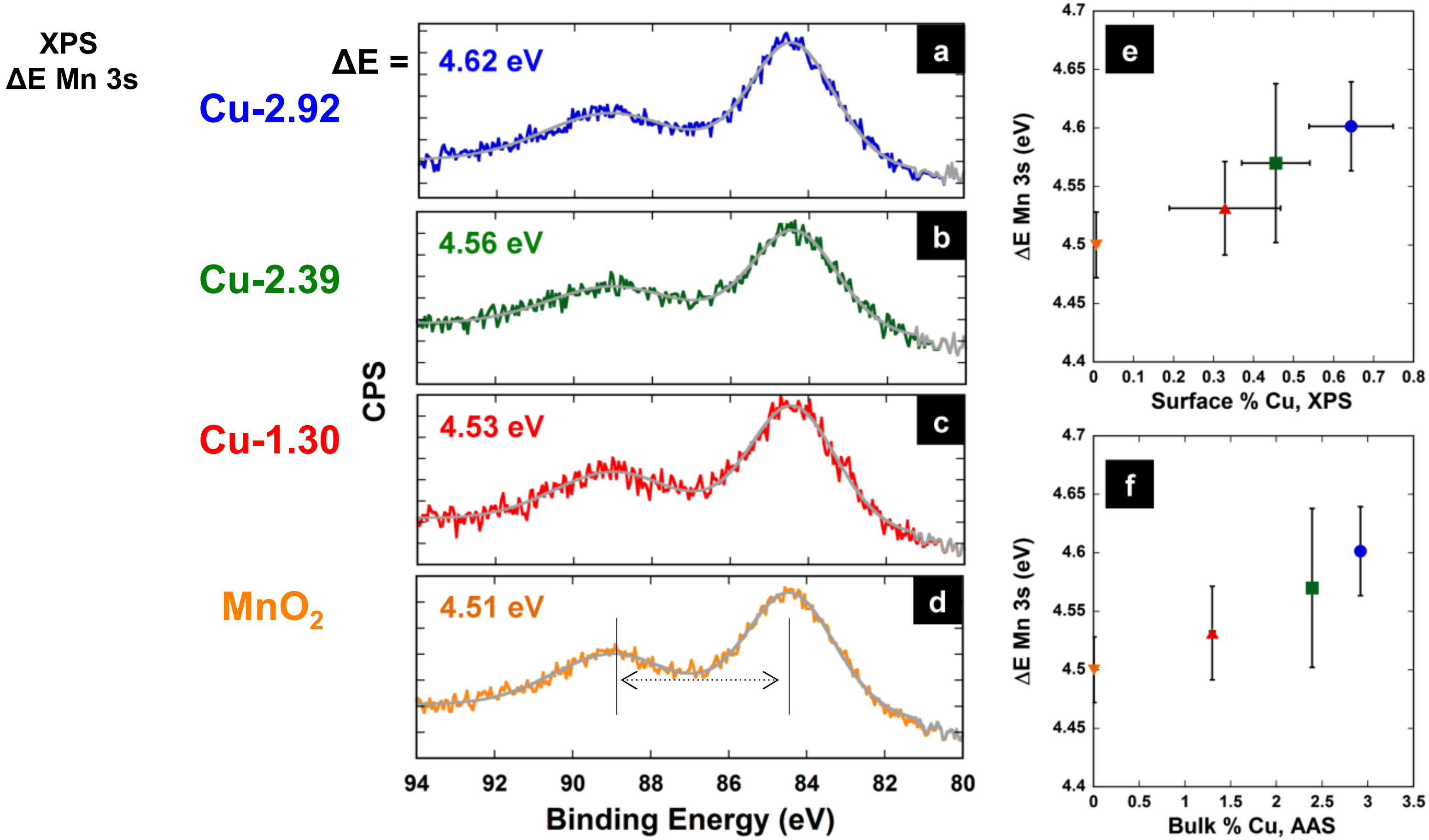
Ratio Mn:Cu	Onset (mV)	n (e-)	Current density (mA/cm^2)	Half-wave (mV)	Rate (cm/s)	Rct (Ω)
1:0.25	-107.7	3.28	-1.93	-312	0.0078	5744
1:0.5	-97.3	3.31	-2.14	-303	0.0097	4380
1:1	-100.3	3.20	-2.82	-292	0.019	3430

- Smaller crystallite size
- Lattice volume expansion
- More Covalent bonding
- Higher Mn^{3+}/Mn^{4+} ratio
- Conductivity ?

D. J. Davis *et al. J. Phys. Chem. C.* **2014**, *118*, 17342-17350.

Electronic Effects of Cu ?

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

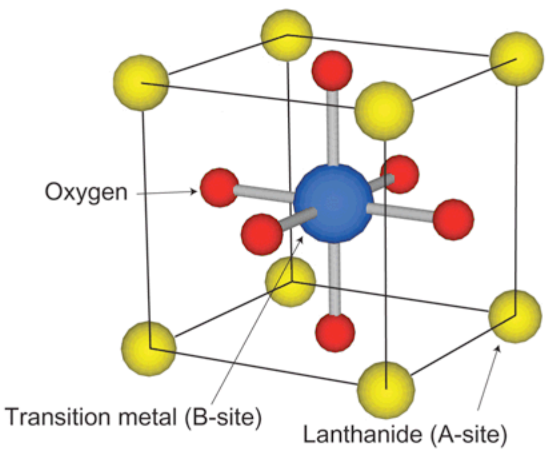


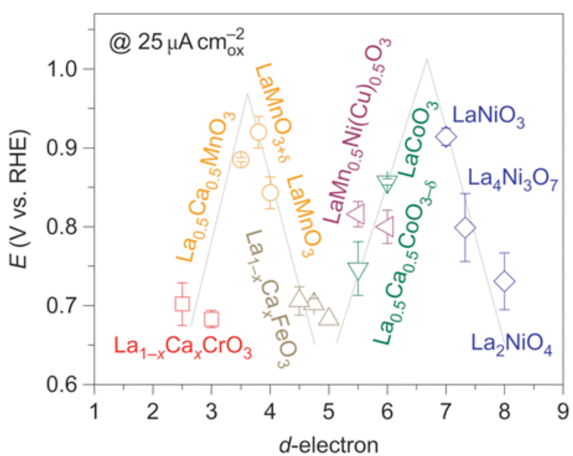
- **Increasing copper leads to increasing surface Mn^{3+}**
- **Increasing Cu leads to better electrocatalyst**

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.

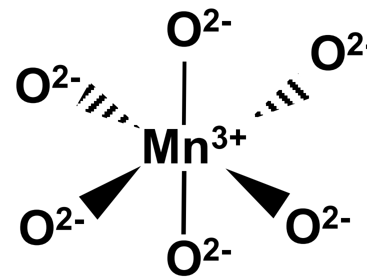
d4 = High Spin in Octahedral coordination

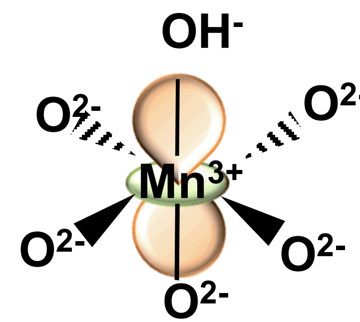




Adapted from J. Suntivich *et al.* Nature Chemistry. **2011.** 3, 546-550.

Mn^{3+}

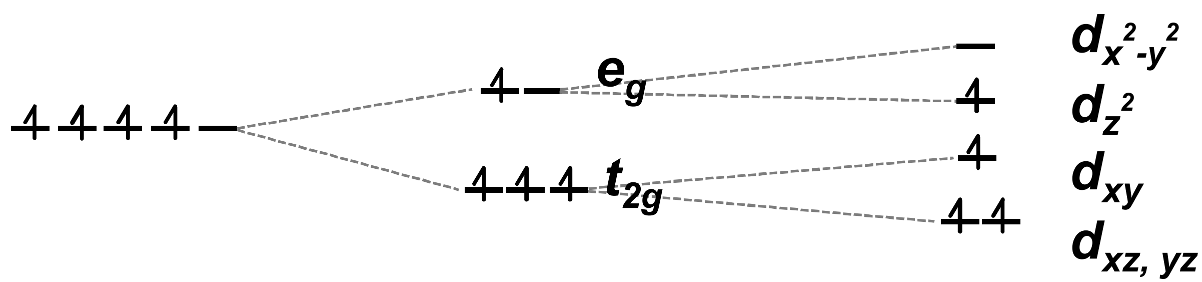




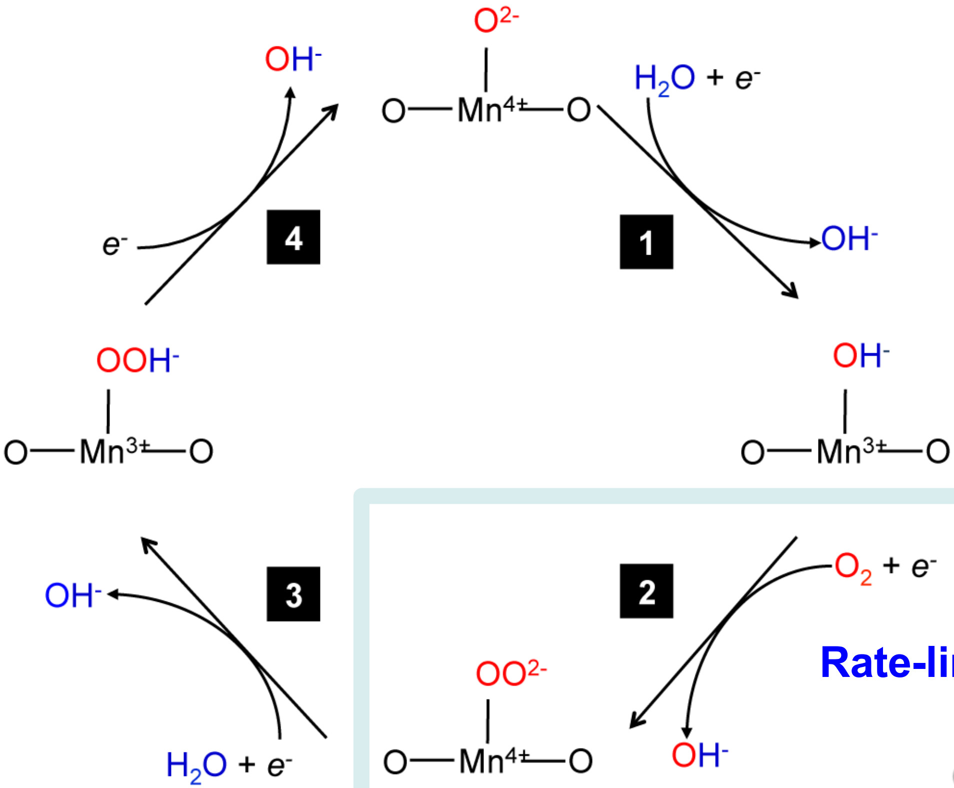
d^4 : *d*-manifold

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

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

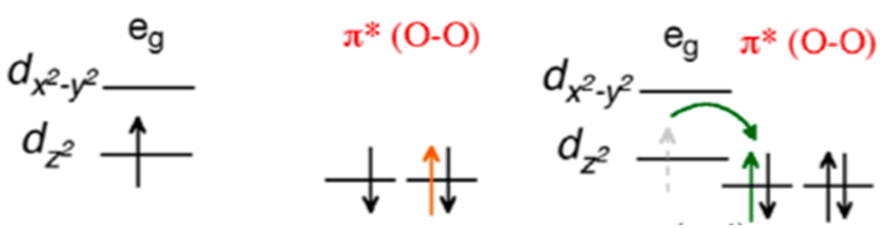


The role of Mn^{3+}/Mn^{4+} Couple



- **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)**

Rate-limiting step



$Mn^{3+}\text{-}OH^- + O_2 + e^- \longrightarrow Mn^{4+}\text{-}OO^{2-} + OH^-$

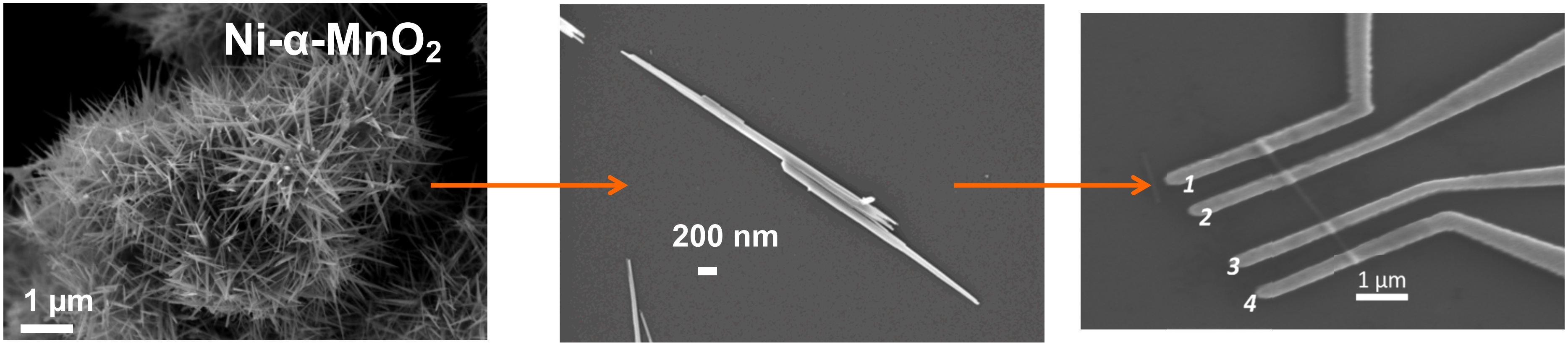
Mn^{3+} : d4 ion =
High Spin in Octahedral coordination

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

Conductivity effects of M^{n+} ?

Charge transfer resistance values suggest increased conductivity

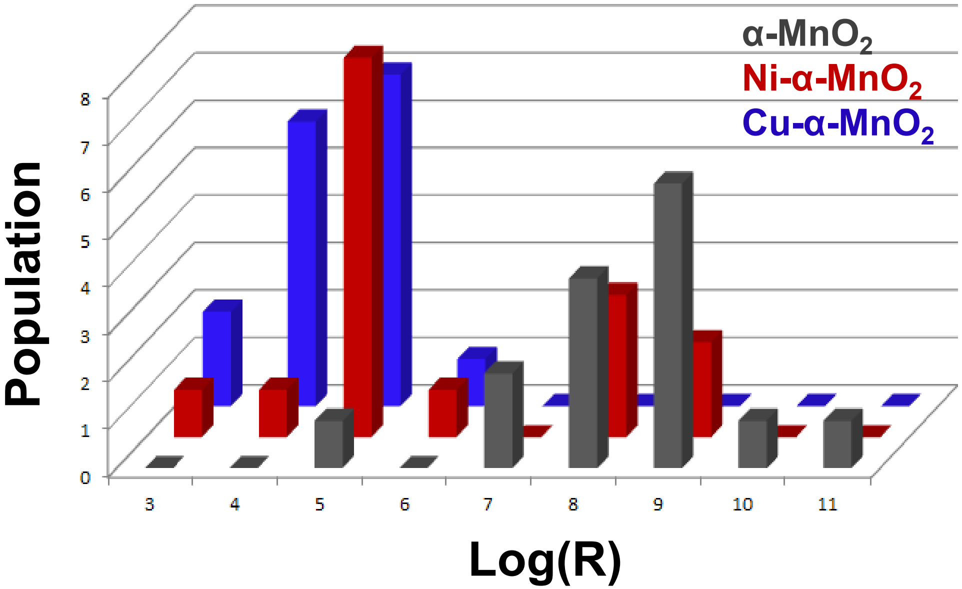
As Prepared | **Dispersed NWs** | **Electrical Contacts**



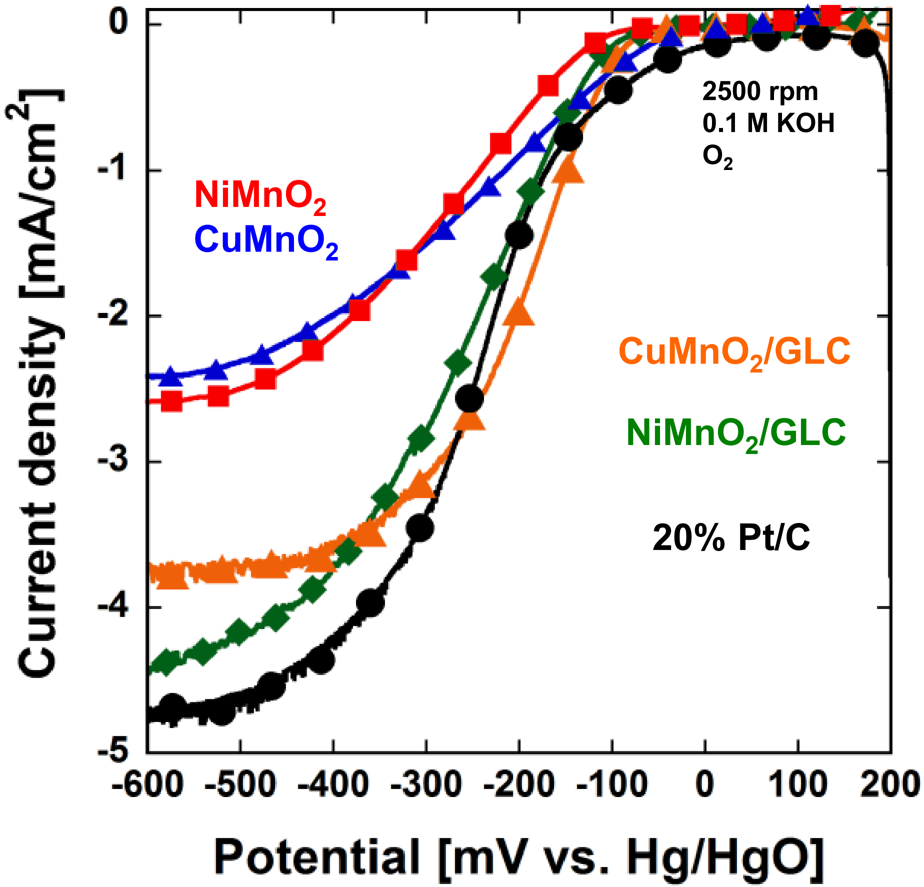
CY15 CINT User Proposal:
w/Brian Swartzentruber
and Collin Delker

47 nanowire devices were prepared and tested ($R = \Delta V / I$)

Temperature Dependent measurements pending



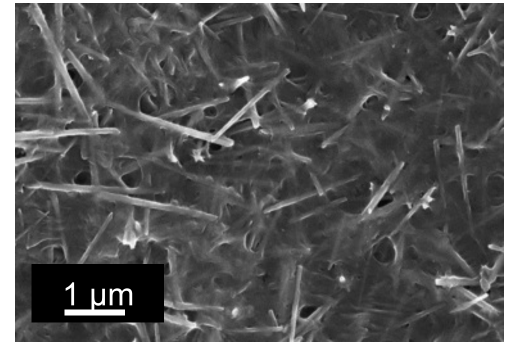
Increase Electrocatalysis with carbon



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
<u>CuMnO$_2$ outperforms</u> Pt/C in the potential range of -127 mV to -267 mV

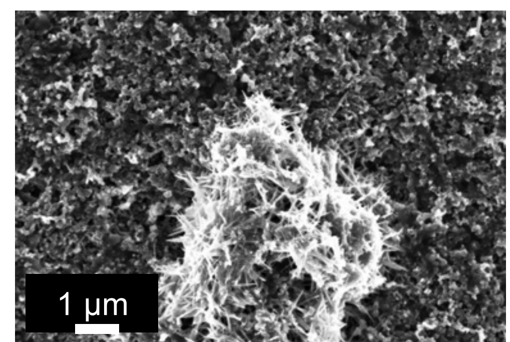
For GLC (Prof. JM Tour@ Rice) synthesis see:
Z. Jin *et al. J. Am. Chem. Soc.* **2010**, 132, 15246–15251.

Cu-α-MnO$_2$ NWs / GLC / Nafion



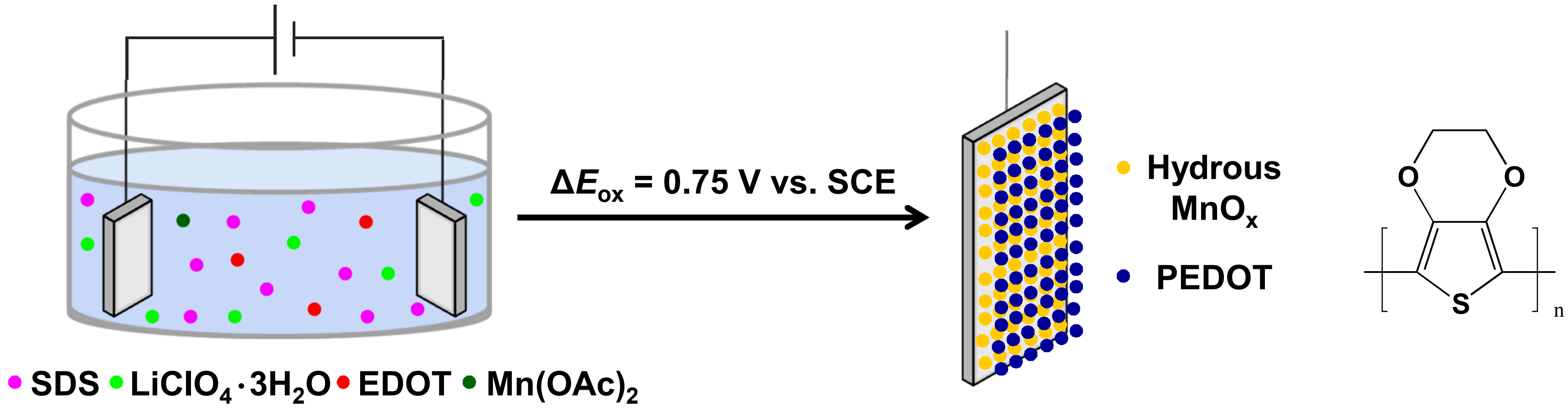
GLC:
Conductivity = 2.59 S/cm
Surface Area (carbon) = 900-1000 m^2/g
Excellent Dispersion of NWs

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

What about intrinsically conductive polymers?

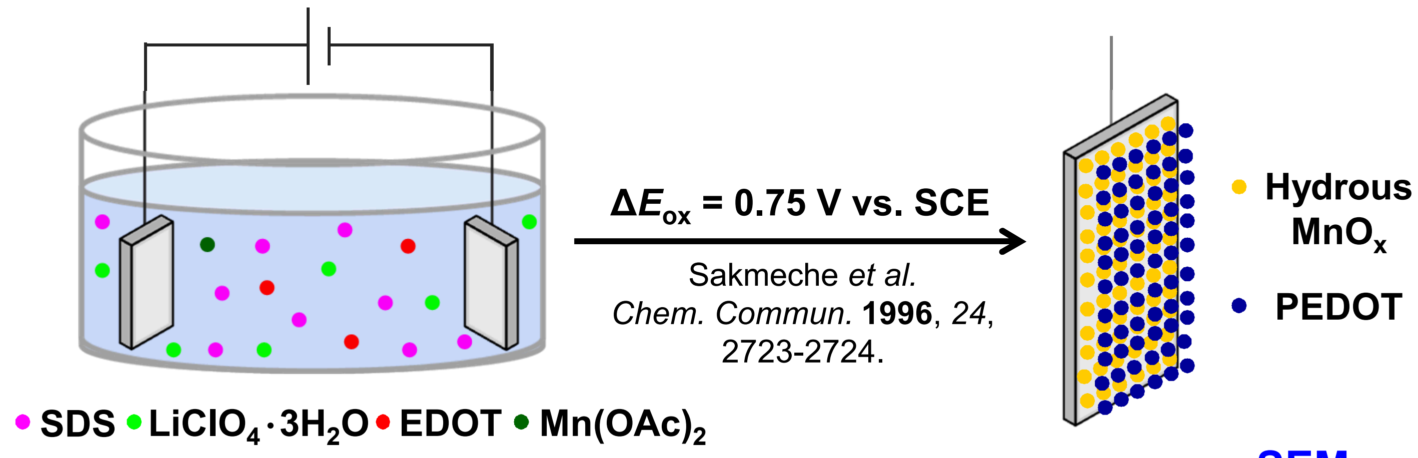


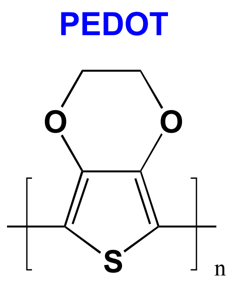
- **PEDOT discovered in 1980's**
- **Prepared via chemical or electrochemical methods**
- **Highly Conductive ~ 1-100 S cm^{-1} and stable**
- **PEDOT/PSS as replacement for Nafion (PEM fuel cells)**
- **PEDOT is catalyst for ORR in alkaline – limited literature**
- **MnOx/PEDOT studied extensively for super-capacitors**
  Core-shell structures *vs.* Good dispersion
- **Perfect Project for a HS Student ! (Kaitlyn Eldred)**

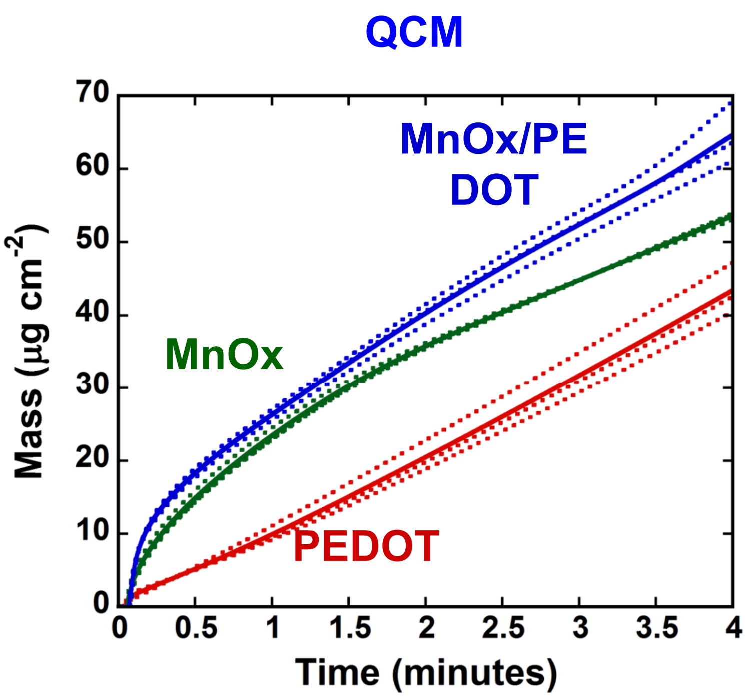
J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

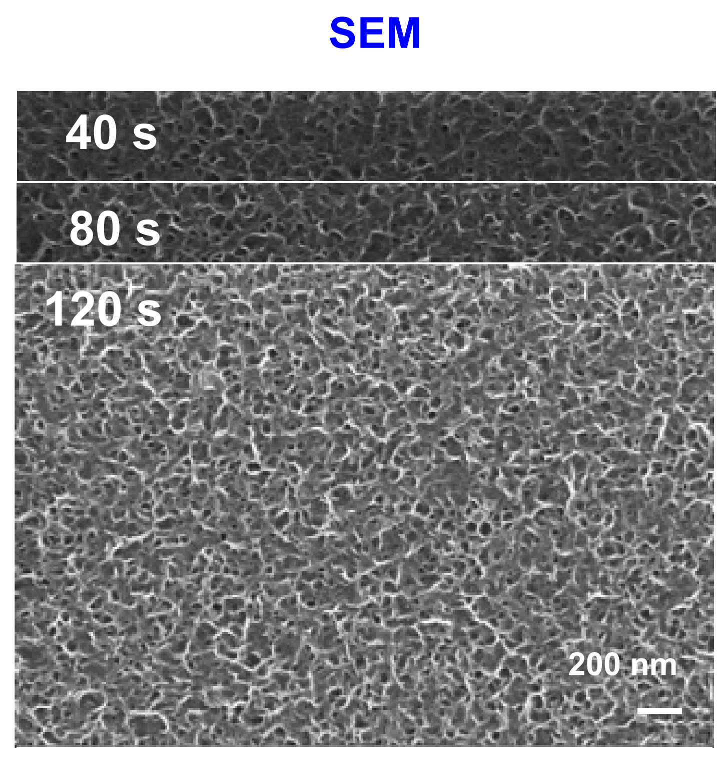
MnOx/PEDOT composite thin films for the ORR

Sandia National Laboratories

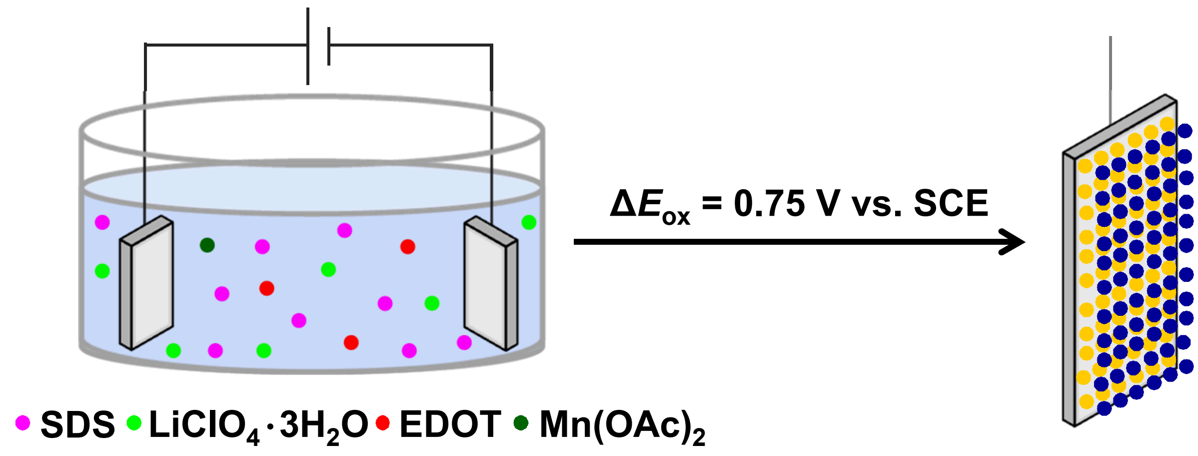


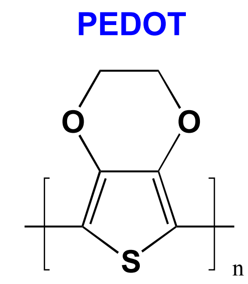


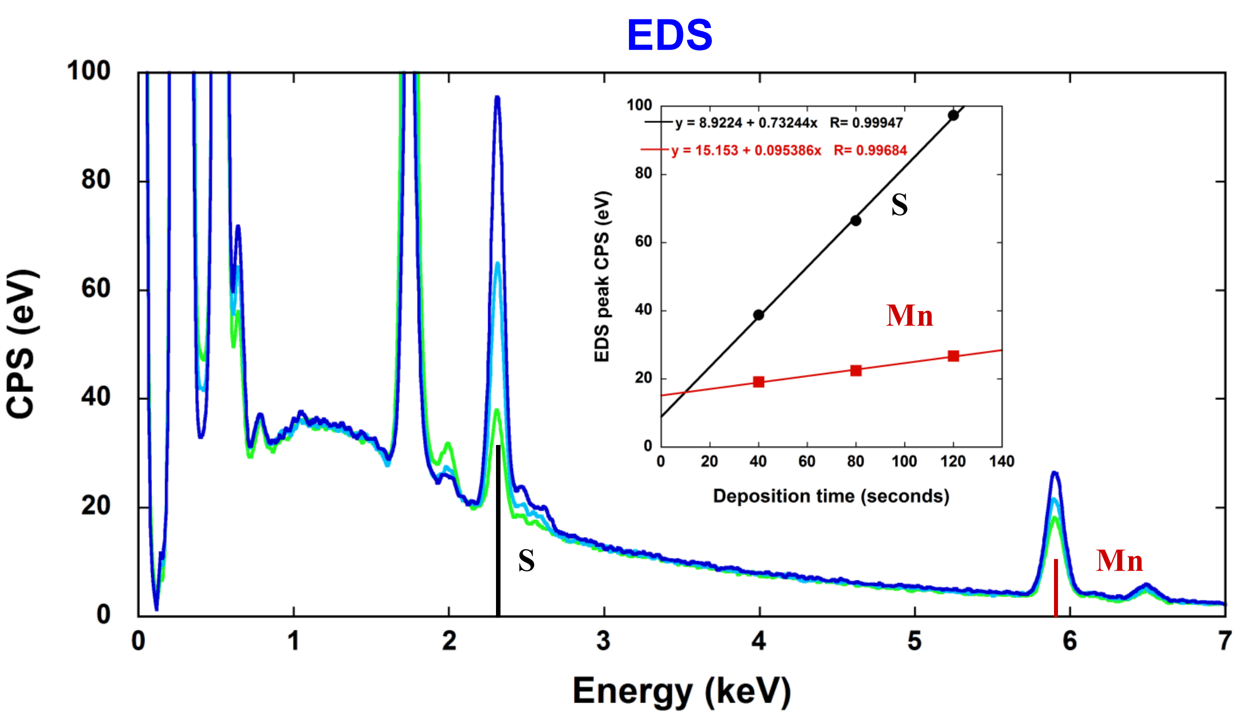


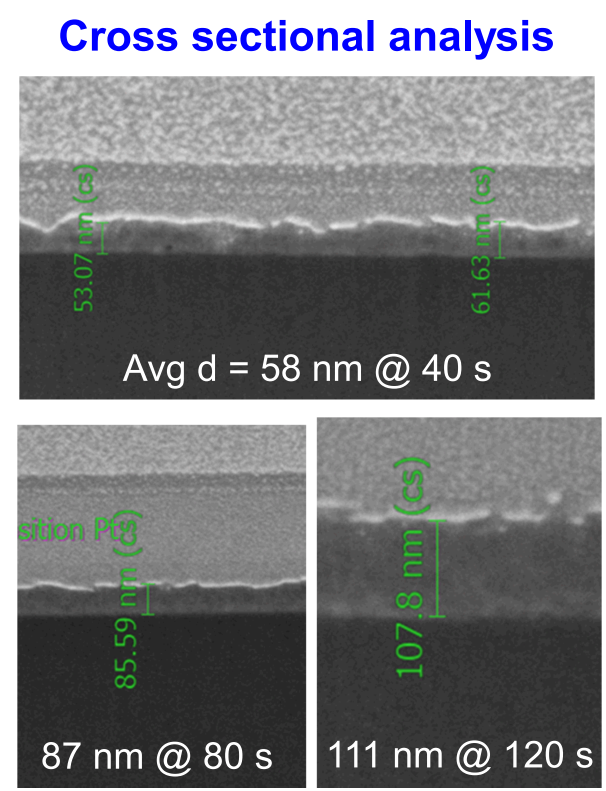


MnOx/PEDOT composite thin films for the ORR



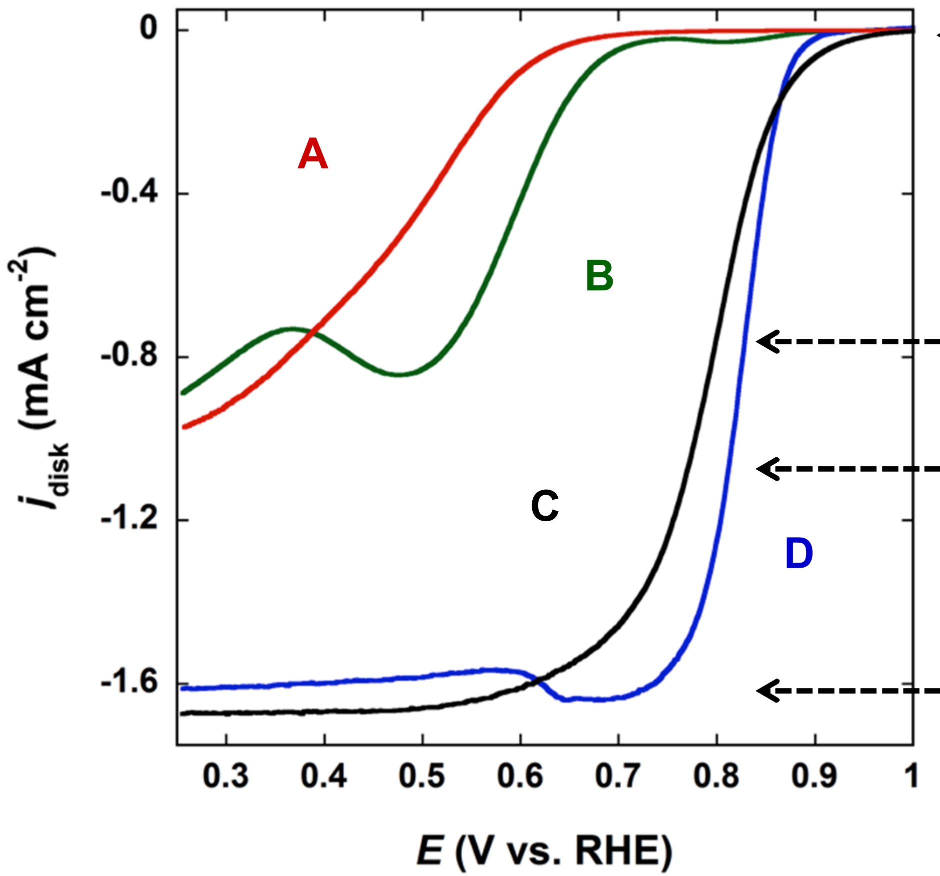






J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

RDE Electrode Data



Onset Value

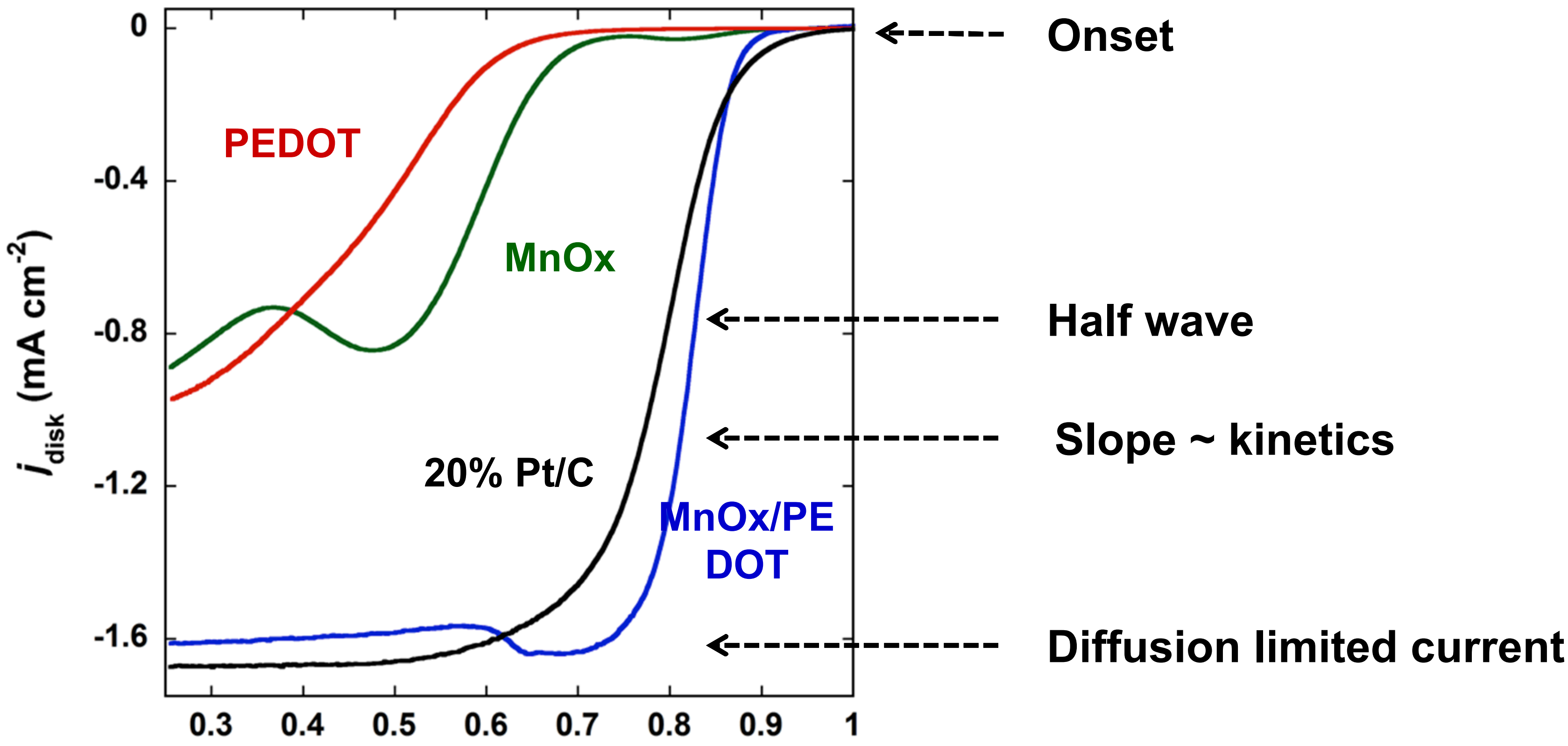
Half wave potential

Slope ~ kinetics

Diffusion limited current

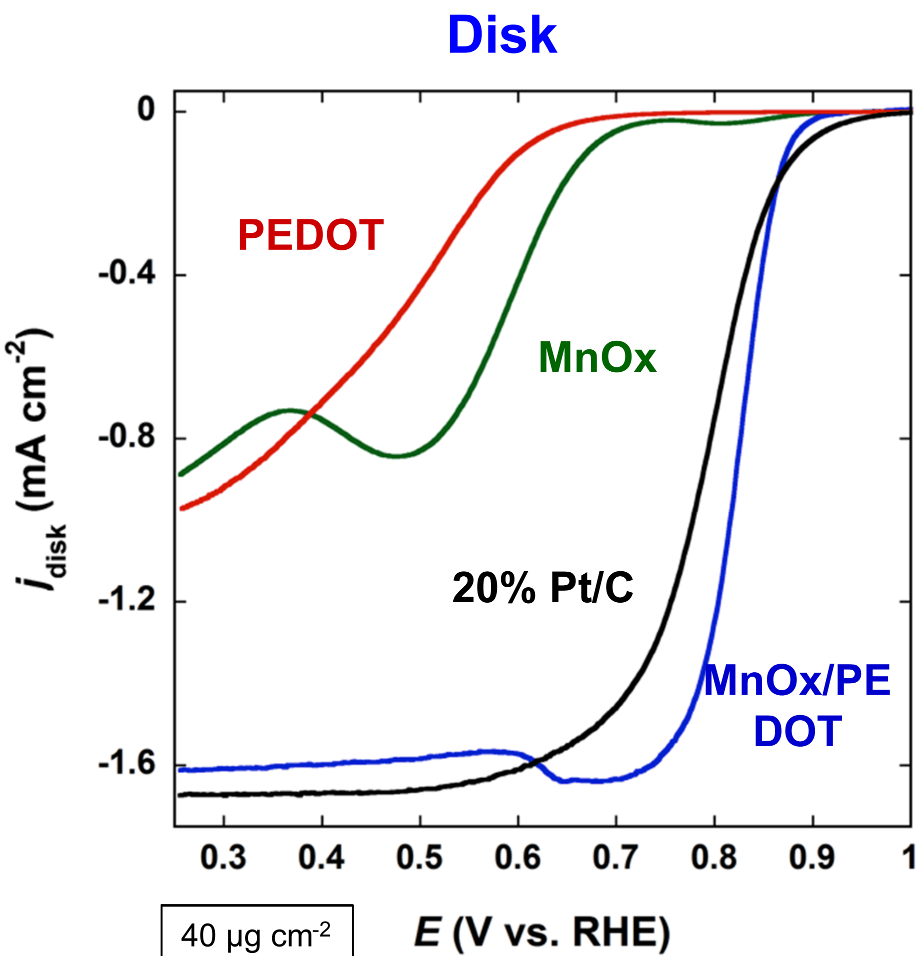
Mass loading
Rotation rate
Scan rate

MnOx/PEDOT composite thin films for the ORR

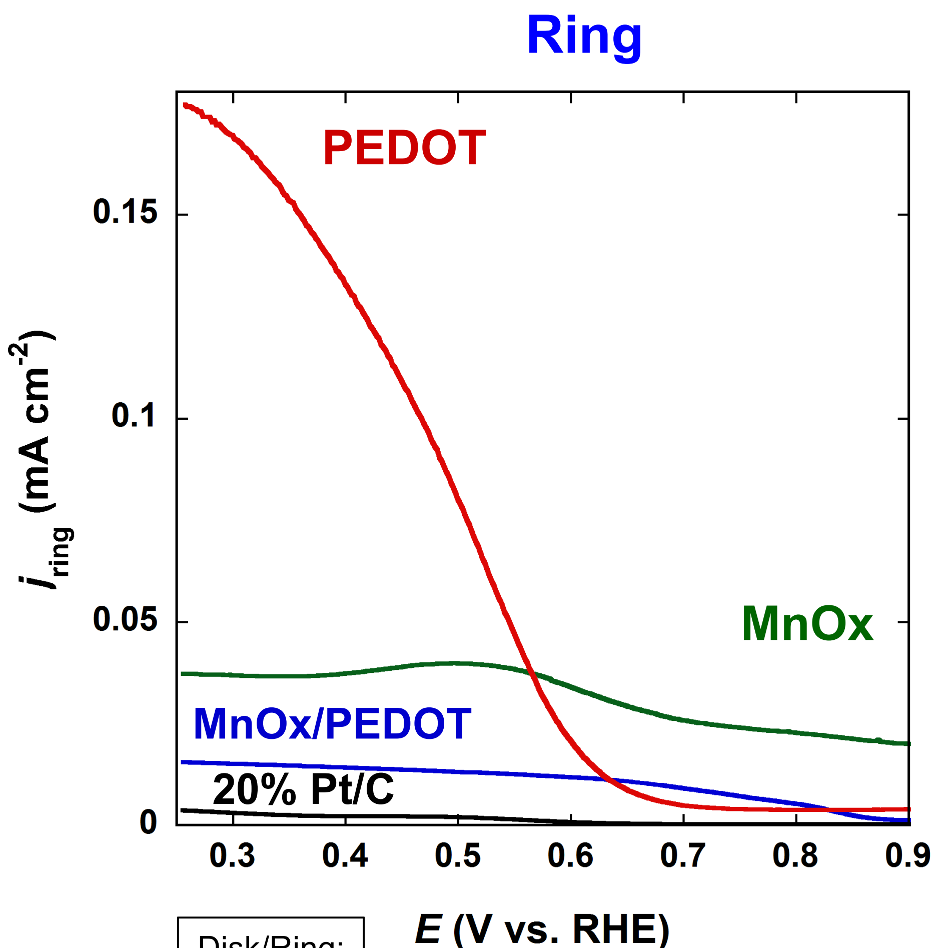


40 μg cm^{-2}
400 rpm
5 mV s^{-1}

MnOx/PEDOT composite thin films for the ORR



40 µg cm^{-2}
400 rpm
2 mV s^{-1}



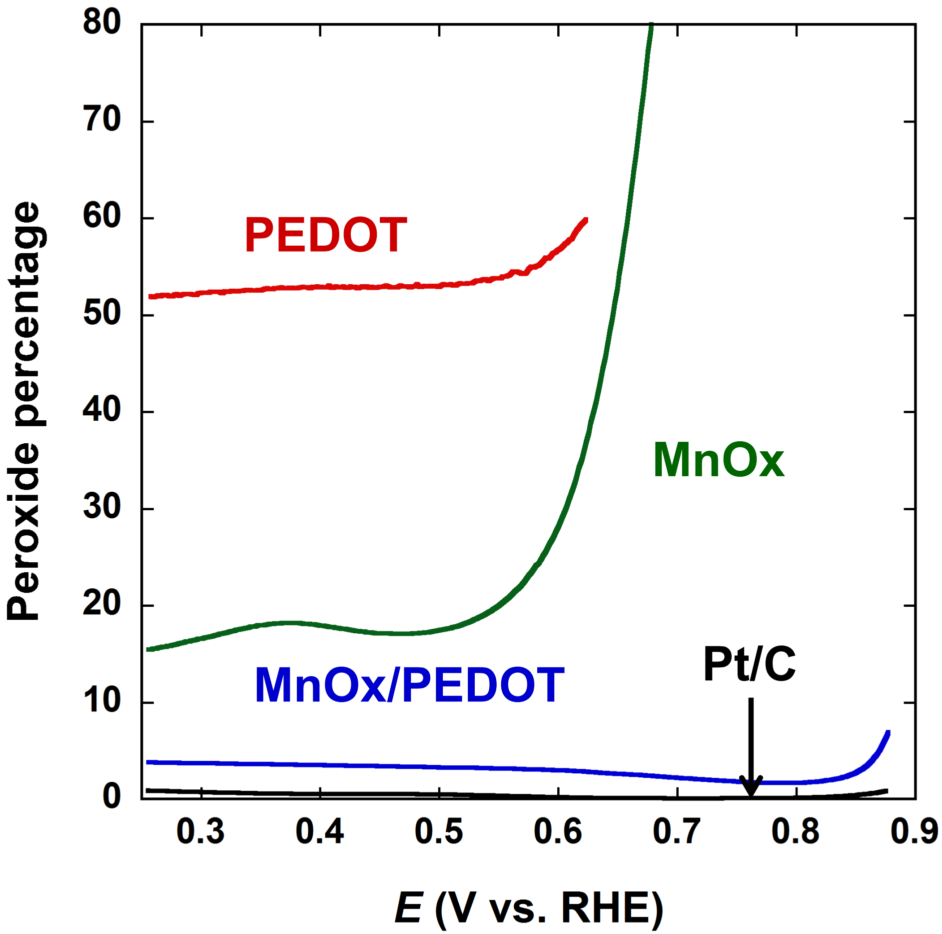
Disk/Ring:
C/Pt
C/Au
C/C

J. A. Vigil *et al.* *ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

MnOx/PEDOT composite thin films for the ORR

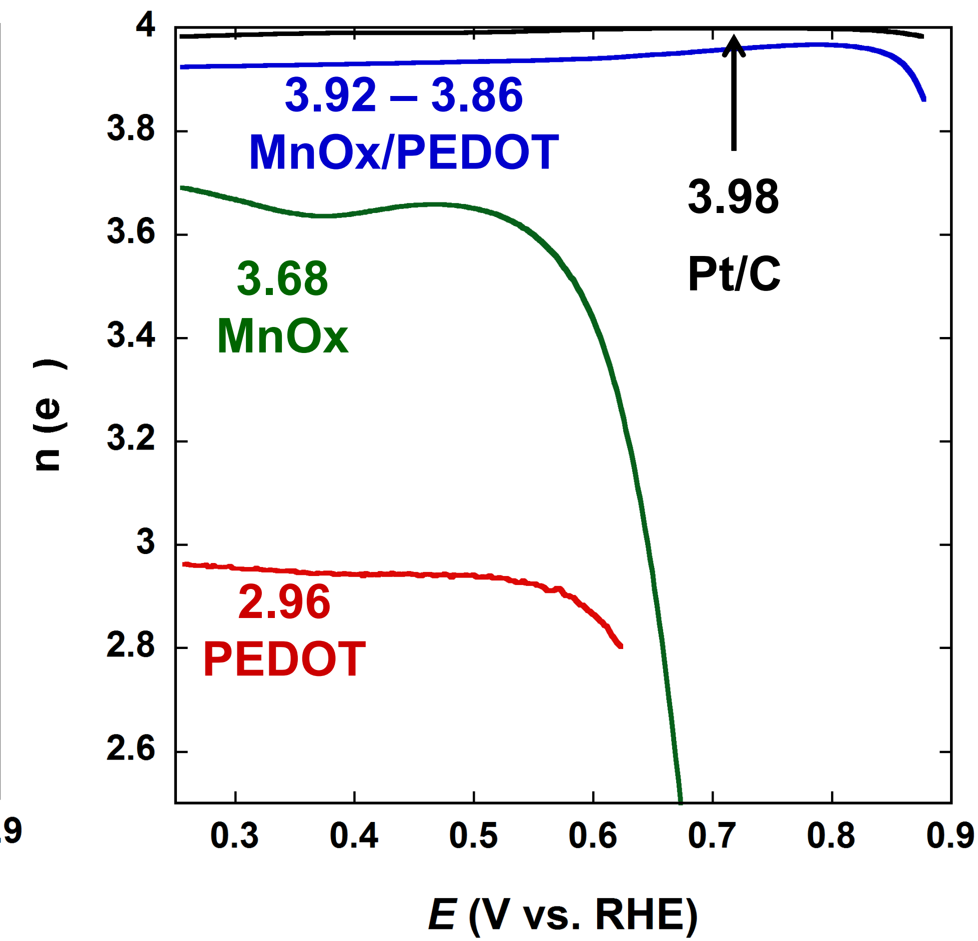
Sandia National Laboratories

Peroxide formed



$$\%H_2O_2 = 200 \ (I_R/N) \ / \ (I_R/N+I_D)$$

n value

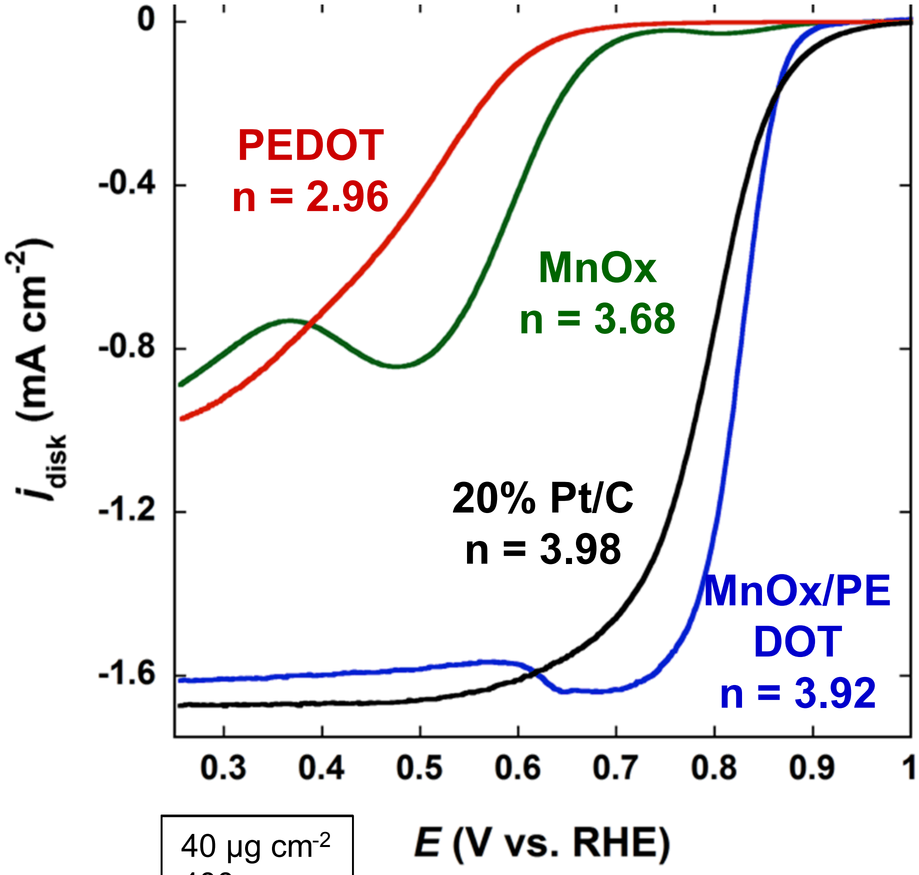


$$n = 4 \ (I_D)/(I_D+I_R/N)$$

J. A. Vigil *et al.* *ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

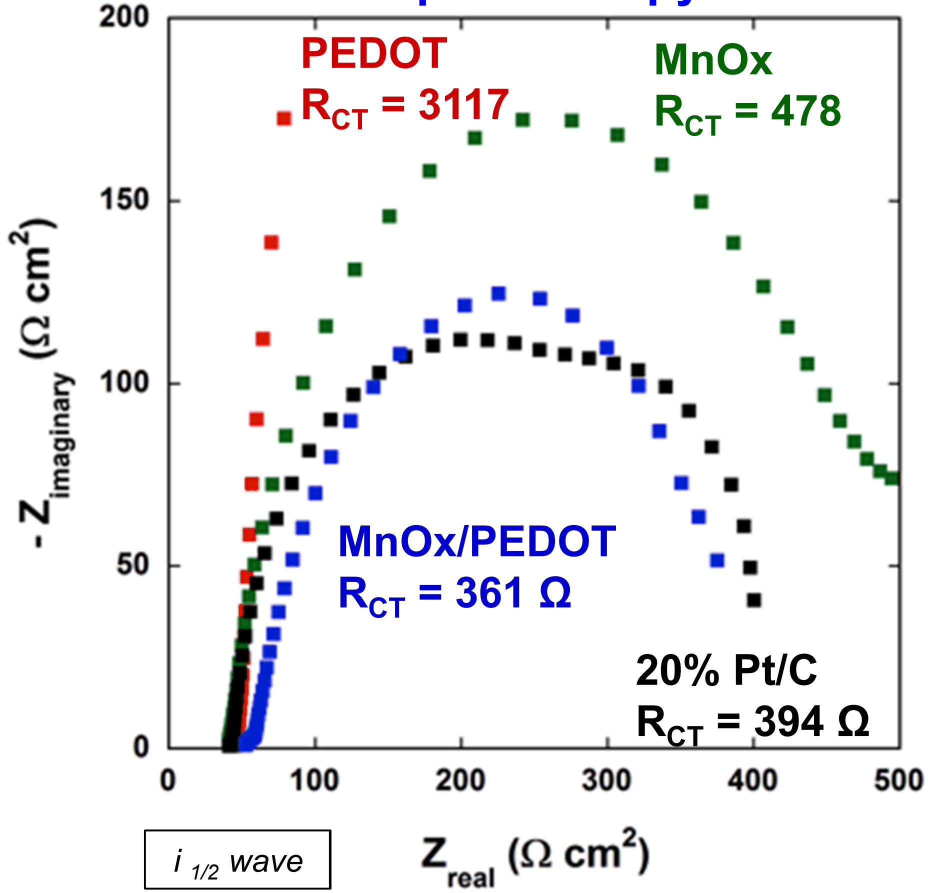
MnOx/PEDOT composite thin films for the ORR

Oxygen reduction reaction
(O_2 + $2H_2O$ + $4e^-$ = $4OH^-$)



40 µg cm^{-2}
400 rpm
2 mV s^{-1}

Electrochemical Impedance Spectroscopy

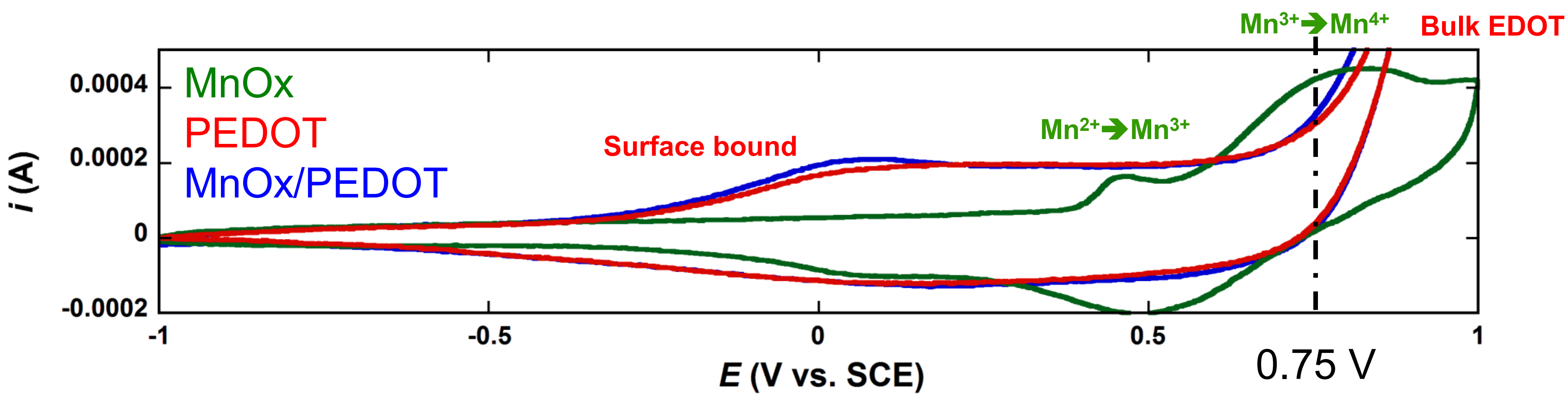


$i_{1/2}$ wave

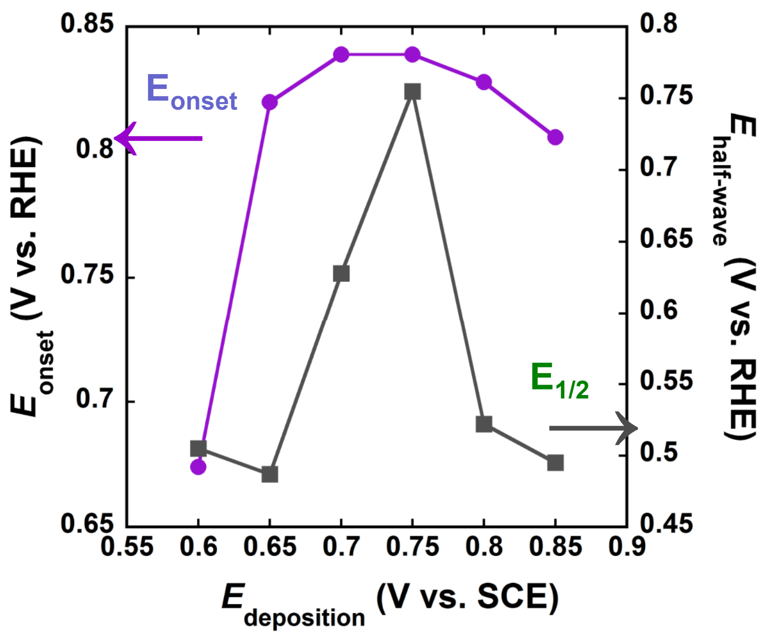
Composite improvement over components alone → synergism

J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

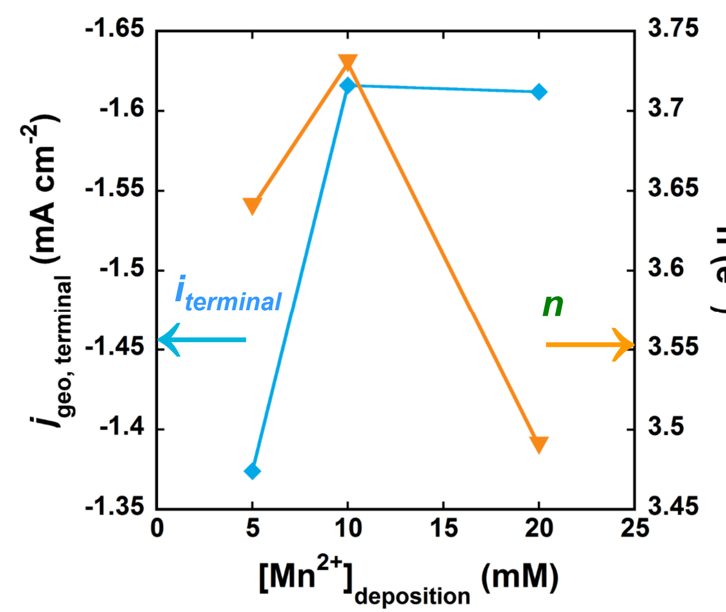
MnOx/PEDOT composite thin films for the ORR



Optimize Potential



Optimize Concentration



MnOx/PEDOT composite thin films for the ORR

Sandia National Laboratories

	ORR onset potential (V vs. RHE)	ORR half wave potential (V vs. RHE)	ORR terminal mass activity (mA mg^{-1}) [terminal potential vs. RHE]	Mass loading (mg cm^{-2})	*n* value (e^-)	Rotation rate (RPM)
MnO_x/PEDOT□	0.877	0.825	-40.425 [0.25 V]	0.040	3.92	400
PEDOT-$CoMn_2O_4$[1]	0.707	0.575	-0.014 [0.26 V]	352.1	3.9	500
PEDOT-hemin20[2]	0.727	0.407	-14.723 [-0.24 V]	0.153	3.8	400
HPCF-800[3]	0.757	0.732	-19.635 [0.16 V]	0.153	3.7	400
PEDOT/rGO/ H_2SO_4[4]	0.807	0.727	-15.833 [0.16 V]	0.120	3.3 – 3.8	400
PEDOT double-layer bowls[5]	0.657	0.557	-3.531 [-0.24 V]	0.354	2.92	900
GC/PEDOTIL[6]	0.635	0.535	ND$^{\Psi}$ [-0.03 V]	ND	2	400
PEDOT[7]	0.702	0.397	-17.0 [0.06 V]	0.1	ND	ND
VPP-PEDOT[8]	0.732	0.544	ND [0.06]	ND	ND	1500

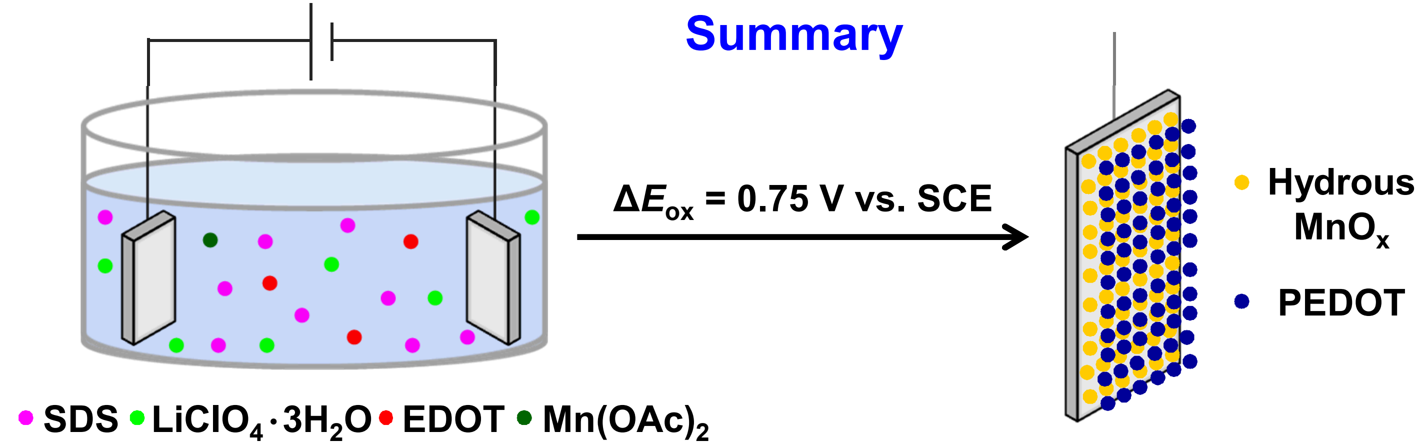
MnOx/PEDOT is most active PEDOT catalysts to date

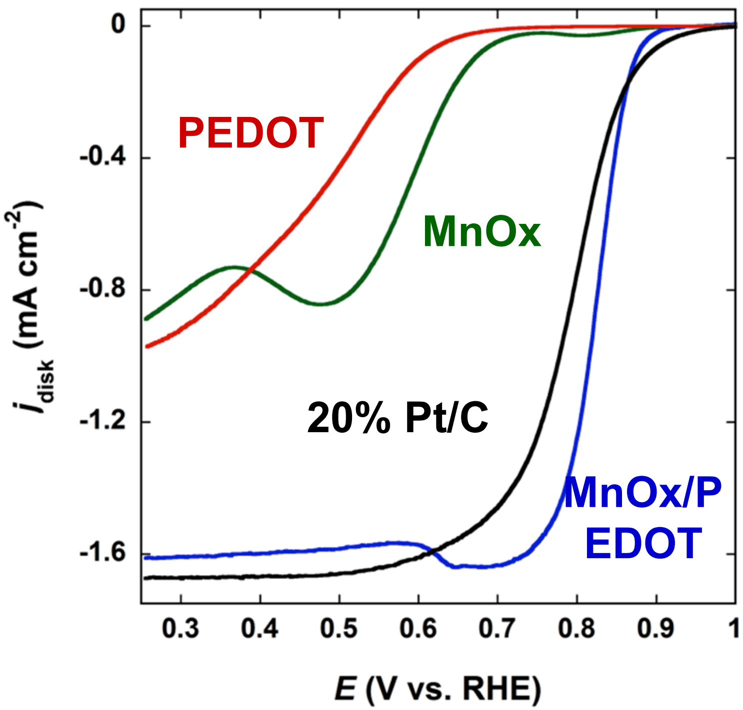
(Onset, half wave and terminal current)

Promising as Pt/C alternative for alkaline ORR

J. A. Vigil *et al.* *ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

PEDOT/MnOx electrocatalysts



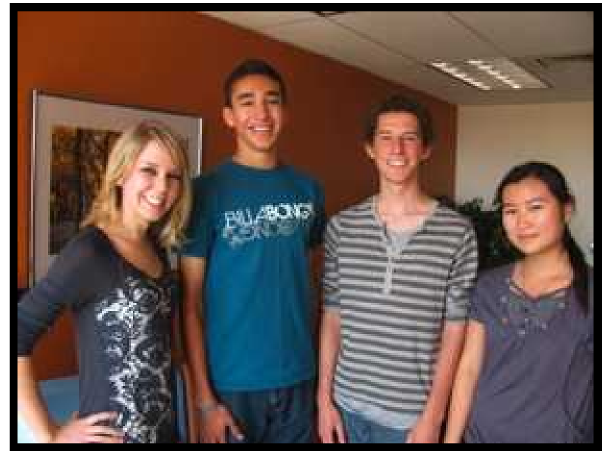


- Simple electrodeposition
- MnO_x/PEDOT >> PEDOT or MnOx
- Synergistic behavior observed
- MnO_x/PEDOT (n = 3.92) on par with Pt/C (n = 3.98)
- ICPs as potential replacement for C ?

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
High School Student

- Additional SNL/CINT collaborators:

Collin Delker, Mark Rodriguez,

Mike Brumbach, Eric Coker,

Paul Kotula, Ben Christensen

Steven Limmer, Ph.D

Patrick Burton, Ph.D.

Madalyn Hungate
High School Student

Kaitlyn Eldred
High School Student

- Rice University collaborators

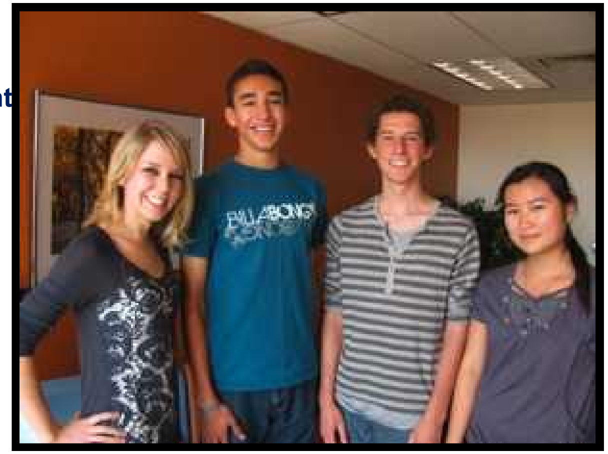
Professor James M. Tour's Group

Thank you

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



Kaitlyn Eldred
Manzano High School

Suzanne White
El Dorado High School

- Additional SNL collaborators:

Mike Brumbach, Eric Coker,

Paul Kotula, Mark Rodriguez,

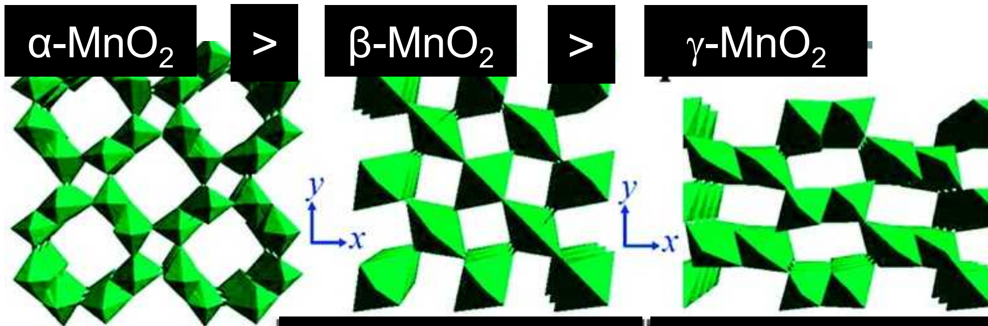
- Rice University collaborators

(Graphene materials):

Professor James M. Tour's Group

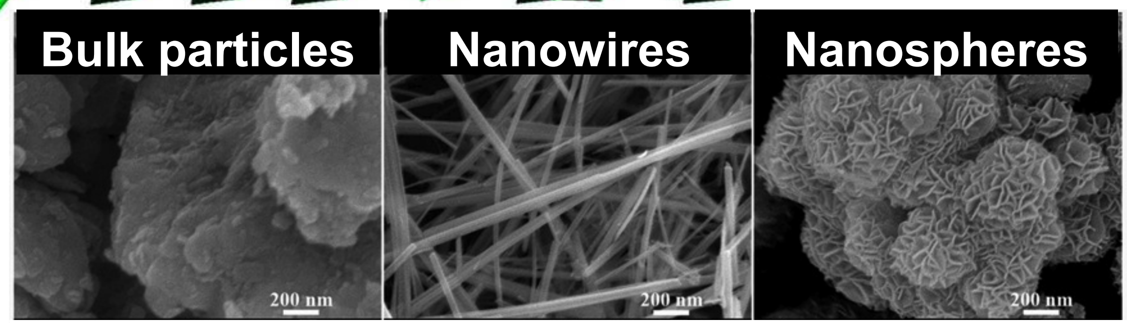
What factors are important ?

- Size: Nano >Micro
- Phase: α-MnO_2 > β-MnO_2 > γ-MnO_2



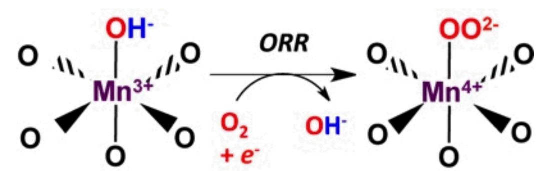
F. Cheng, *et al.*
Chem. Mater. **2010**, *22*, 898–905

- Morphology



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

- Valency: Mn(III)/Mn(IV) ratio

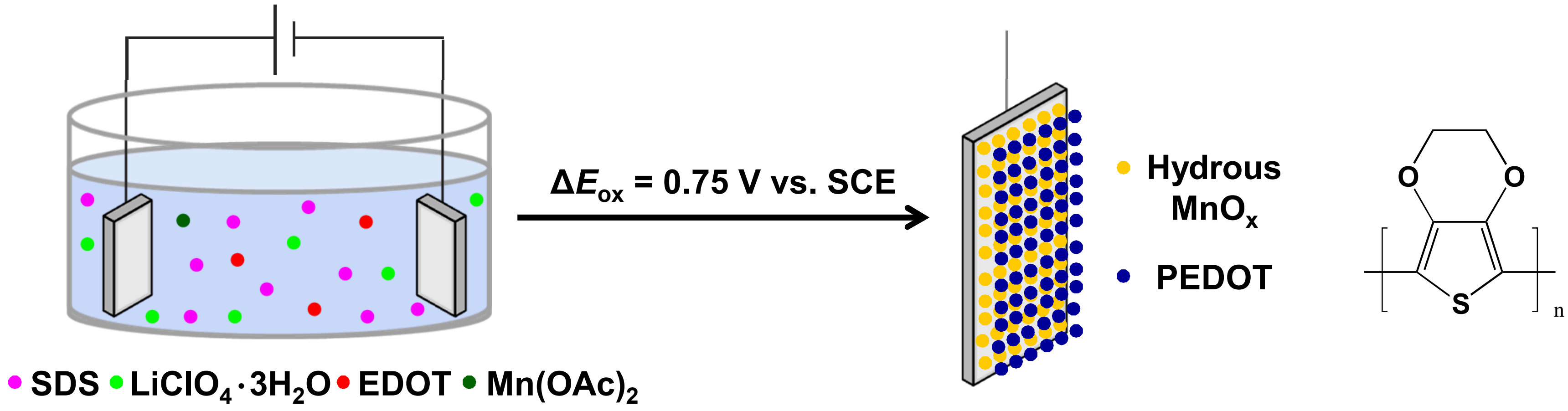


- Conductivity (Doping, Hybridize with NPs, carbon)

D. J. Davis *et al. J. Phys. Chem. C.* **2014**, *118*, 17342-17350.

What about intrinsically conductive polymers?

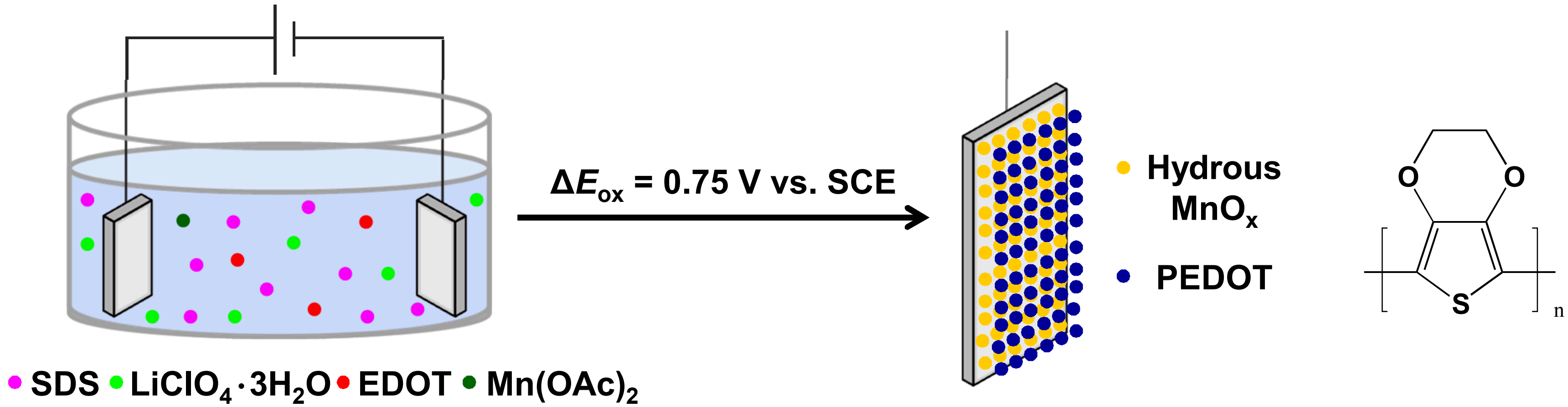
Sandia National Laboratories



- PEDOT discovered in 1980's
- Prepared via chemical or electrochemical methods
- Highly Conductive ~ 1-100 S cm^{-1} and stable
- PEDOT/PSS as replacement for Nafion (PEM fuel cells)
- PEDOT is catalyst for ORR in alkaline – limited literature
- MnOx/PEDOT studied extensively for super-capacitors
- Perfect Project for a HS Student ! (Kaitlyn Eldred)

J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

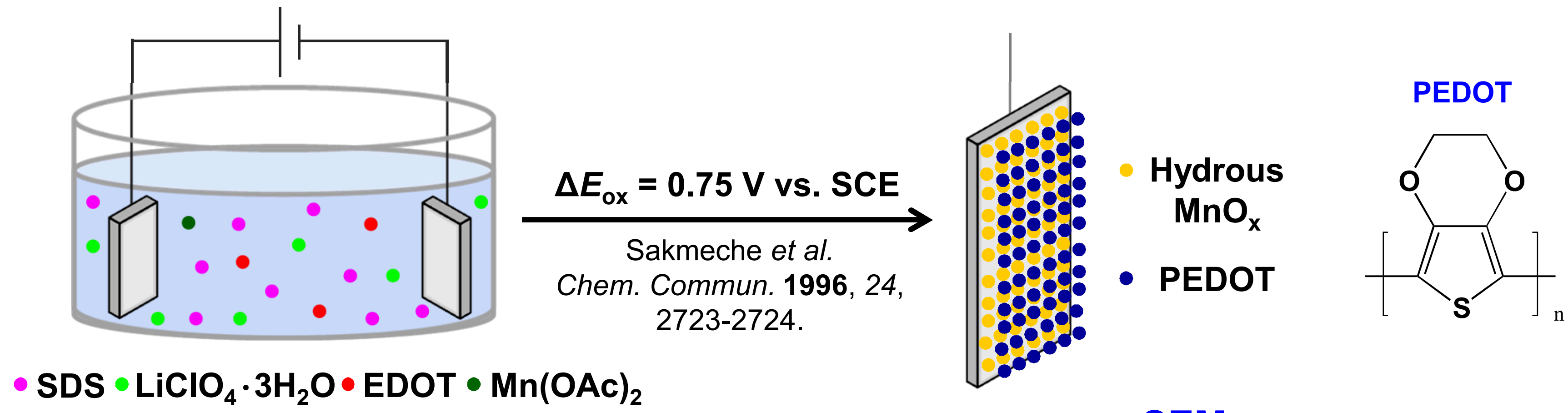
What about intrinsically conductive polymers?



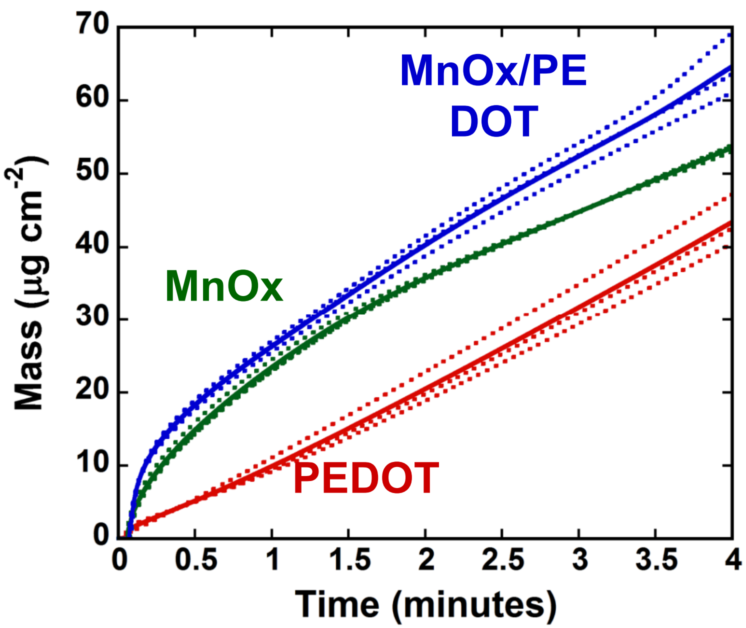
- **PEDOT discovered in 1980's**
- **Prepared via chemical or electrochemical methods**
- **Highly Conductive ~ 1-100 S cm^{-1} and stable**
- **PEDOT/PSS as replacement for Nafion (PEM fuel cells)**
- **PEDOT is catalyst for ORR in alkaline – limited literature**
- **MnOx/PEDOT studied extensively for super-capacitors**
- **Perfect Project for a HS Student ! (Kaitlyn Eldred)**

J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

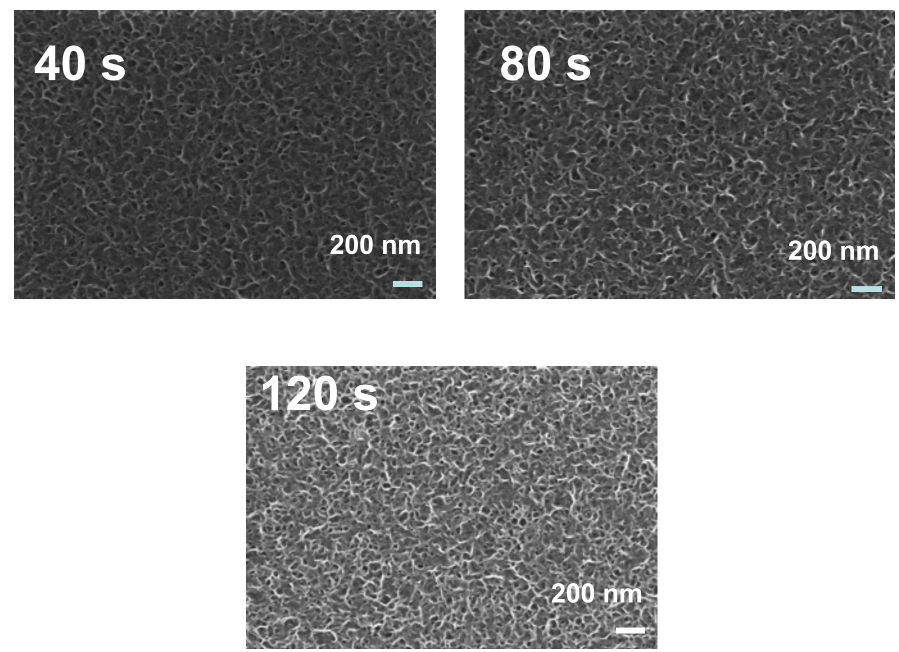
MnOx/PEDOT composite thin films for the ORR



QCM



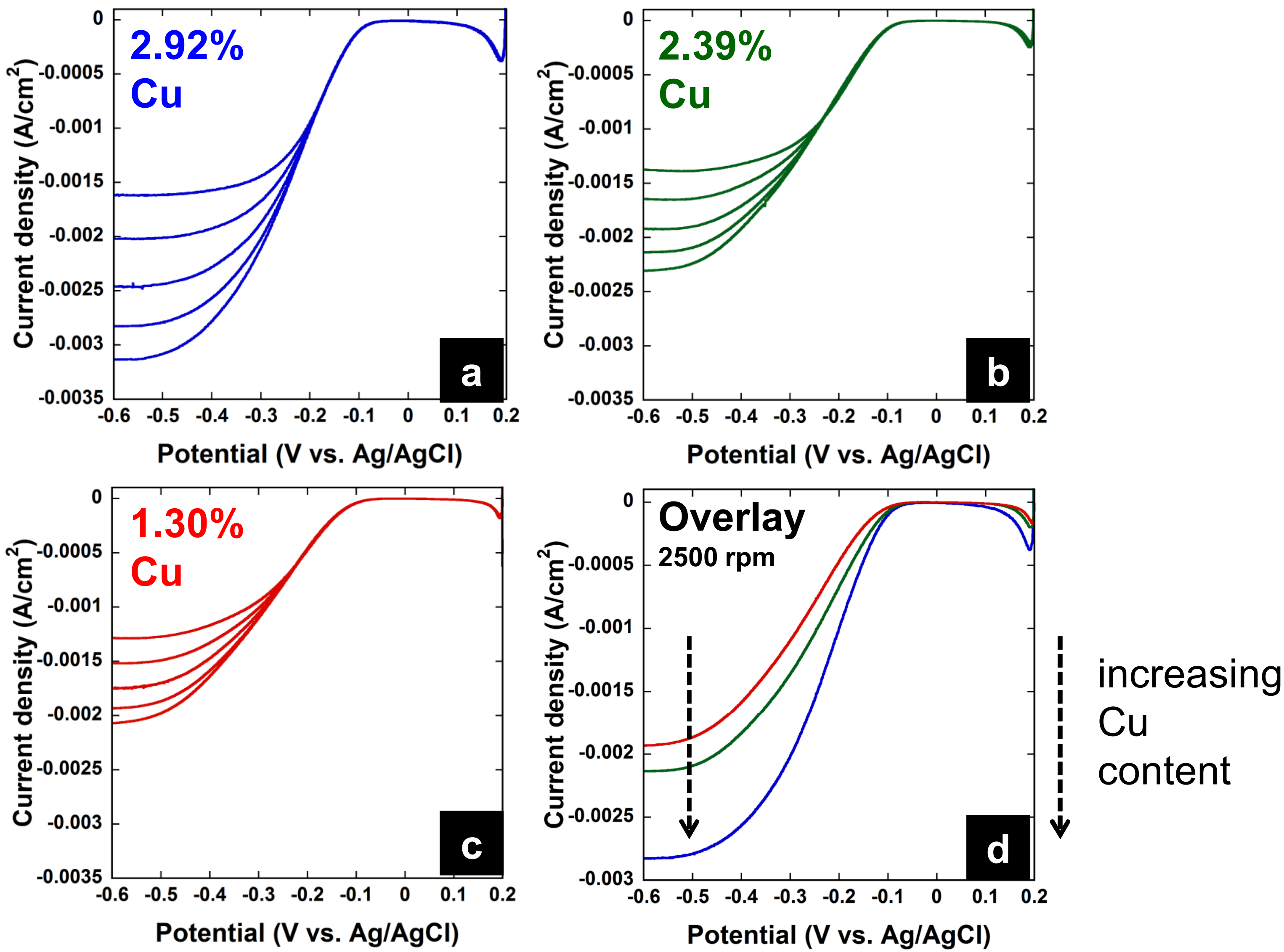
SEM



J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

Electrochemical Analysis

Rotating Disk Electrode (RDE) Studies

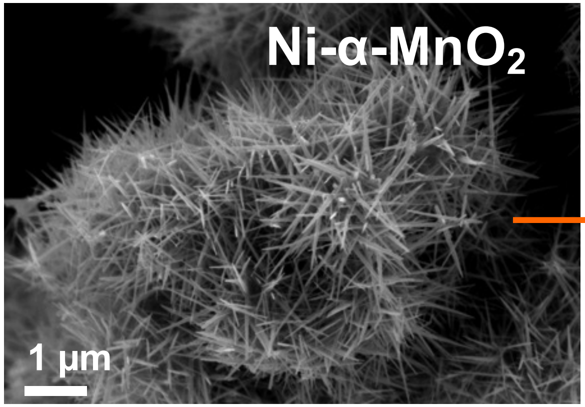


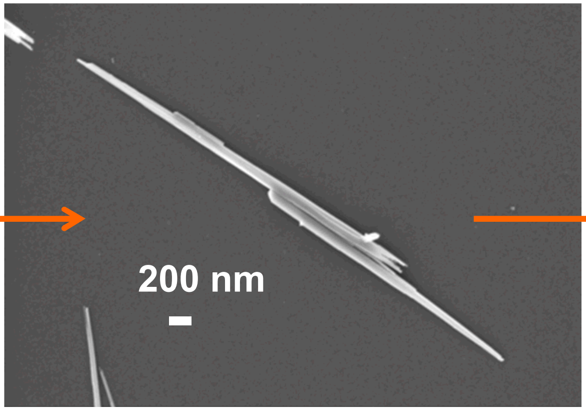
Conductivity effects of M^{n+} ?

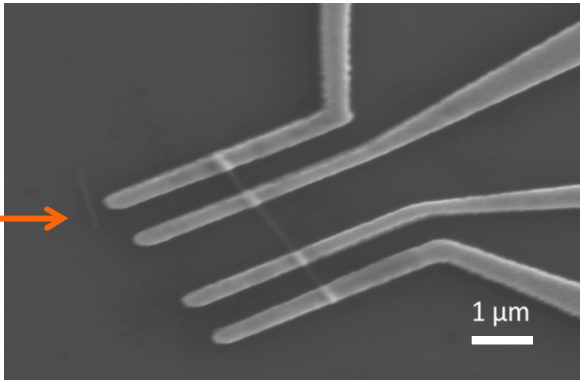
Charge transfer resistance values suggest increased conductivity

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**







4-point conductivity measurements

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

** as determined from EDS

Conductivity effects of M^{n+} ?