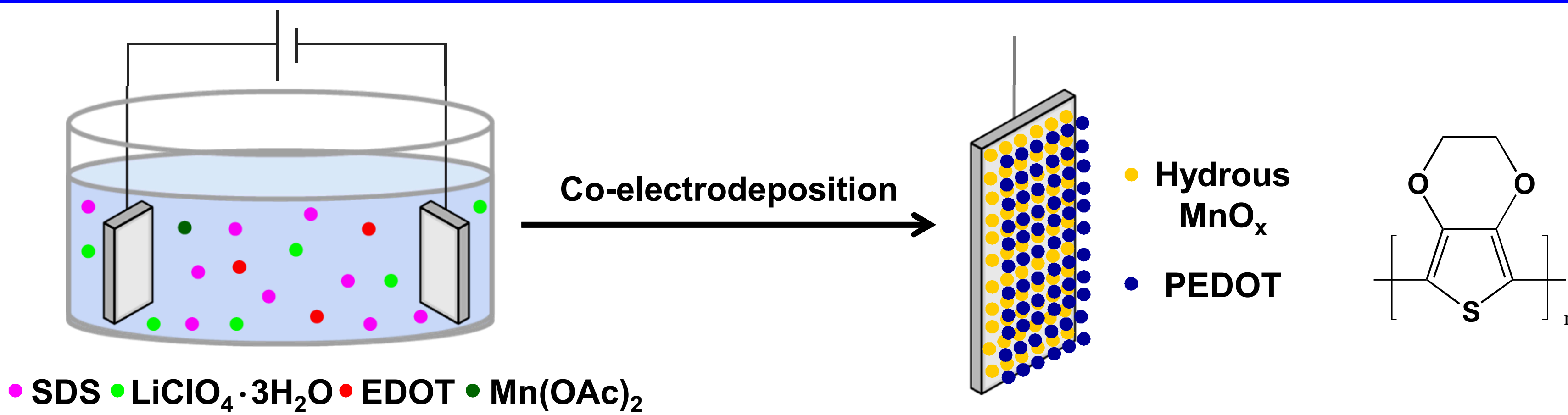
SAND2016-3944C

Exceptional service in the national interest

Sandia National Laboratories

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



MnOx/PEDOT hybrid thin films as ORR electrocatalysts

2016 Spring E-MRS Meeting

May 6th, 2016: Lille, France

Timothy N. Lambert and Julian A. Vigil

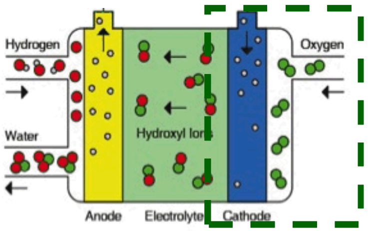
U.S. DEPARTMENT OF ENERGY

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

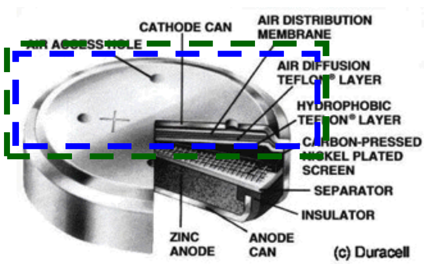
Sandia National Laboratories



Fuel cell schematic

Alkaline fuel cell:

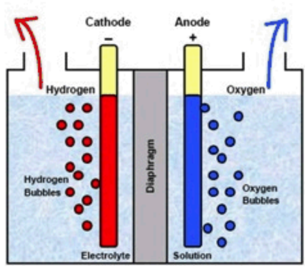
Anode:	$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$	
Cathode:	$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$	Oxygen Reduction Reaction (ORR)
Overall:	$2H_2 + O_2 \longrightarrow 2H_2O$	



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:

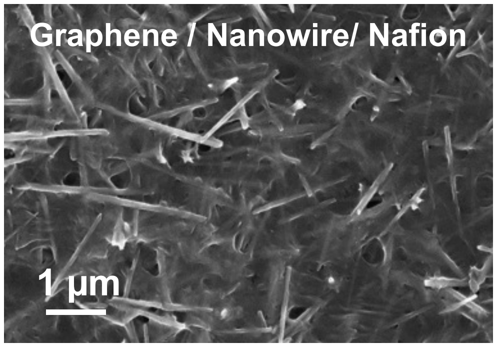
Anode:	$4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$	OER
Cathode:	$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$	Hydrogen Evolution Reaction (HER)
Overall:	$4H_2O \longrightarrow 2H_2 + O_2$	

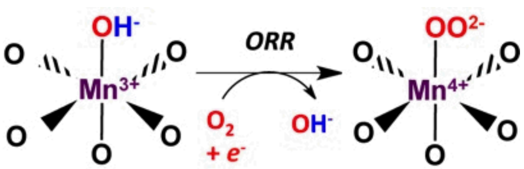
Catalysts: environmentally benign, earth-abundant, and overall potentially cost effective

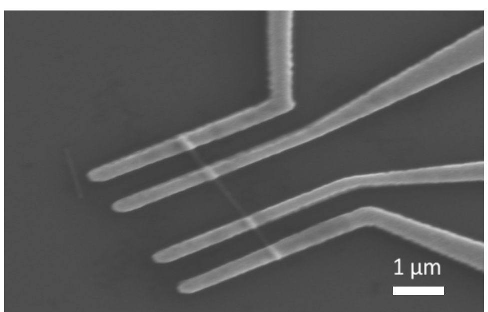
Nanoscale Electrocatalysts

Approach: Develop new nanoscale non-PGM electrocatalysts

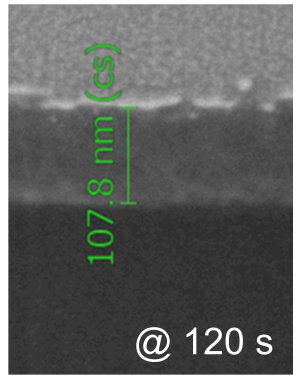
Graphene/Ni-α-MnO_2 Cu-α-MnO_2 Nanowires



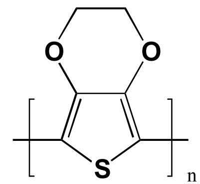


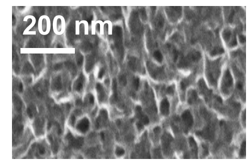


MnOx/PEDOT Thin Films

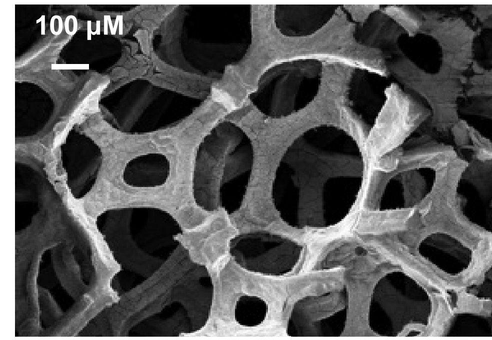


PEDOT

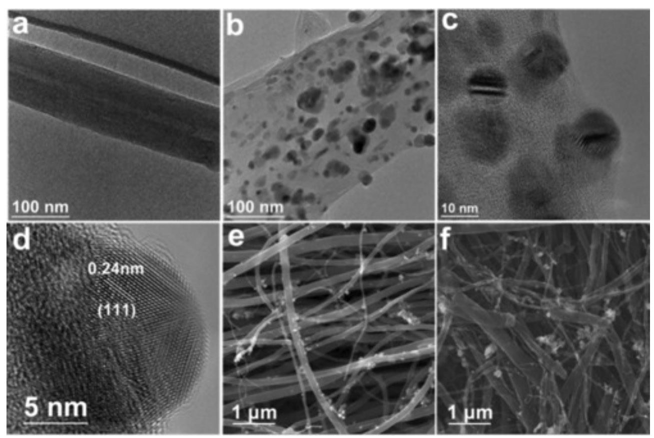




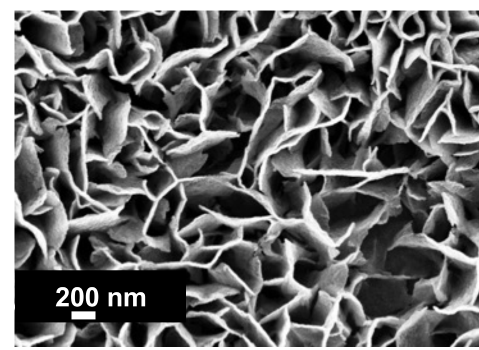
$Ni_xCo_{3-x}O_4$ Thin Films



Graphene Nanoribbon/Ag



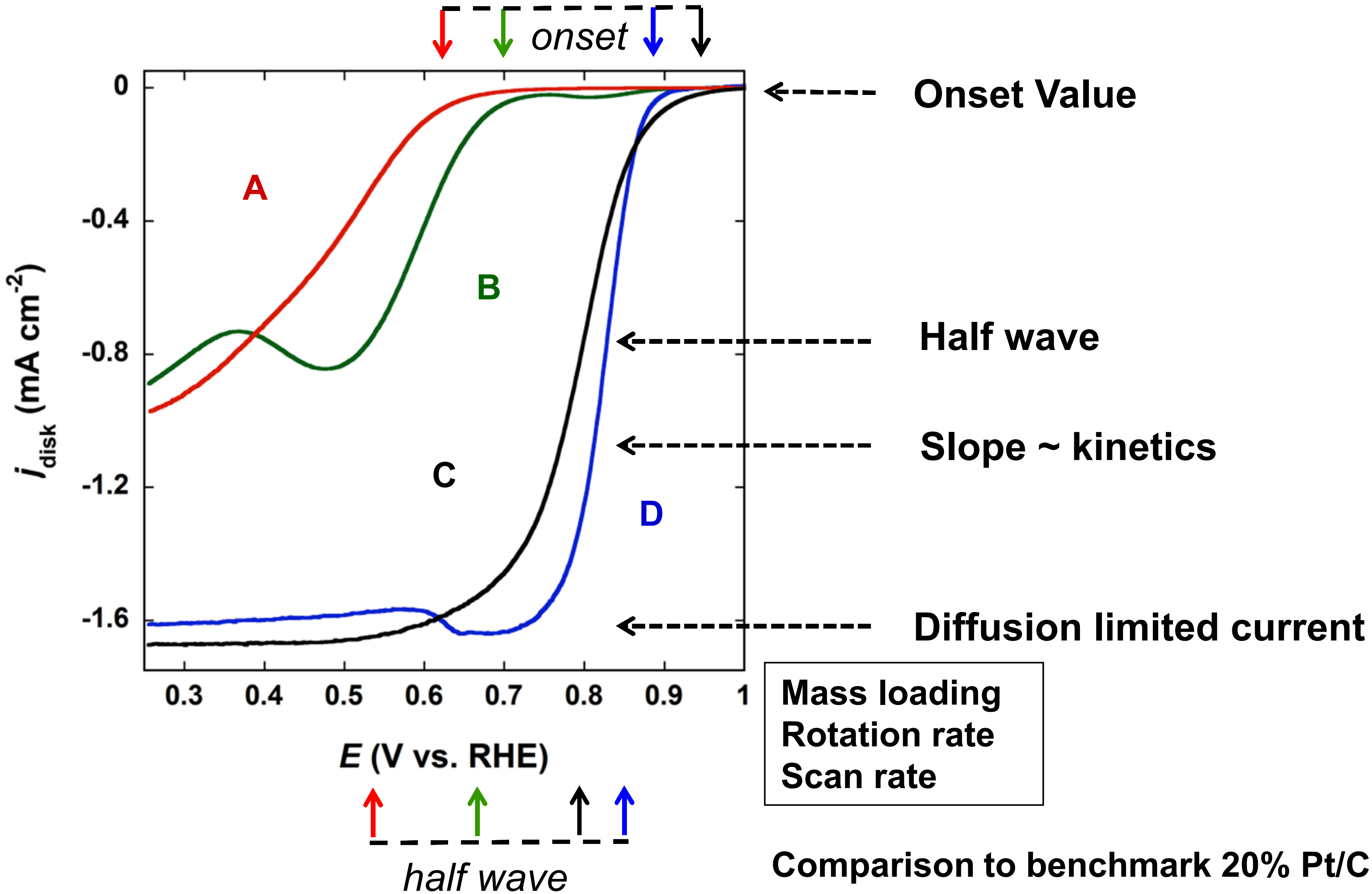
CoP Thin Films and NPs



(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**, RSC Adv. **2015**

RDE Electrode Data

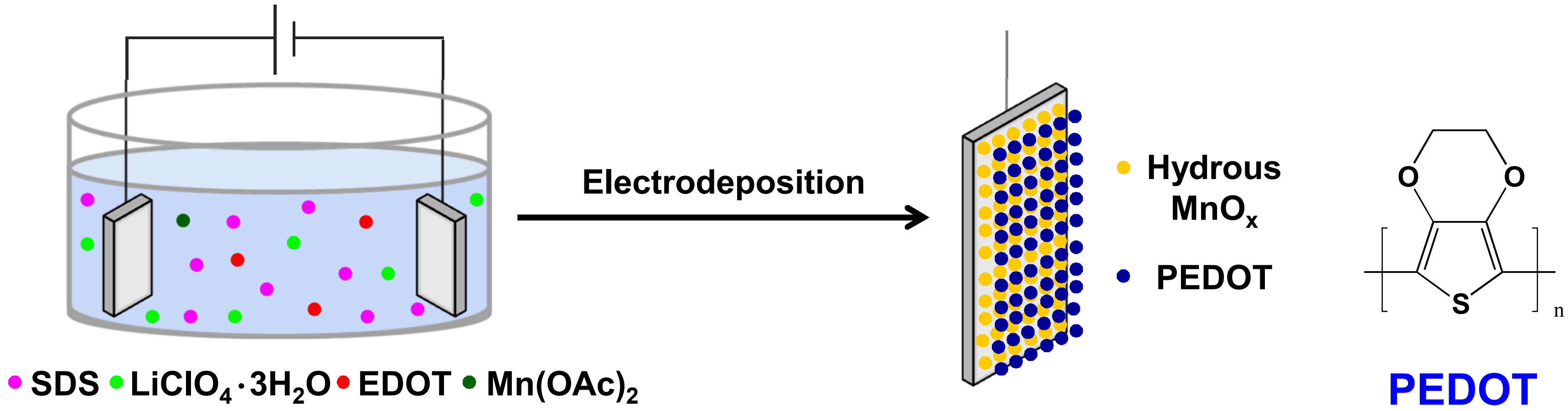
ORR: $O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$ $E° = 1.23$ V vs. RHE



Mass loading
Rotation rate
Scan rate

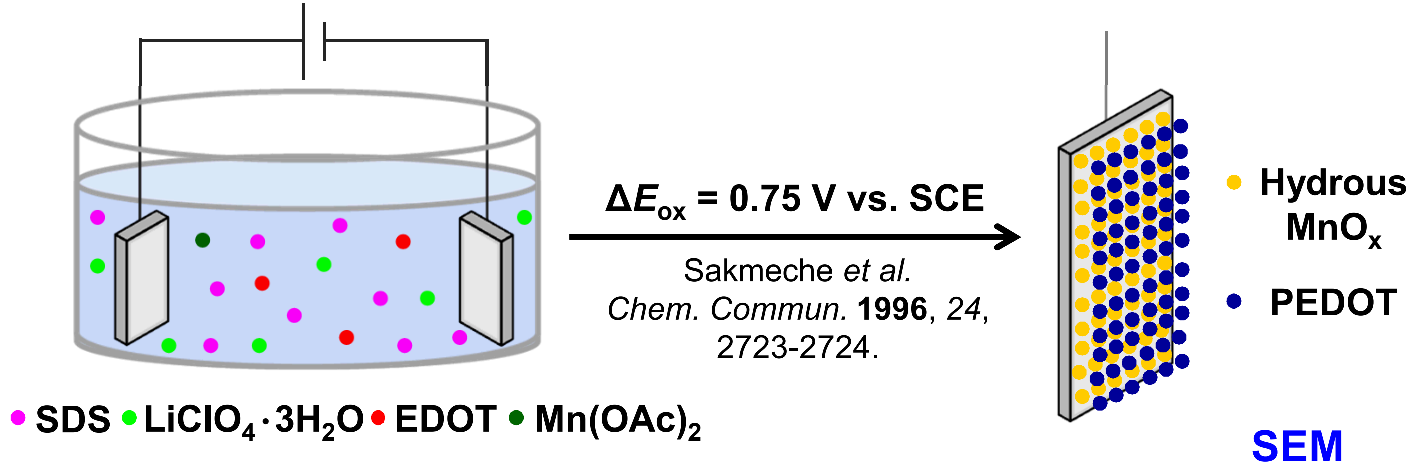
Comparison to benchmark 20% Pt/C

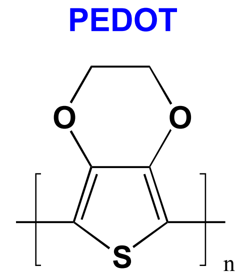
What about intrinsically conductive polymers?

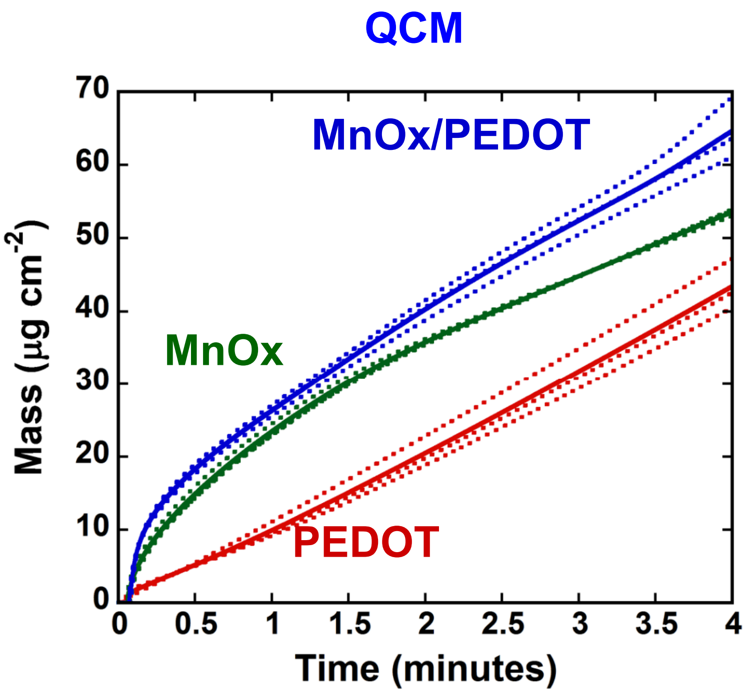


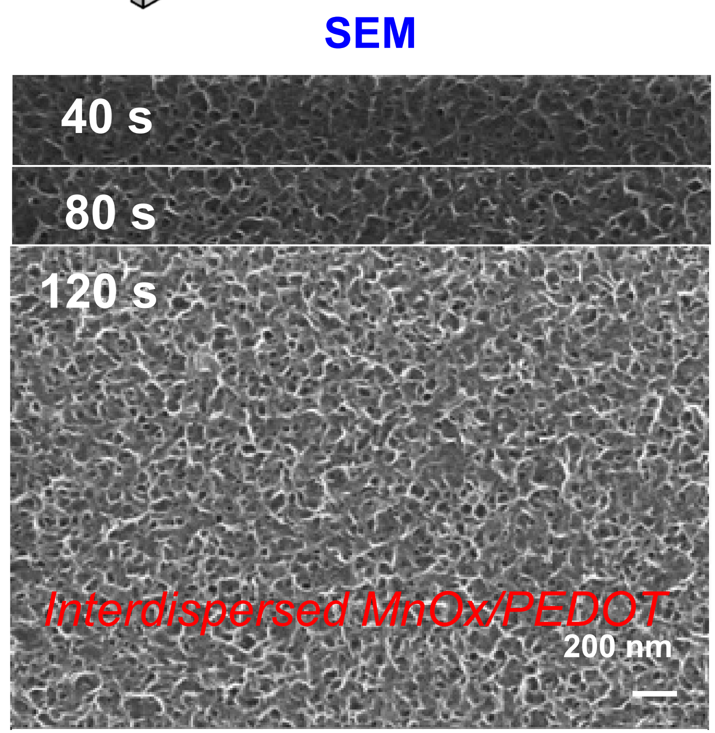
- **PEDOT discovered in 1980's**
- **Prepared via chemical or electrochemical methods**
- **Highly Conductive ~ 1-100 S cm^{-1} and stable**
- **PEDOT/PSS as replacement for Nafion (PEM fuel cells)**
- **PEDOT is catalyst for ORR in alkaline – limited literature**
- **MnOx/PEDOT studied extensively for super-capacitors**
  Core-shell structures vs. Structures with good dispersion/inter-mixing

MnOx/PEDOT composite thin films for the ORR

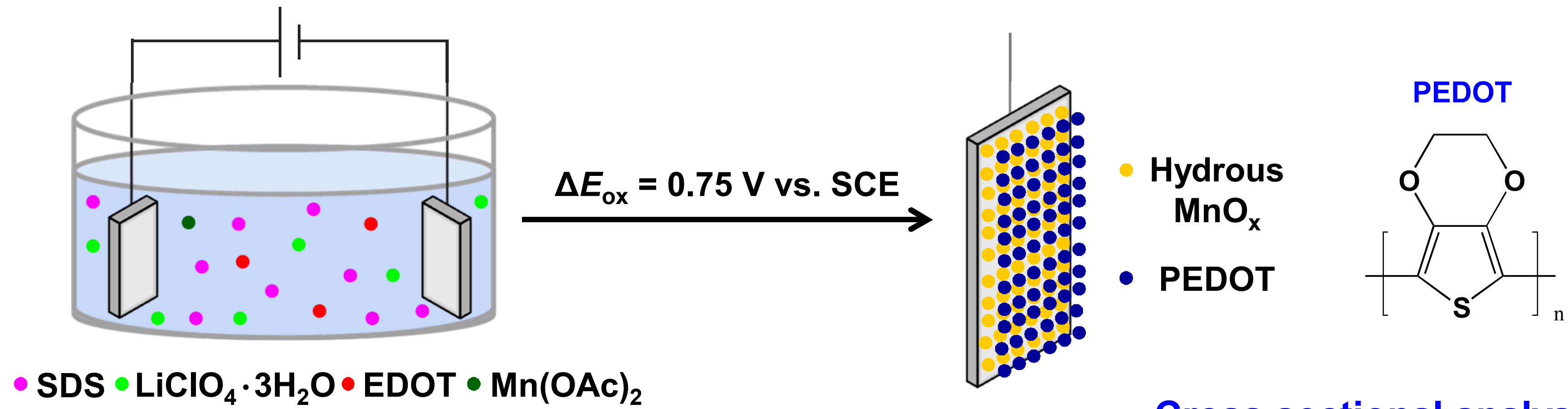




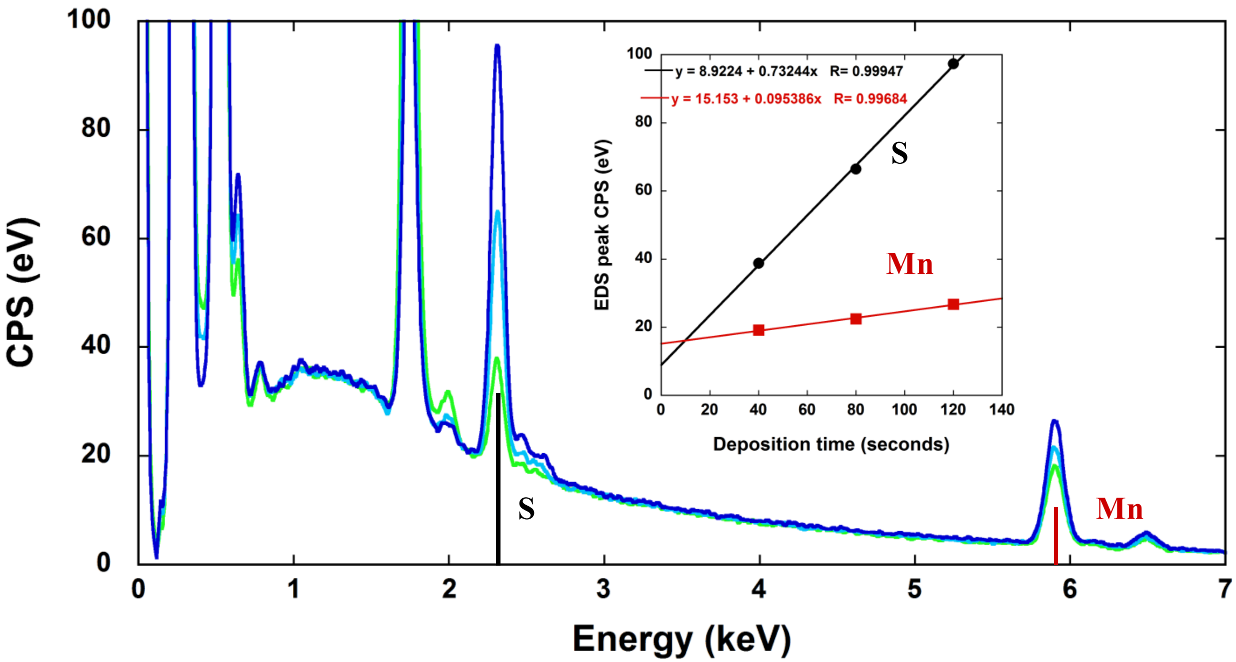




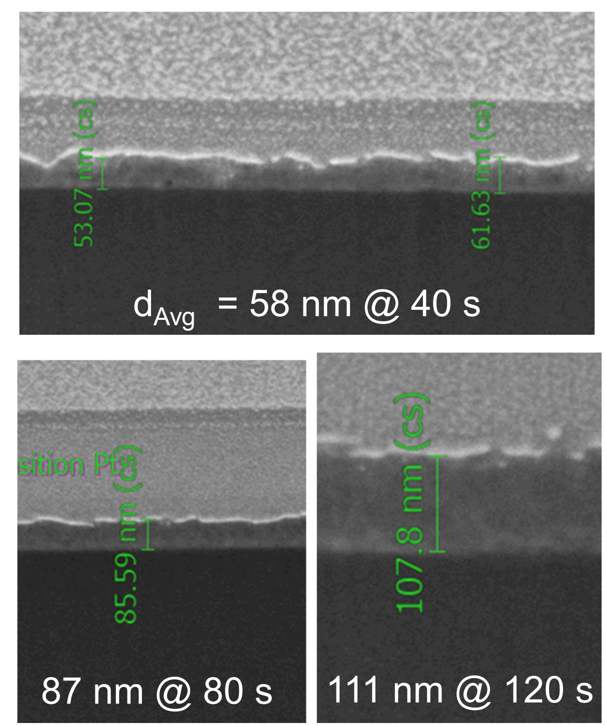
MnOx/PEDOT composite thin films for the ORR



EDS



Cross sectional analysis

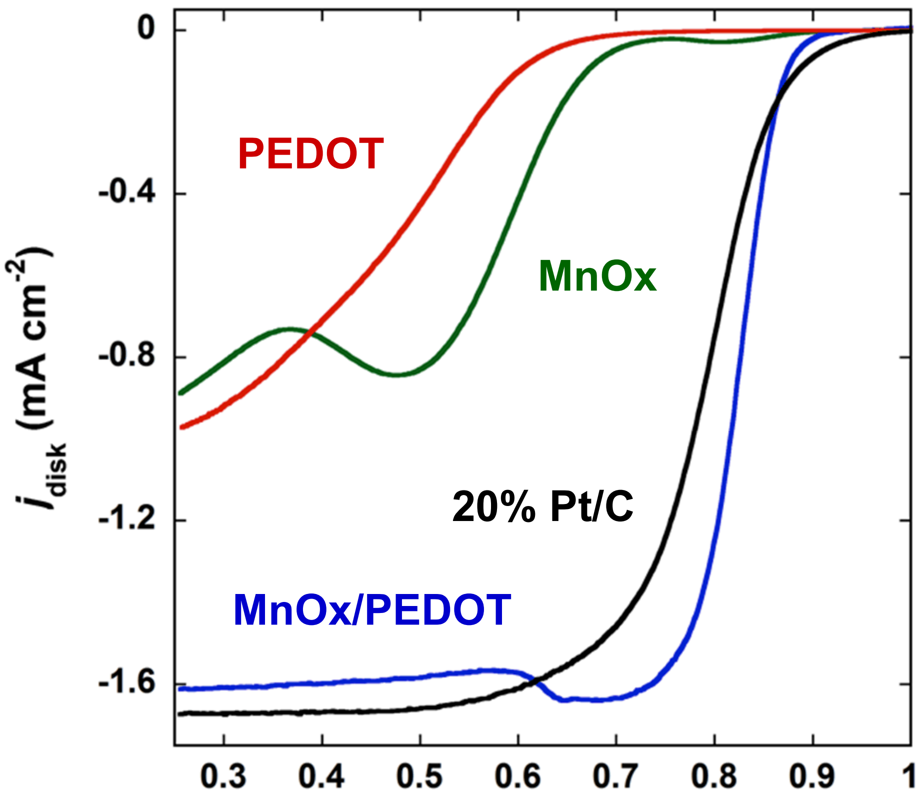


J. A. Vigil *et al.* *ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

MnOx/PEDOT composite thin films for the ORR

Sandia National Laboratories

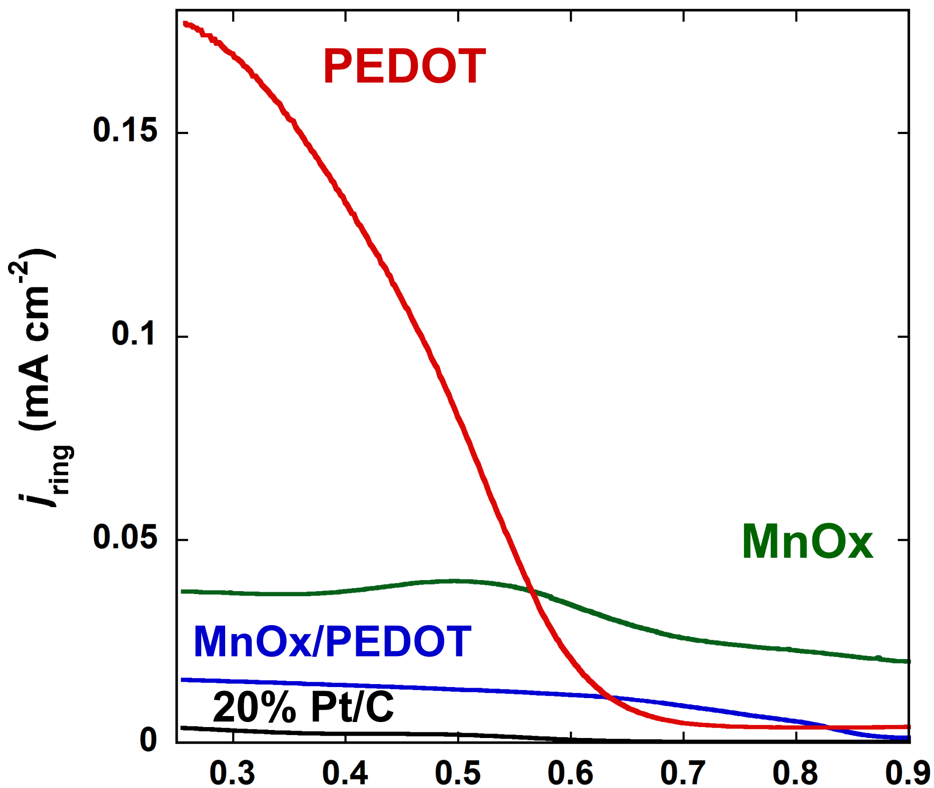
Disk



40 µg cm^{-2}
400 rpm
2 mV s^{-1}

E (V vs. RHE)

Ring

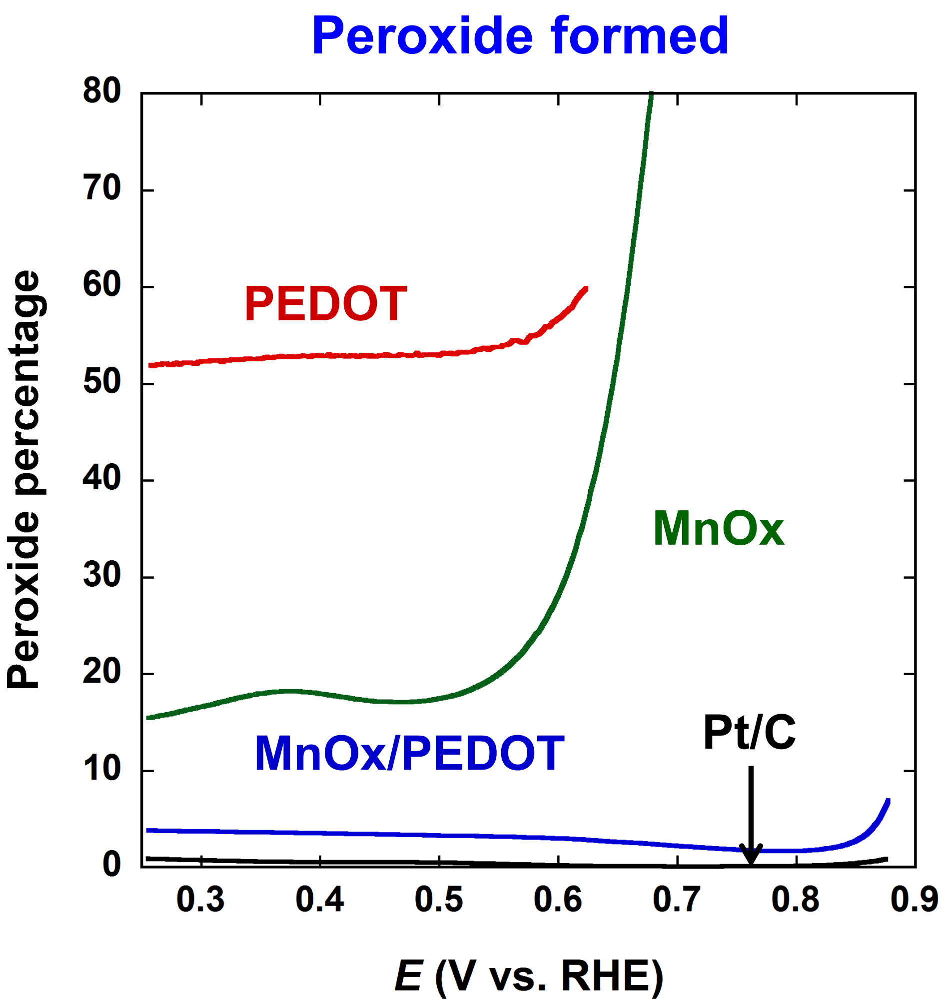


E (V vs. RHE)

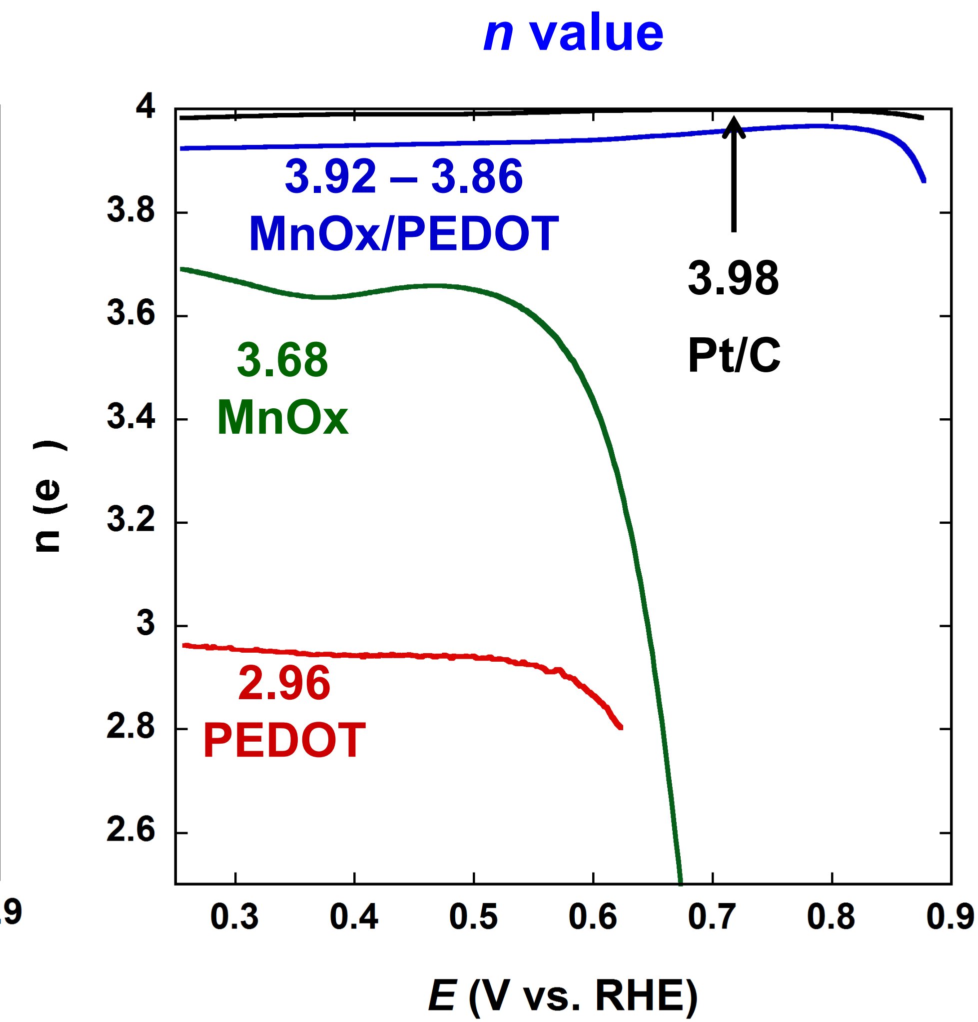
Disk/Ring:
C/Pt
C/Au
C/C

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

MnOx/PEDOT composite thin films for the ORR



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

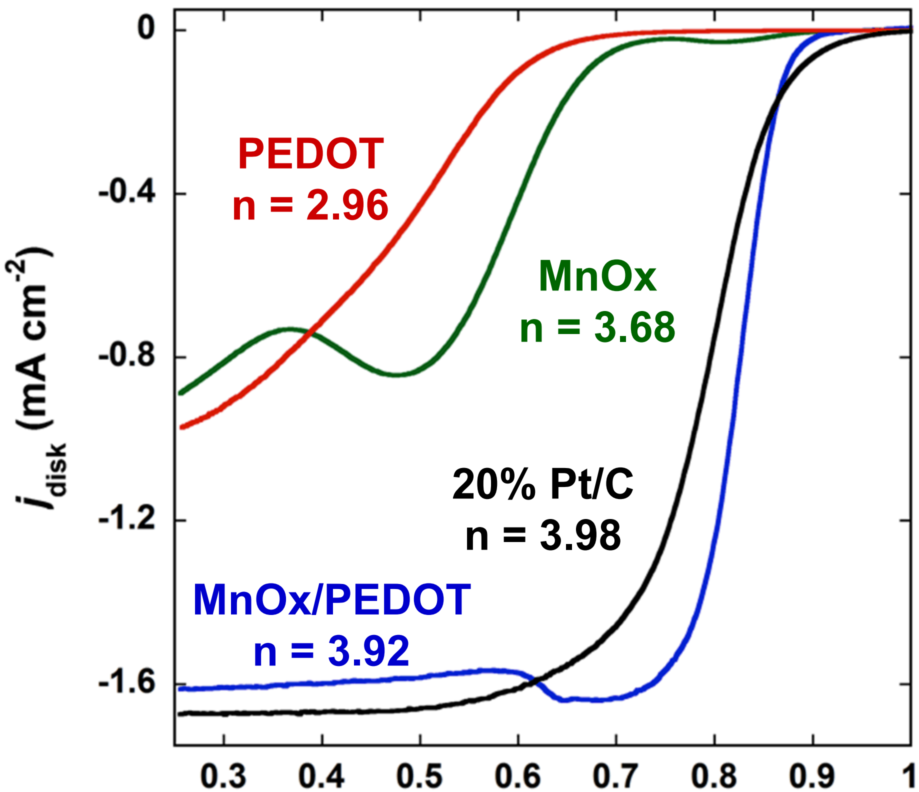


$n = 4 \, (I_D)/(I_D + I_R/N)$

MnOx/PEDOT composite thin films for the ORR

Sandia National Laboratories

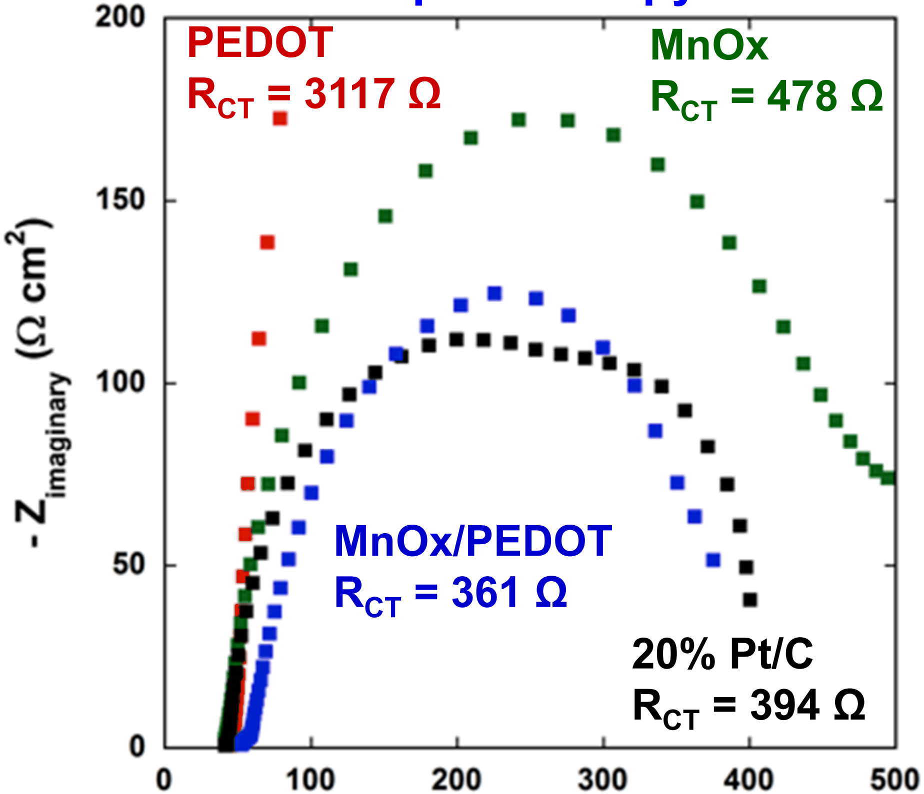
Oxygen reduction reaction
(O_2 + $2H_2O$ + $4e^-$ = $4OH^-$)



40 μg cm^{-2}
400 rpm
2 mV s^{-1}

E (V vs. RHE)

Electrochemical Impedance Spectroscopy



i $_{1/2}$ *wave*

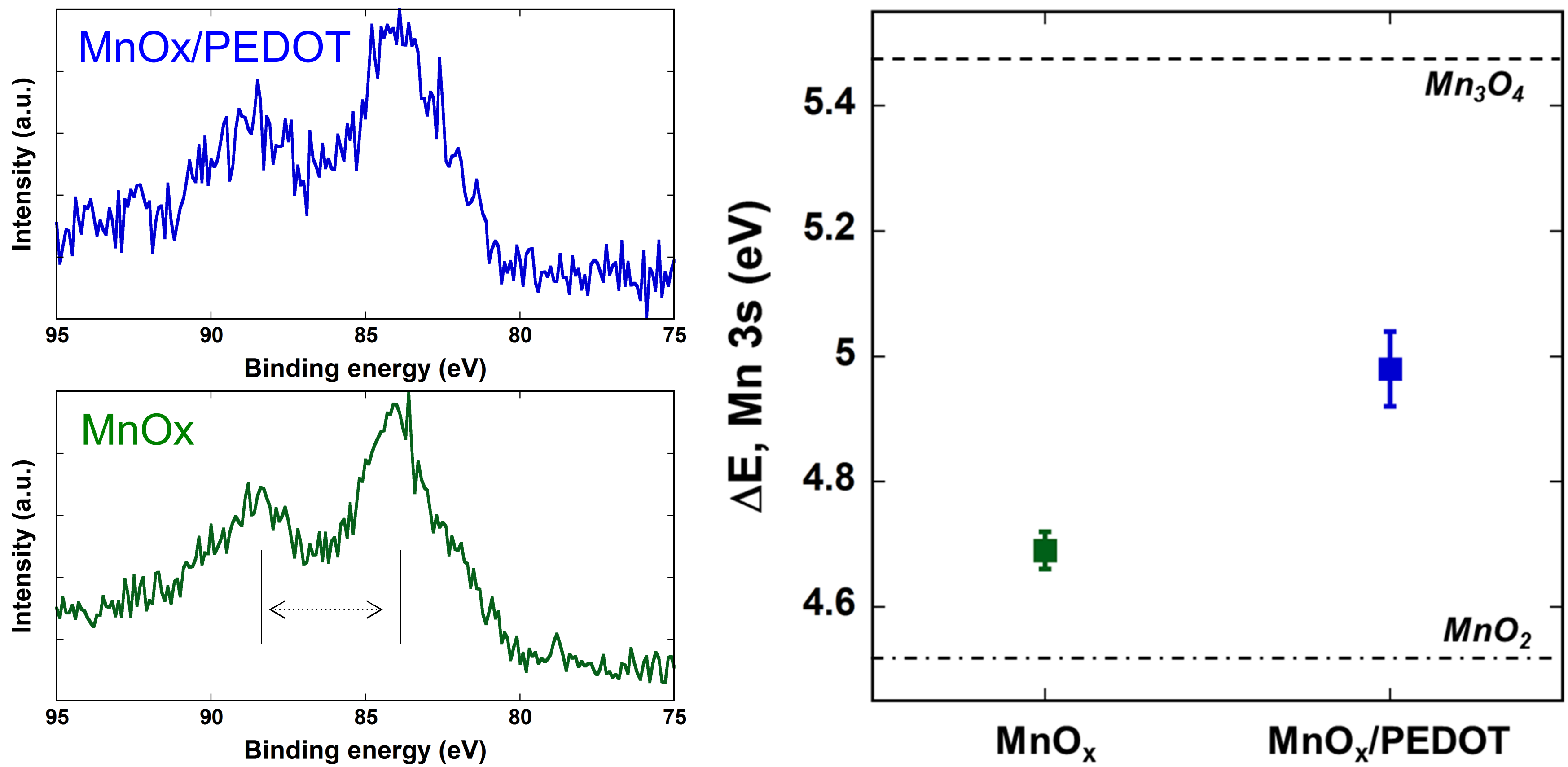
Z_{real} (Ω cm^2)

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

Origin of synergism ?

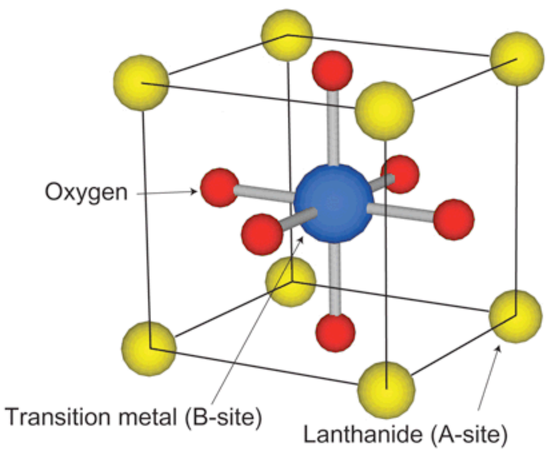


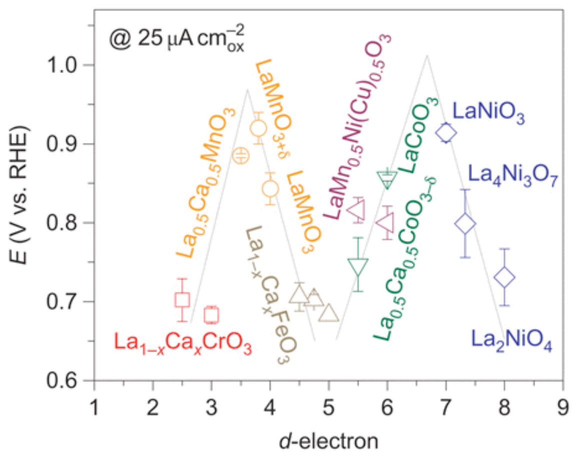
- Co-polymerization w/ PEDOT leads to increased surface Mn^{3+}
- Increasing Mn^{3+} leads to better electrocatalyst

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.

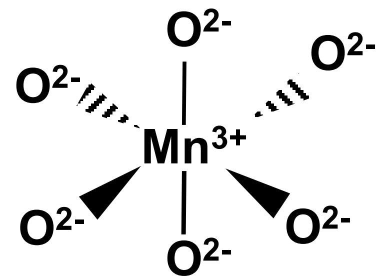
d4 = High Spin in Octahedral coordination

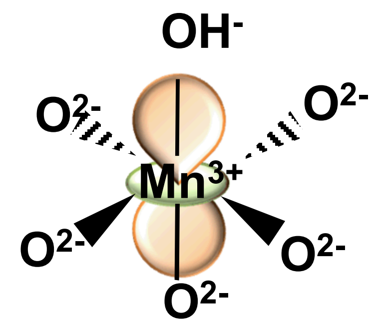




Adapted from J. Suntivich *et al.* Nature Chemistry. **2011.** 3, 546-550.

Mn^{3+}

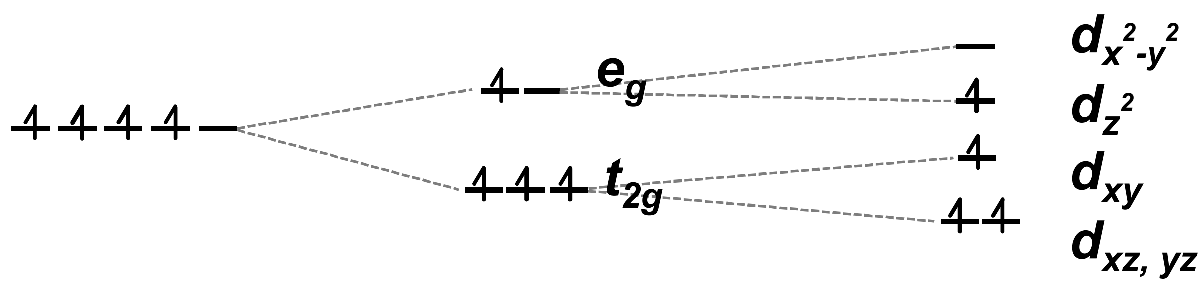




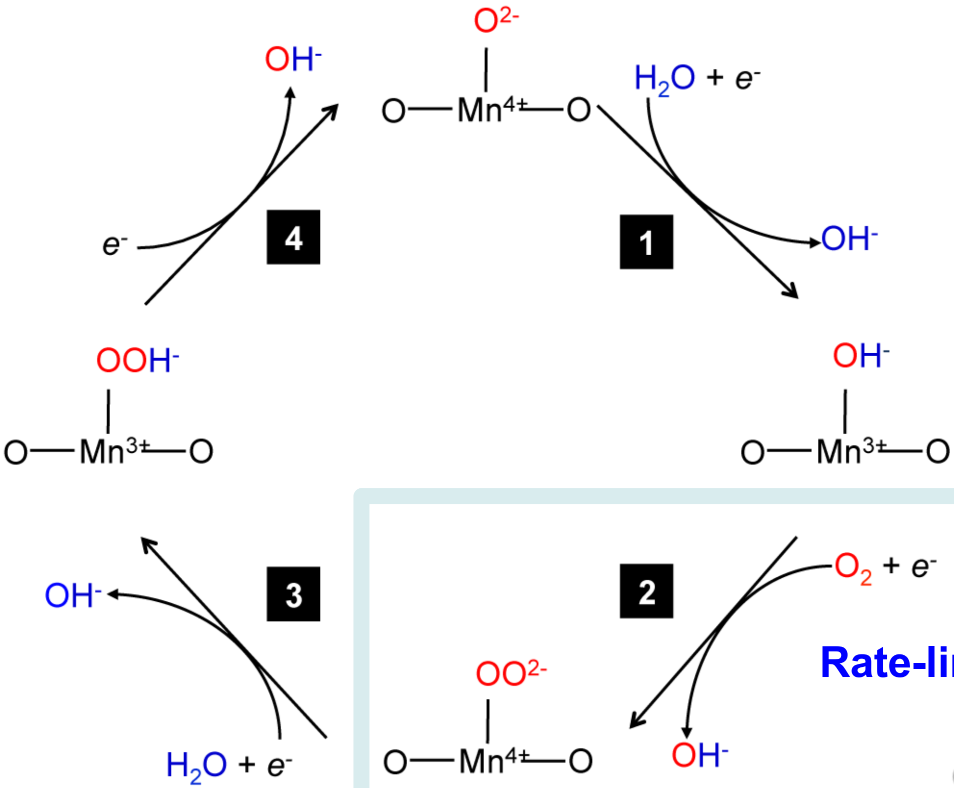
d^4 : *d*-manifold

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

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

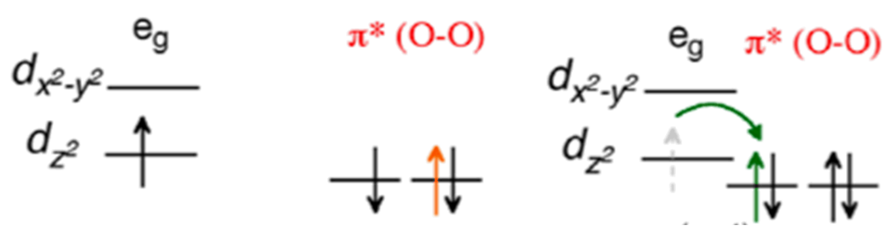


The role of Mn^{3+}/Mn^{4+} Couple



- **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

Rate-limiting step

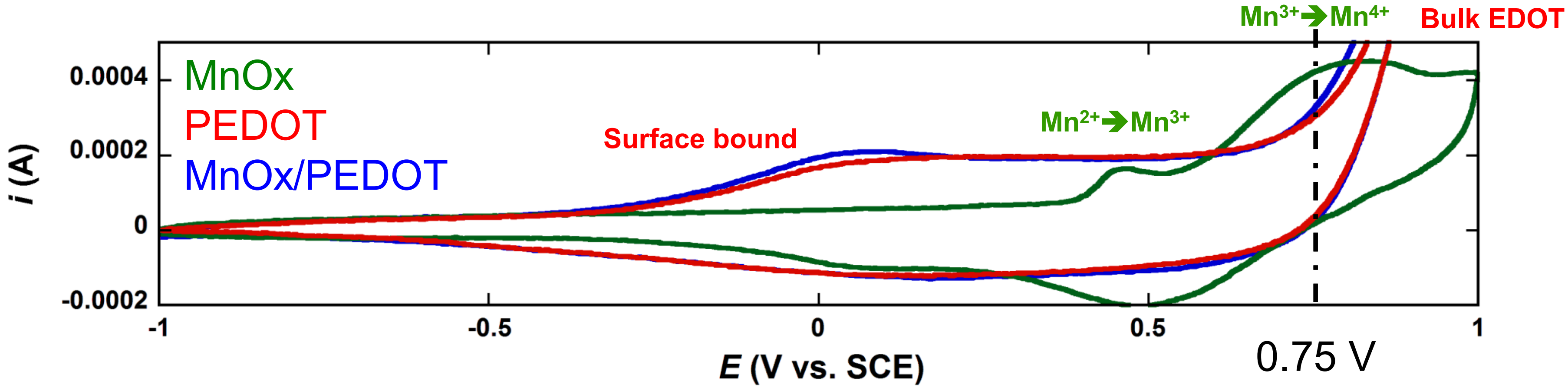


$$Mn^{3+}\text{-}OH^- + O_2 + e^- \longrightarrow Mn^{4+}\text{-}OO^{2-} + OH^-$$

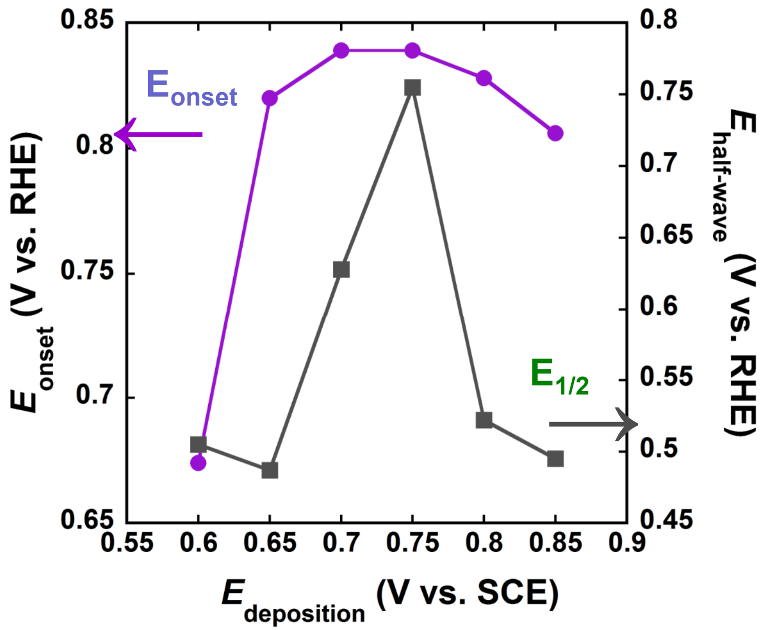
Mn^{3+}: d4 ion = High Spin in Octahedral coordination

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

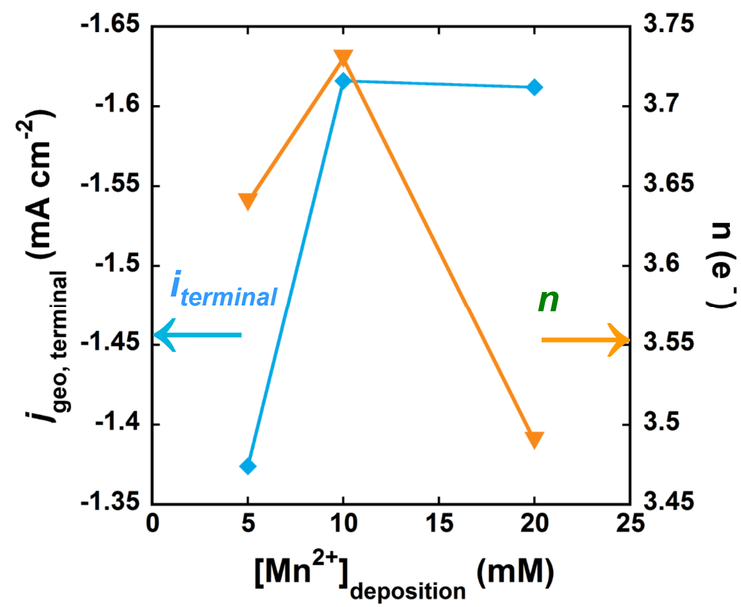
MnOx/PEDOT composite thin films for the ORR



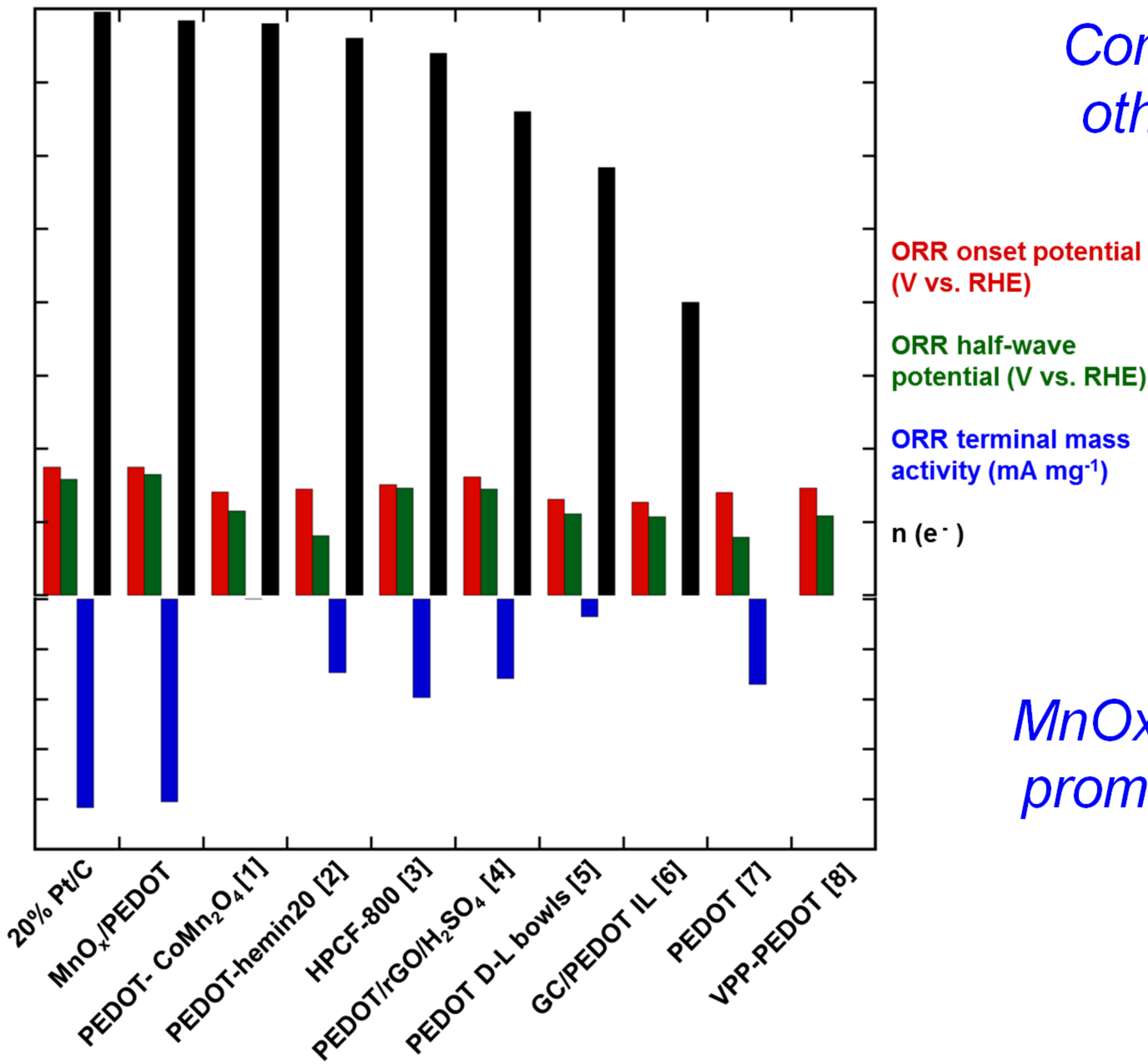
Optimize Potential



Optimize Concentration



MnOx/PEDOT composite thin films for the ORR



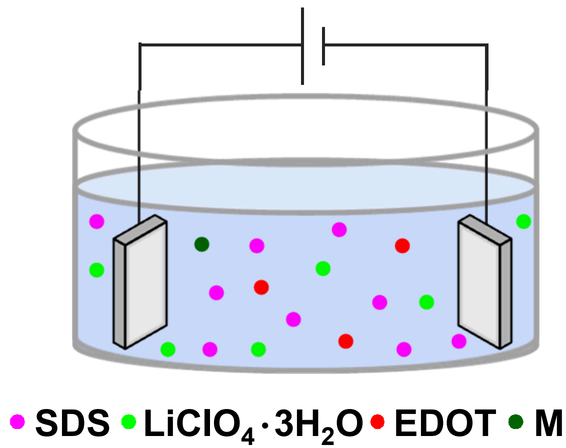
Comparison to Pt/C and other PEDOT systems

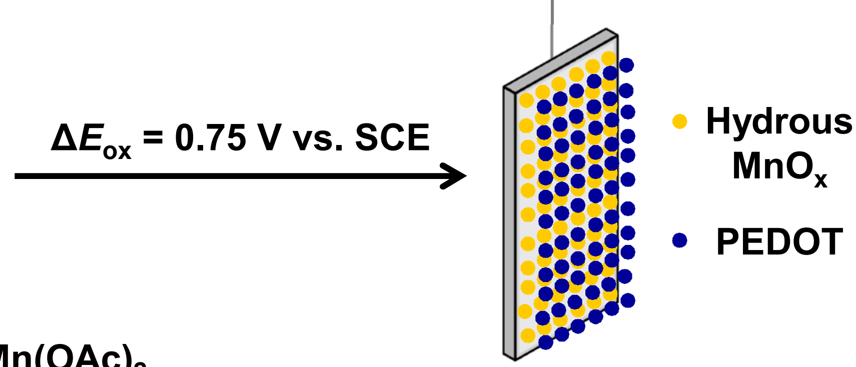
MnOx/PEDOT materials are promising replacements for Pt/C

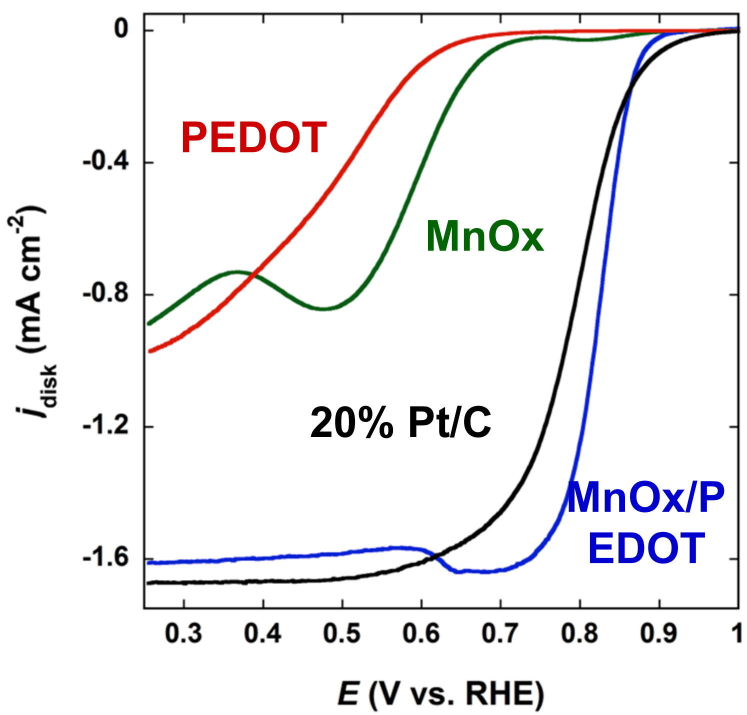
J. A. Vigil *et al. ACS Appl. Mater. Interfaces* **2015**, 7 (41), 22745–22750.

PEDOT/MnOx electrocatalysts

Summary







- 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 ?
- Synergism, Stability ➔ Future Work

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

Acknowledgements

Pictured Left to Right:

Julian Vigil
UNM Undergraduate

Ben Christensen
California Polytechnic State University

Me
SNL

Colin Delker
Postdoc SNL/CINT

Suzanne White
El Dorado High School

Maria Kelly
UNM Undergraduate

Kaitlyn Eldred
Manzano High School

- Sandia National Laboratories ($$)   Laboratory Directed Research and Development (LDRD)
- SNL STAR Program
- Michael Brumbach (XPS)
- Michael Rye (TEM)
- Bonnie McKenzie (SEM)

Thank you

Oxygen Reduction Reaction

Sandia National Laboratories

Direct 4 e^- reduction $n = 4$

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

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

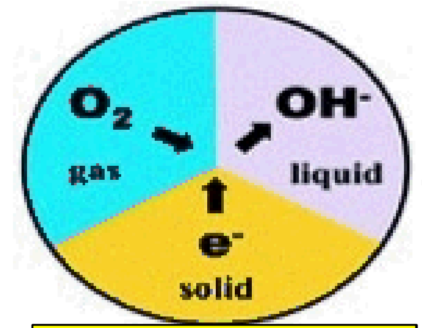
$$O_{2\,(g)} + H_2O_{\,(l)} + 2e^- \rightarrow HO_2^-{}_{(aq)} + OH^-_{\,(aq)}$$

Indirect 2 + 2 = 4 e^- $n = 4$

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

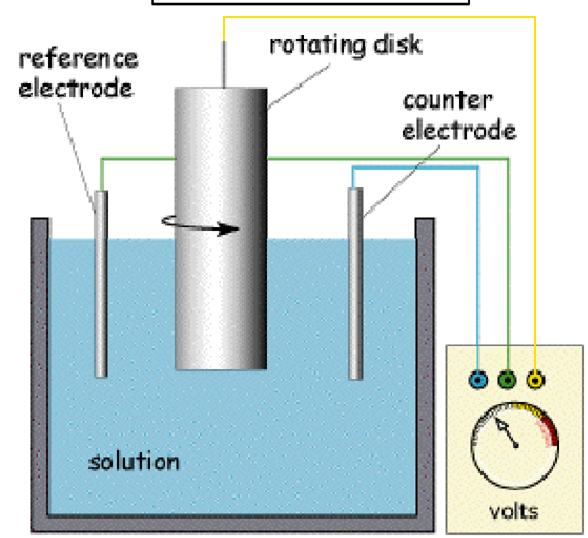
Disproportionation

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



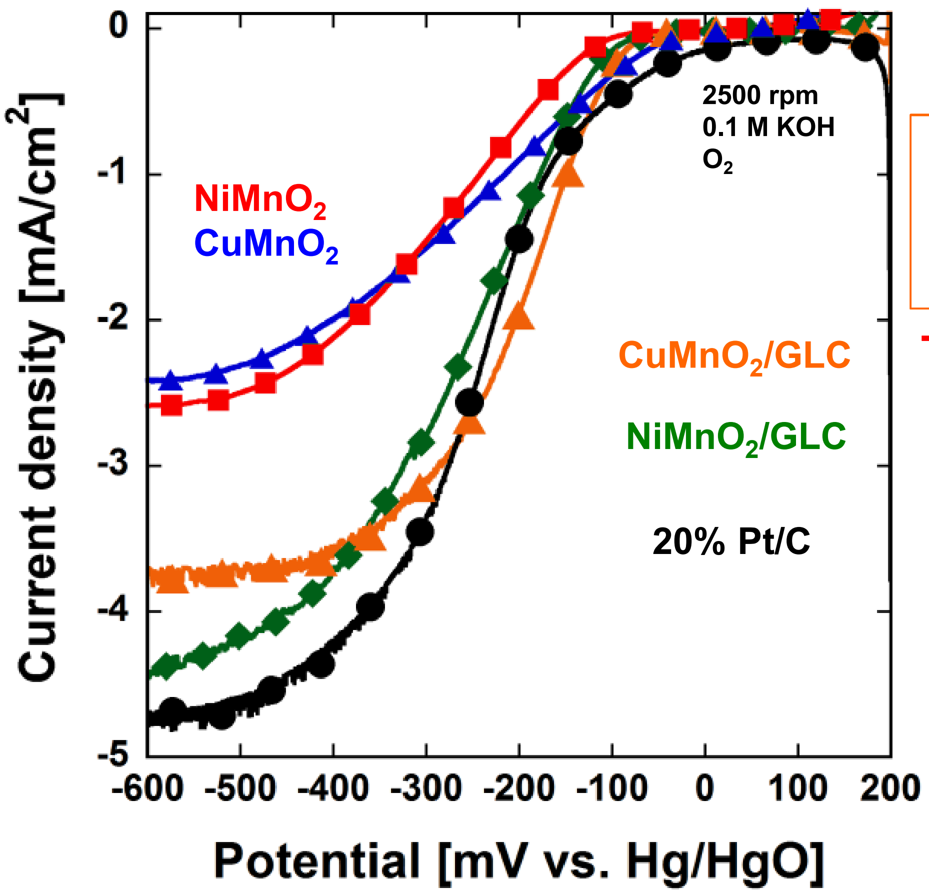
Electrocatalyst

RDE/RRDE methodology



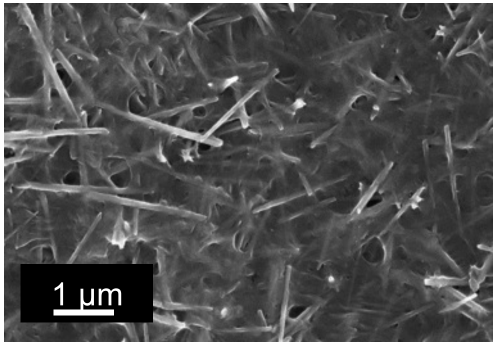
Increase Electrocatalysis with carbon

Sandia National Laboratories



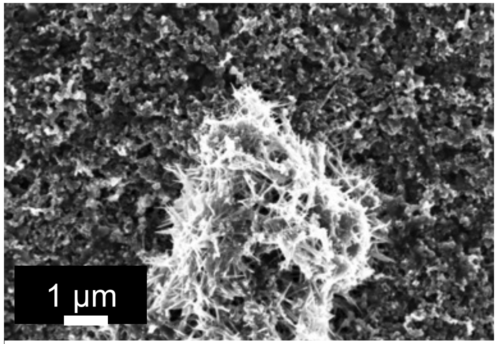
Good dispersion of catalyst

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

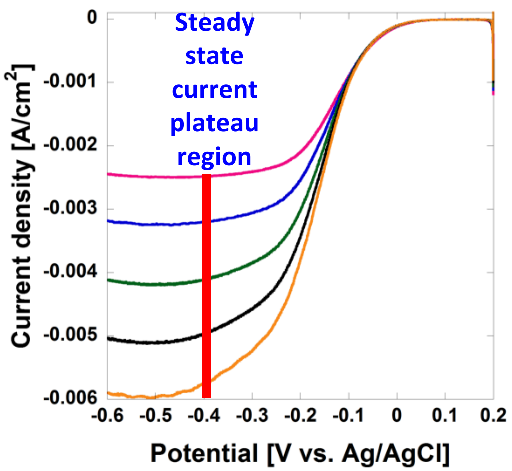
Cu-MnO_2: 78% of current obtained by Pt/C, *n* = 3.9
Ni-MnO_2: 91% of current obtained by Pt/C, rate = 3.50 x 10^{-2} cm/s
Pt/C rate = 3.24 x 10^{-2} cm/s
<u>$CuMnO_2$ outperforms</u> Pt/C in the potential range of -127 mV to -267 mV

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

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

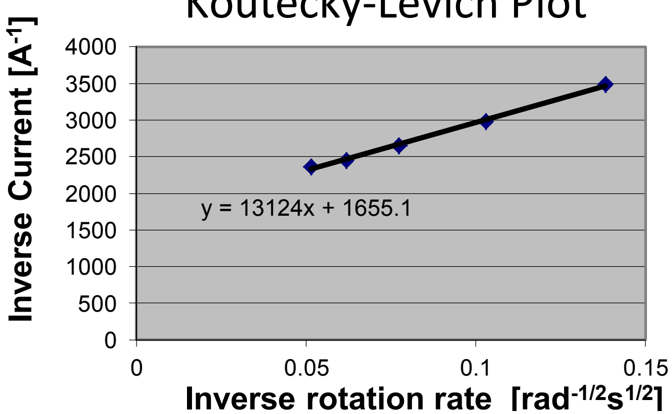
Analyzing the Catalytic Performance

Linear Scanning Voltammogram (LSV)



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

Koutecky-Levich Plot



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

Koutecky-Levich Equation

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

$$= -\frac{1}{\boxed{n}FA\boxed{k}C^0} - \frac{1}{0.62\boxed{n}FAD_{O_2}^{2/3}\upsilon^{-1/6}C^0\omega^{1/2}}$$

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

Importance of O_2 Electrochemistry

Sandia National Laboratories

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

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

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

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

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

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

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**

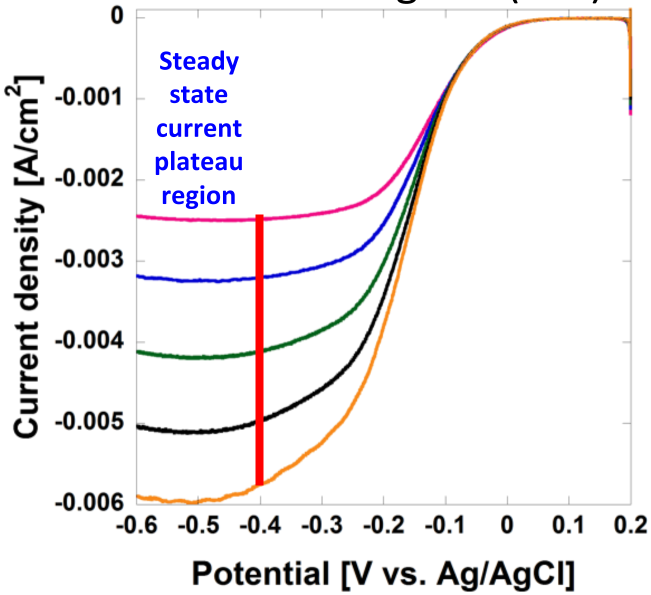
Gorlin *et al. J. Am. Chem. Soc.* **2010**, 132, 13612-13614

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

Analyzing the Catalytic Performance

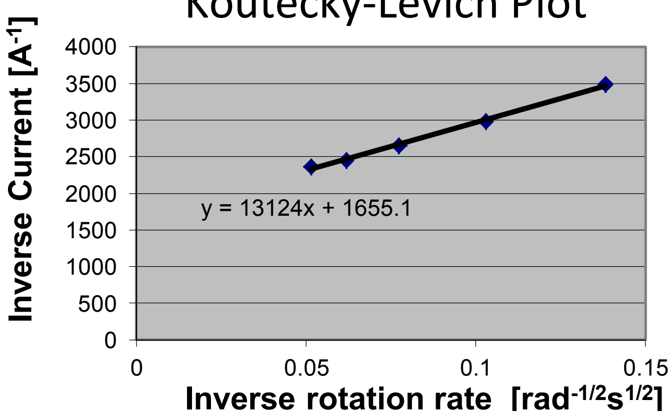
Sandia National Laboratories

Linear Scanning Voltammogram (LSV)



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

Koutecky-Levich Plot



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

Koutecky-Levich Equation

$$1/j = 1/j_L + 1/j_K = 1/(B\omega^{1/2}) + 1/j_K \qquad (1)$$

$$B = (0.62\, n\, \mathrm{F\, A\, D_{O2}}^{2/3}\, \omega^{1/2}\, v^{-1/6}\, \mathrm{C}° \qquad (2)$$

$$j_K = n\, \mathrm{F\, A\, k\, C}° \qquad (3)$$

$\boldsymbol{j_L}$ = diffusion limiting current density

$\boldsymbol{j_k}$ = kinetic limiting current density

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

1/$\boldsymbol{j_L}$ = slope of K-L plot

1/$\boldsymbol{j_K}$ = *intercept; k = heterogeneous rate constant*

F = Faraday constant

A = geometric electrode area (cm^2)

k = rate constant for oxygen reduction

C° = saturated concentration of O_2 in 0.1 M KOH

$\boldsymbol{D_{O2}}$= diffusion coefficient of oxygen

v = kinetic viscosity of electrolyte solution

ω = angular velocity (= 2π*N*, N rotation in rpm)