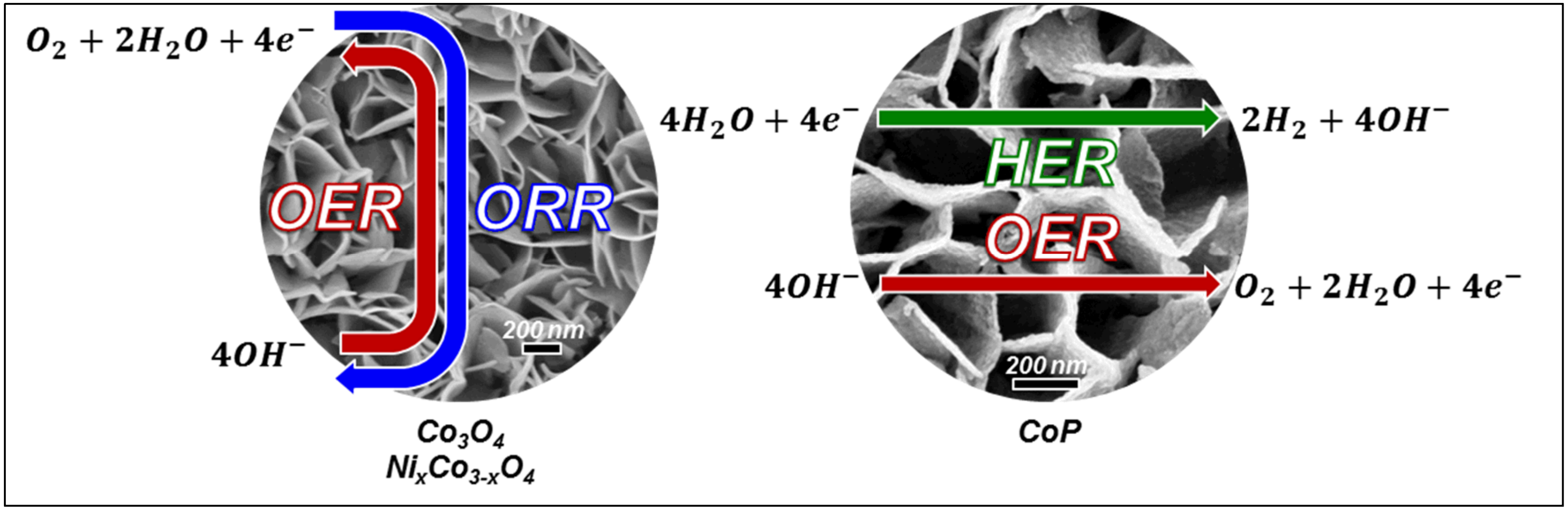
SAND2016-3155C

Exceptional service in the national interest

Sandia National Laboratories

Cobalt-based catalysts for bifunctional electrochemistry: ORR/OER and HER/OER



2016 EMN Electrocatalysis

February 16th, 2015: Orlando, Florida

Timothy N. Lambert and Julian A. Vigil

U.S. DEPARTMENT OF ENERGY NNSA National Nuclear Security Administration

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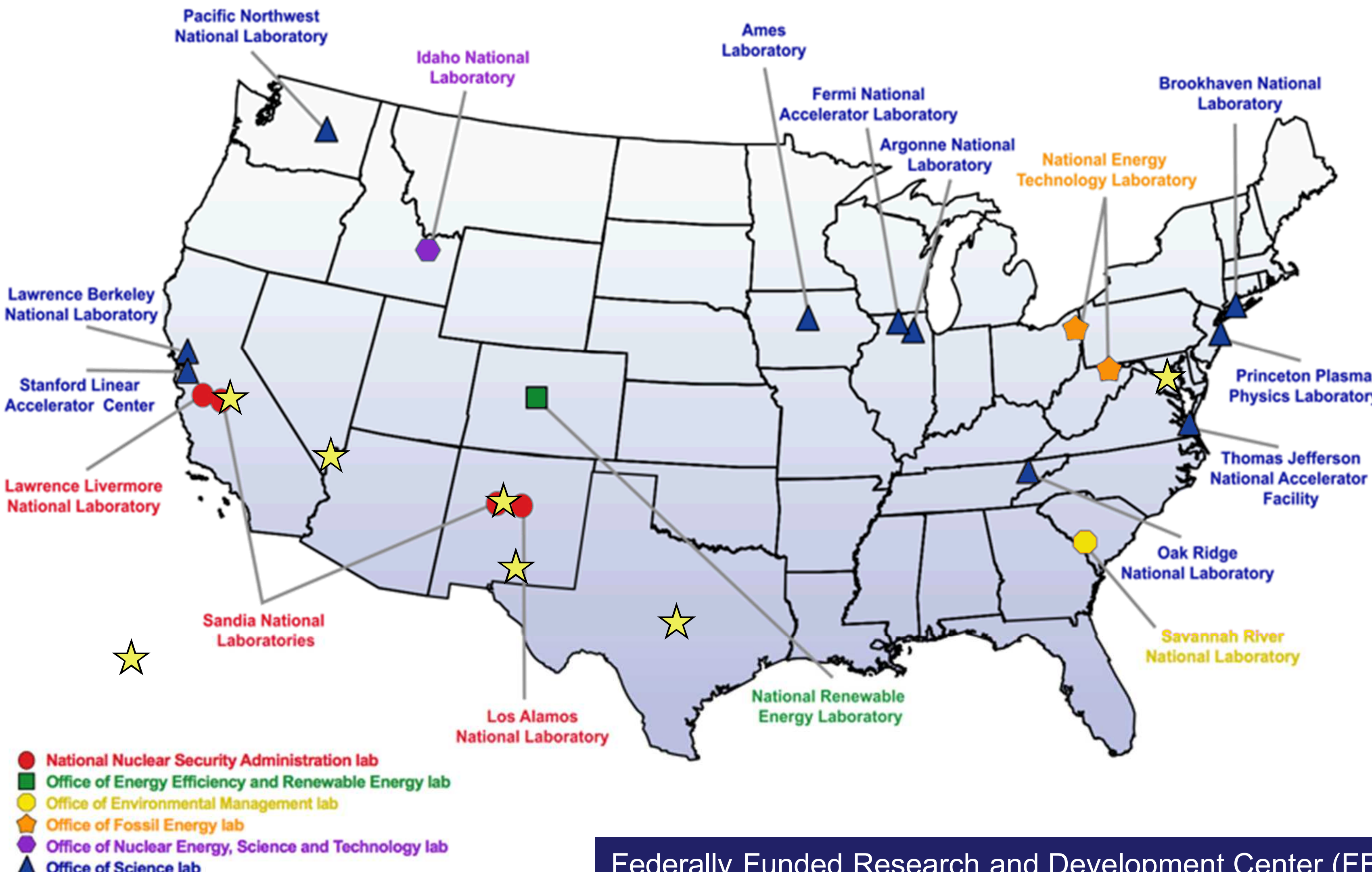
Department of Energy National Laboratories



Federally Funded Research and Development Center (FFRDC)
Government Owned/Contractor Operated (GO/CO)

Sandia National Laboratory sites are located across the nation

Albuquerque, New Mexico

Livermore, California

SNL's major facilities are located at Albuquerque, New Mexico; Livermore, California; and at a test range near Tonopah, Nevada.

Kauai, Hawaii

Waste Isolation Pilot Plant, Carlsbad, New Mexico

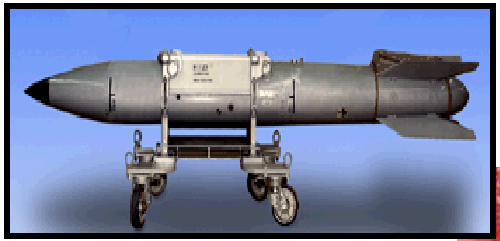
Pantex, Texas

Tonopah, Nevada

188,300 acres.

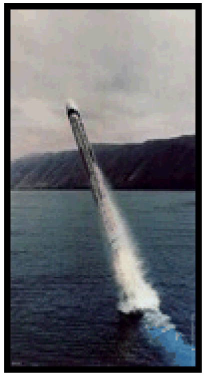
Sandia is a National Security Laboratory

Nuclear Weapons

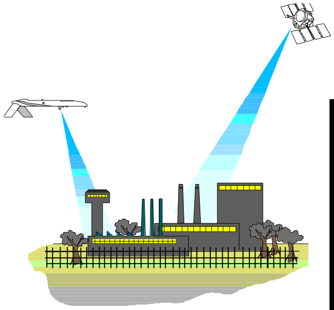


*Safe, Secure,
Reliable Weapons*

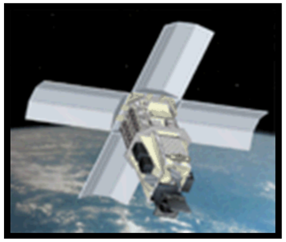
Defense Systems & Assessments



Defense

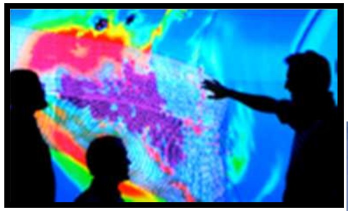


Detection

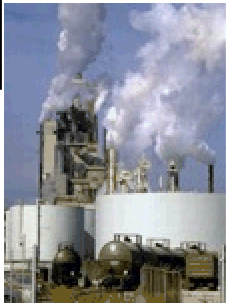


Surveillance

Energy, Climate, & Infrastructure Security



*Modeling
& Analysis*



Energy

Transportation

International, Homeland, & Nuclear Security

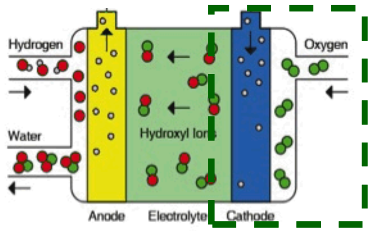
Incident response

*Biological risk
management*

*Anti-crime and anti-
Terrorism technology*

Science, Technology, & Engineering

Electrocatalysis in energy devices



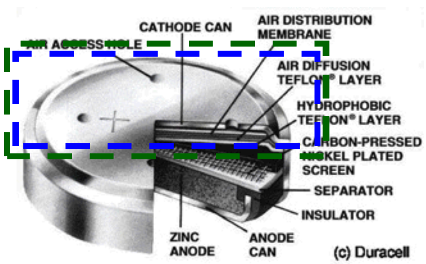
Fuel cell schematic

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

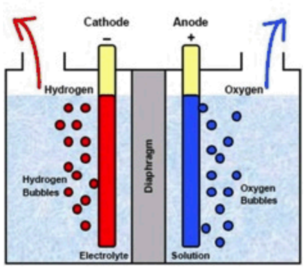
Overall: $2Zn_{(s)} + O_2 + 2H_2O \rightarrow 2Zn^{2+} + 4OH^-$

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)

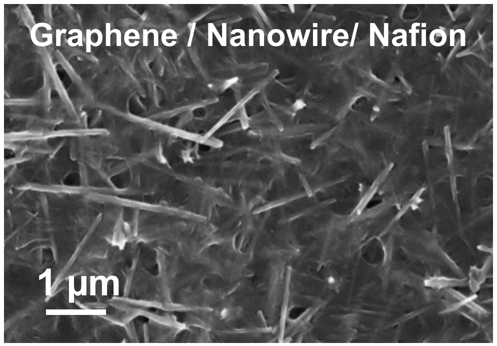
Overall: $4H_2O \longrightarrow 2H_2 + O_2$

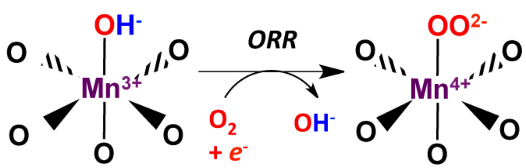
Catalysts: environmentally benign, earth-abundant, and overall potentially cost effective

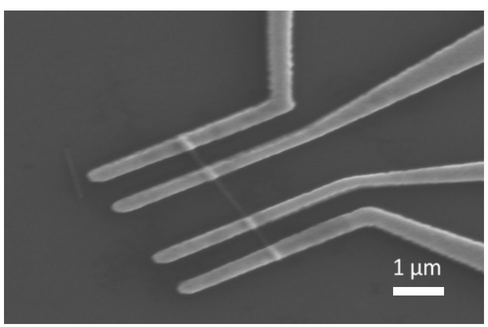
Nanoscale Electrocatalysts

Approach: Develop new nanoscale non-PGM electrocatalysts

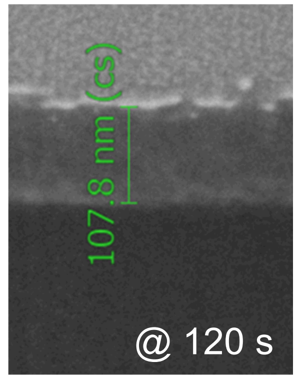
Graphene/Ni-α-MnO_2 Cu-α-MnO_2 Nanowires



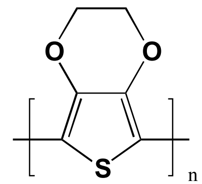


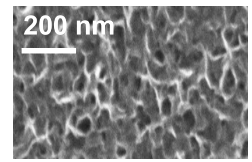


MnOx/PEDOT Thin Films

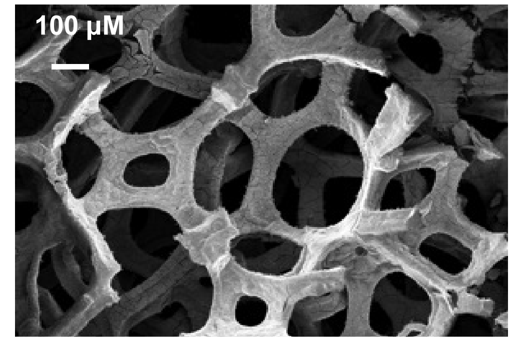


PEDOT

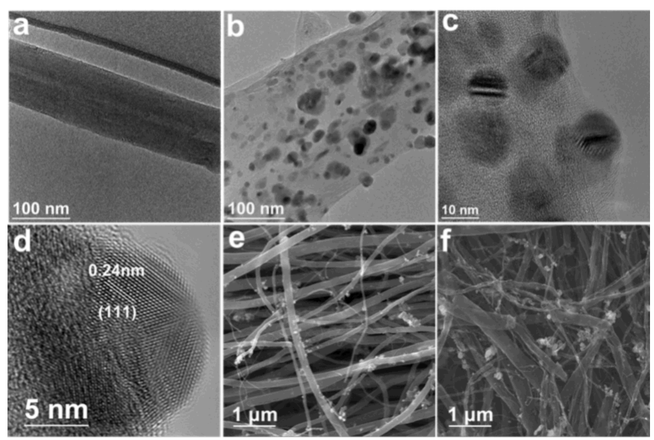




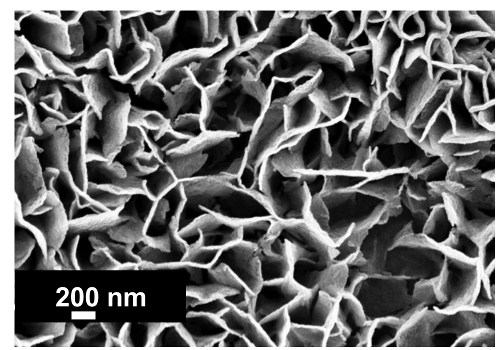
$Ni_xCo_{3-x}O_4$ Thin Films



Graphene Nanoribbon/Ag

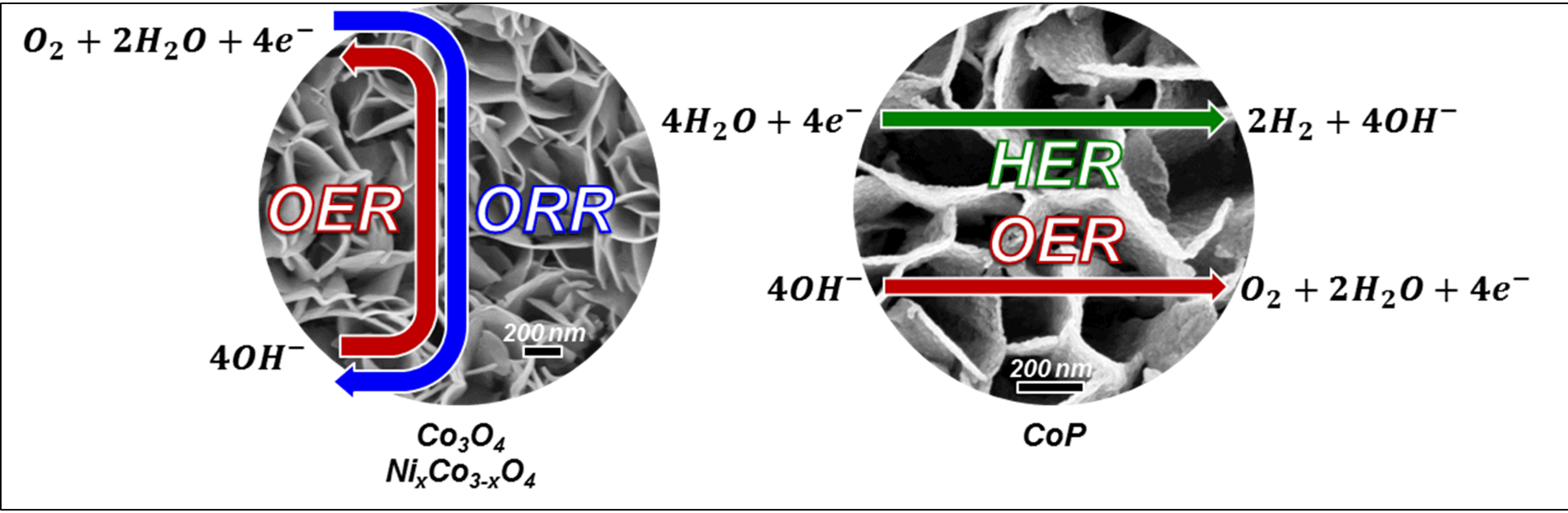


CoP Thin Films



(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**

Cobalt based catalysts for bifunctional electrochemistry:



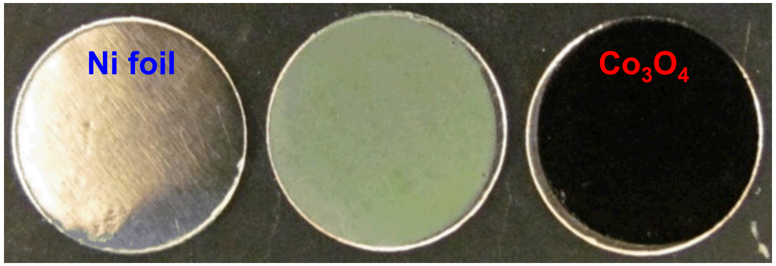
- **Synthesis and Characterization**
- **Electrocatalysis**

Synthesis of $Ni_xCo_{3-x}O_4$ Spinel Films

$$Co(NO_3)_2 \xrightarrow{e^-} Co(OH)_{2-x}(NO_3)_x \cdot y(H_2O) \xrightarrow{\Delta} Co_3O_4$$

$$Co(NO_3)_2 + Ni(NO_3)_2 \xrightarrow{e^-} Co_{1-z}Ni_z(OH)_{2-x}(NO_3)_x \bullet y(H_2O) \xrightarrow{\Delta} Ni_xCo_{3-x}O_4$$

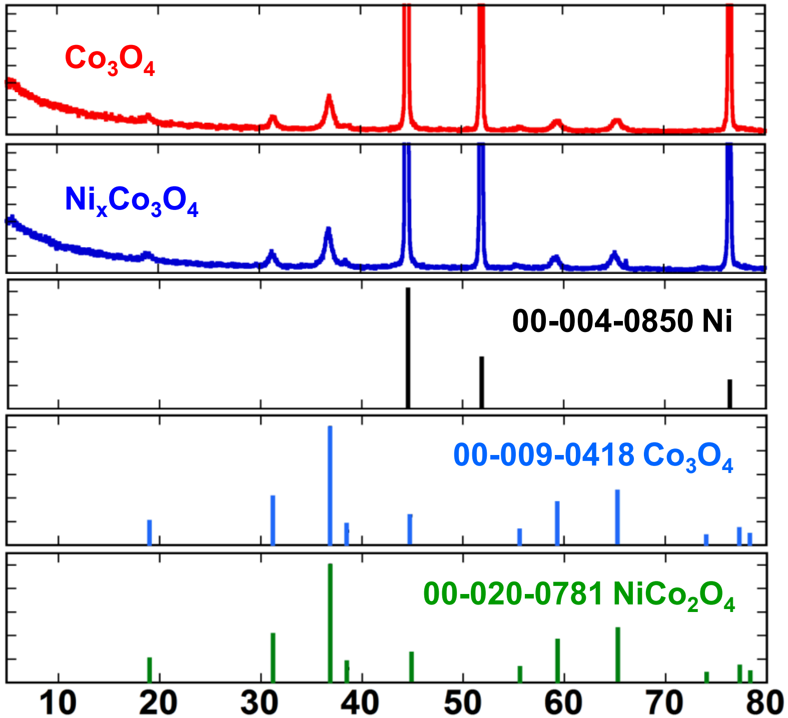
Co:Ni = 1:0.5 = $NiCo_2O_4$ (theoretically)



$Co(OH)_{2-x}(NO_3)_x \cdot y(H_2O)$

E. B. Castro *et al. Int. J. Hydrogen Energ.* **2004**, *29*, 255-261.
J.-S. Do and R.-F. Dai, *J. Power Sources* **2009**, *189*, 204-210.

Variety of substrates, scalable, no carbon and no binder



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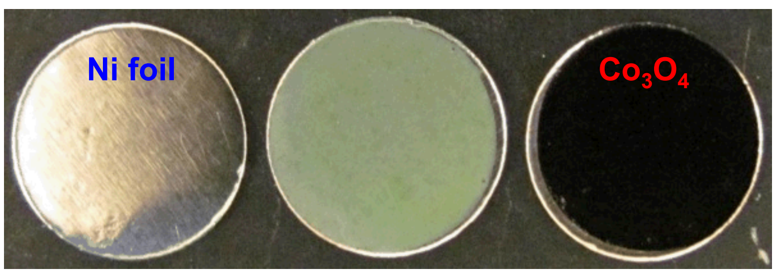
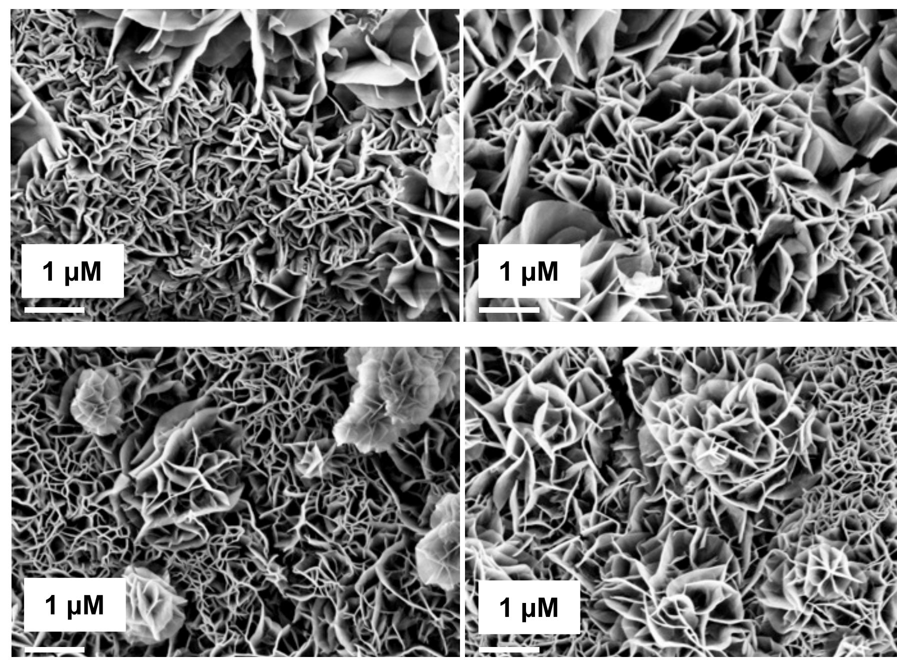


$Co(OH)_{2-x}(NO_3)_x \cdot y(H_2O)$

E. B. Castro *et al. Int. J. Hydrogen Energ.* **2004**, *29*, 255-261.
J.-S. Do and R.-F. Dai, *J. Power Sources* **2009**, *189*, 204-210.

High surface area and porosity

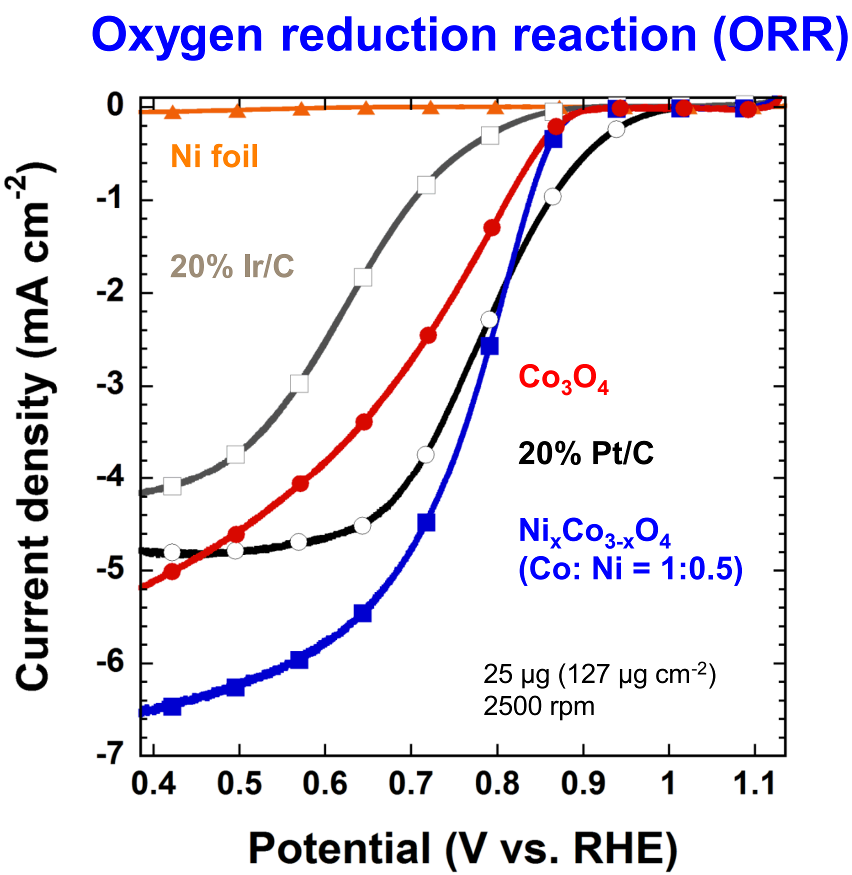
$Co(OH)_{2-x}(NO_3)_x \cdot y(H_2O)$ **Co_3O_4**

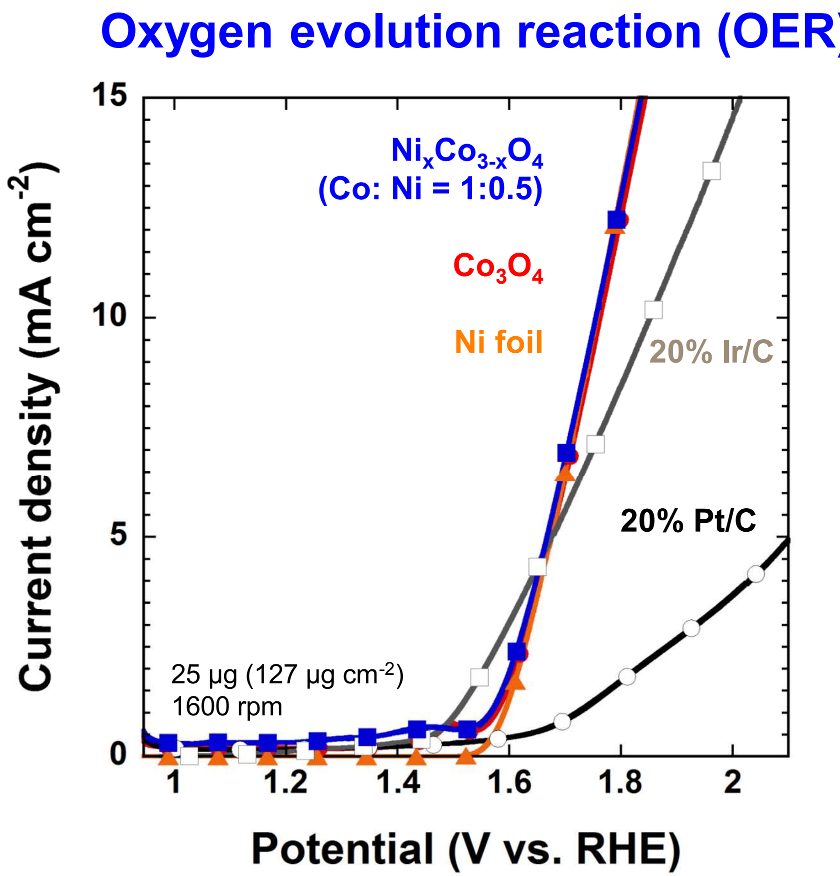


$Co_{1-z}Ni_z(OH)_{2-x}(NO_3)_x \bullet y(H_2O$ **$Ni_xCo_{3-x}O_4$**

T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

Electrocatalysis of ORR & OER

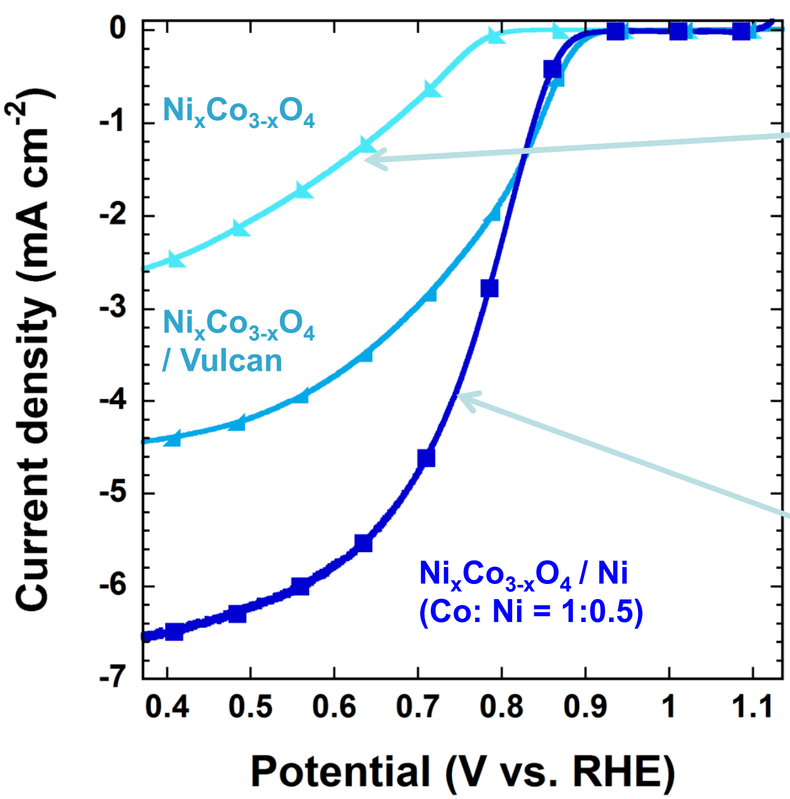


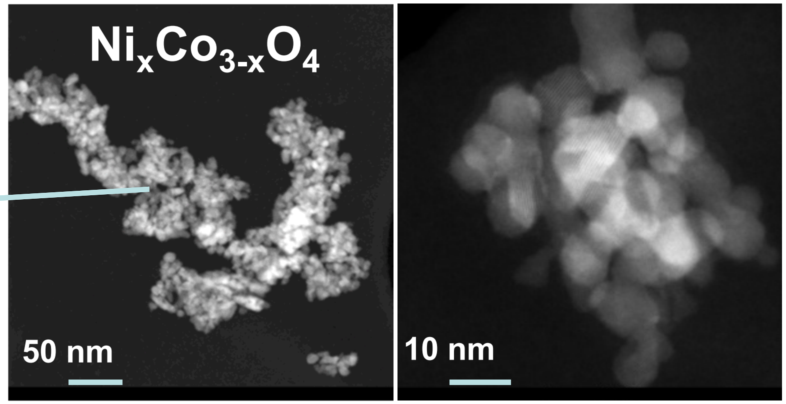


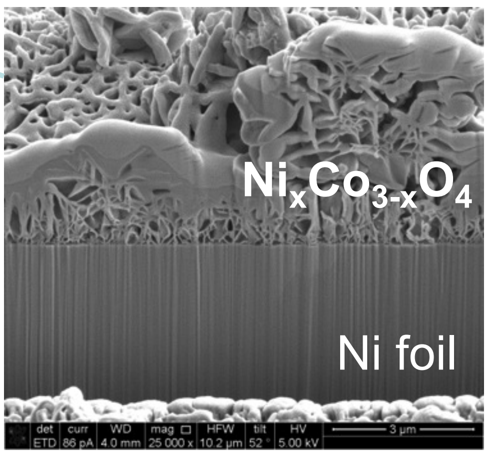
$Ni_xCo_{3-x}O_4$ performs well against the commercial benchmarks
20% Pt/C (ORR)
20% Ir/C (OER)

T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

Co_3O_4 and $Ni_xCo_{3-x}O_4$ Spinel Films







High activity is a result of nanostructure and attachment to Ni foil

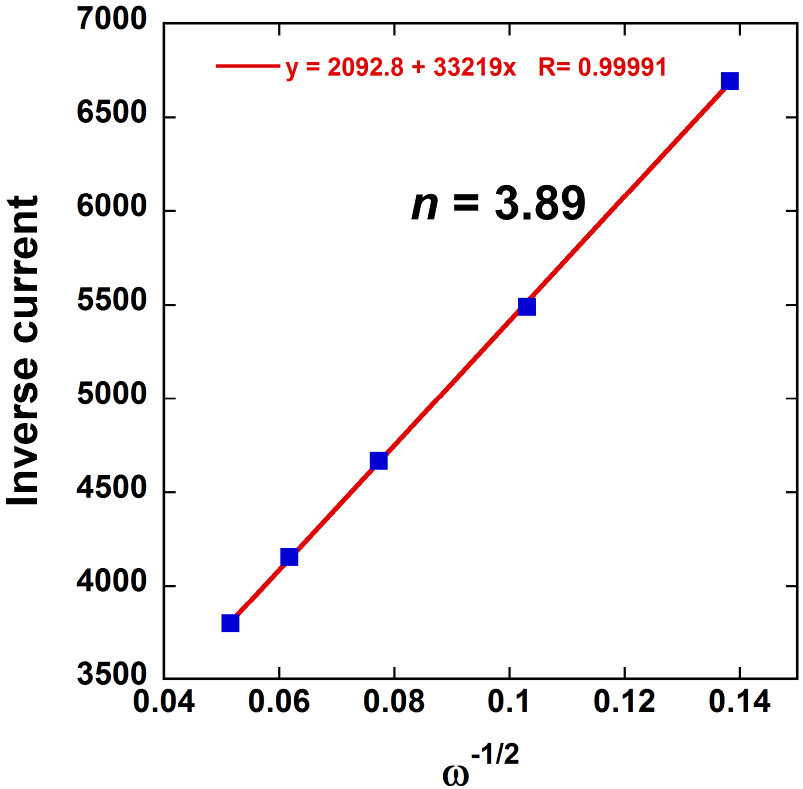
T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

Reaction Order (*n* value)

$Ni_xCo_{3-x}O_4$ from (Co: Ni = 1:0.5)

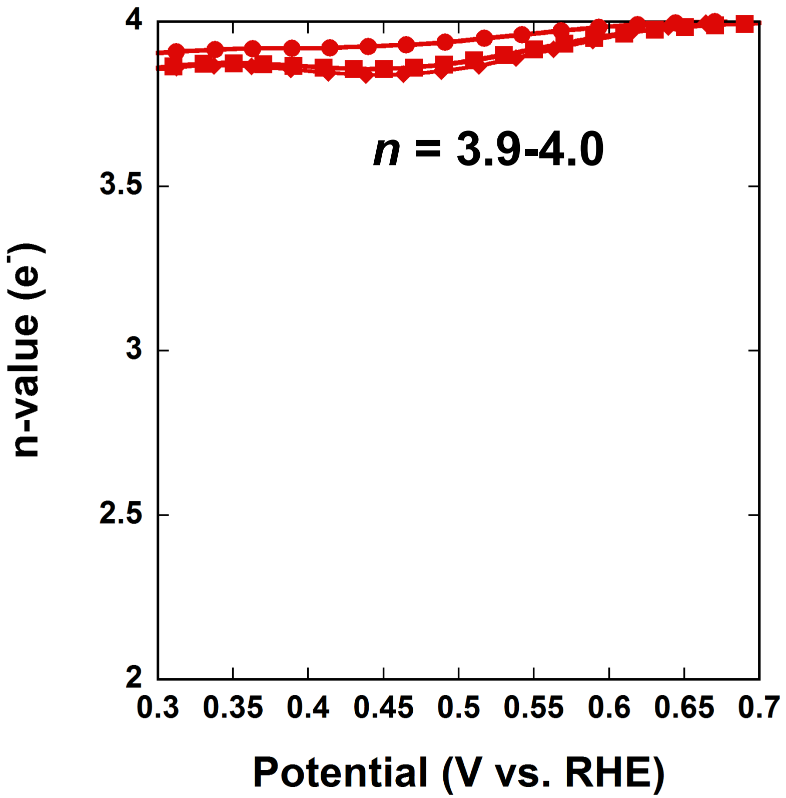
Koutecky-Levich Analysis

$Ni_xCo_{3-x}O_4$ / Vulcan



RRDE Analysis

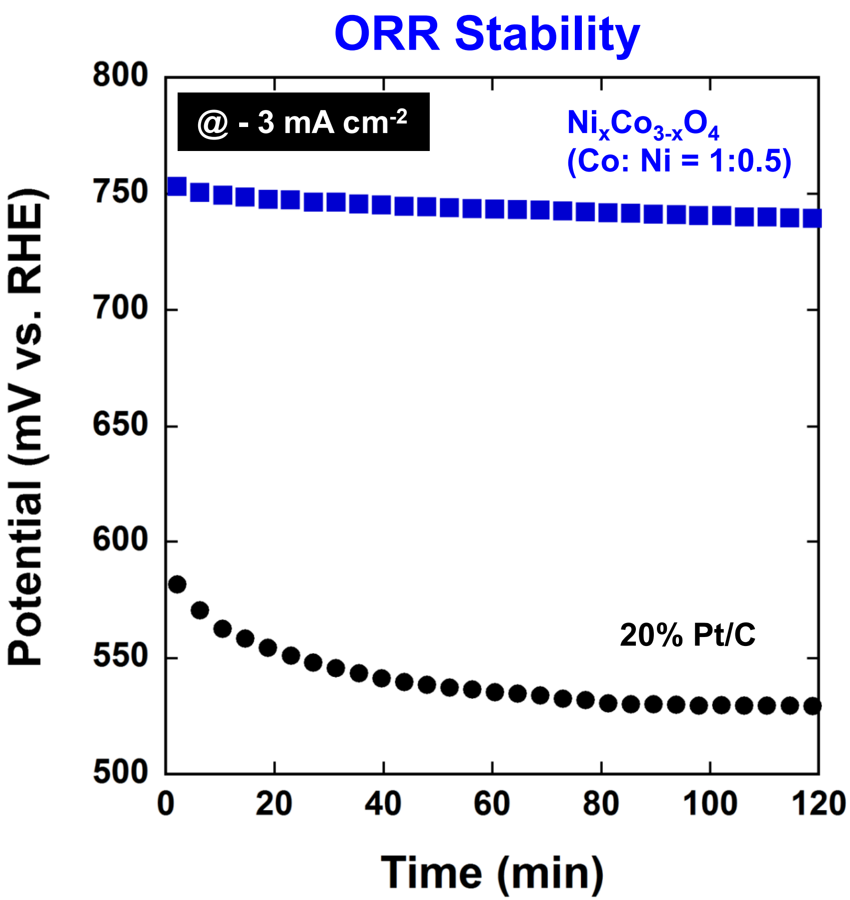
$Ni_xCo_{3-x}O_4$

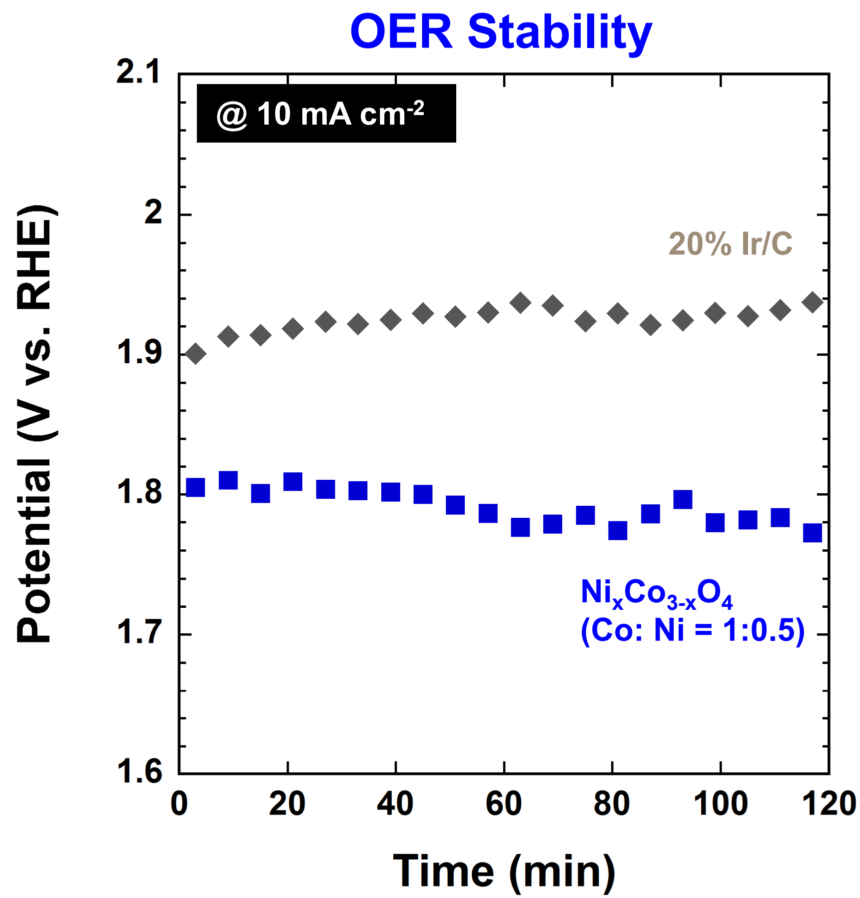


ORR proceeds via an efficient 4e⁻ process

T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

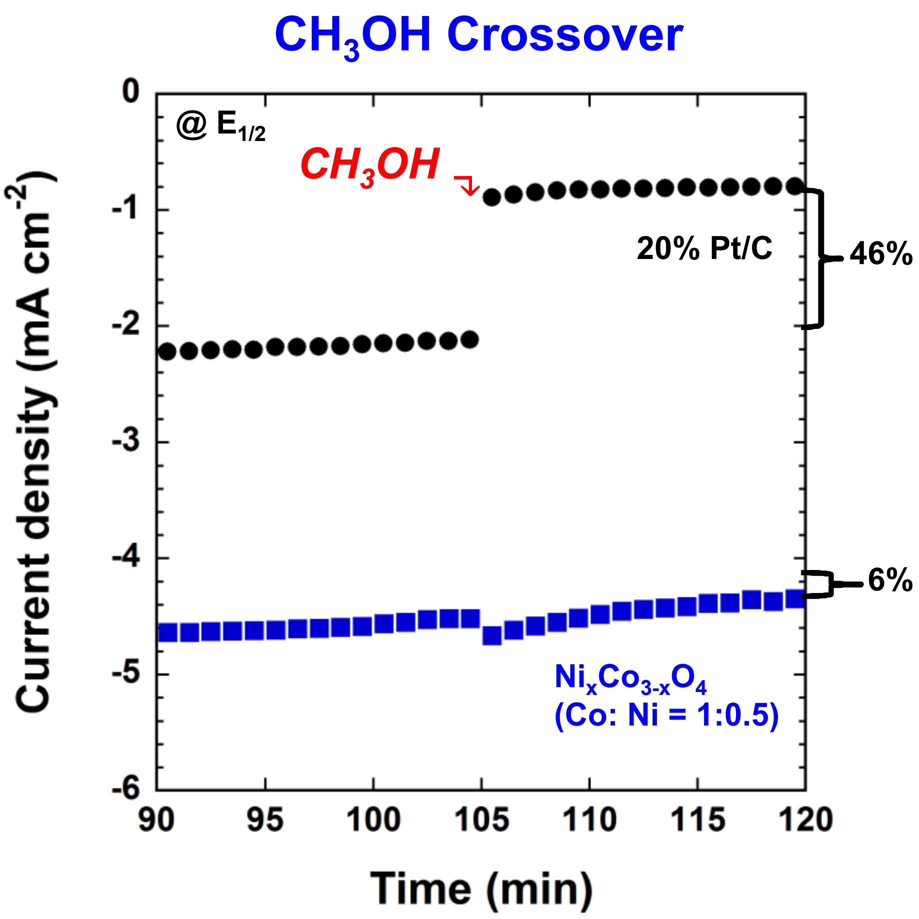
ORR and OER Stability





$Ni_xCo_{3-x}O_4$ exhibits better stability than
20% Pt/C (ORR)
20% Ir/C (OER)

Electrocatalytic Selectivity

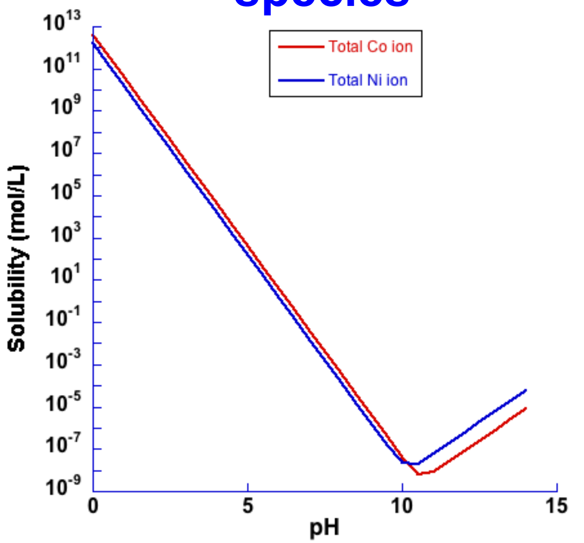


- Preliminary probe to examine crossover effects in alkaline methanol fuel cells
- Arrow indicates injection of methanol (2 wt.% final)
- 20% Pt/C suffers a ~46% decrease in current
- $Ni_xCo_{3-x}O_4$ only shows a ~6% decrease in current

Synthesis of $Ni_xCo_{3-x}O_4$ Spinel Films

$$Co(NO_3)_2 + Ni(NO_3)_2 \xrightarrow{e^-} Co_{1-z}Ni_z(OH)_{2-x}(NO_3)_x \bullet y(H_2O) \xrightarrow{\Delta} Ni_xCo_{3-x}O_4$$

Calculated Solubility vs. pH for Co^{2+} and Ni^{2+} species



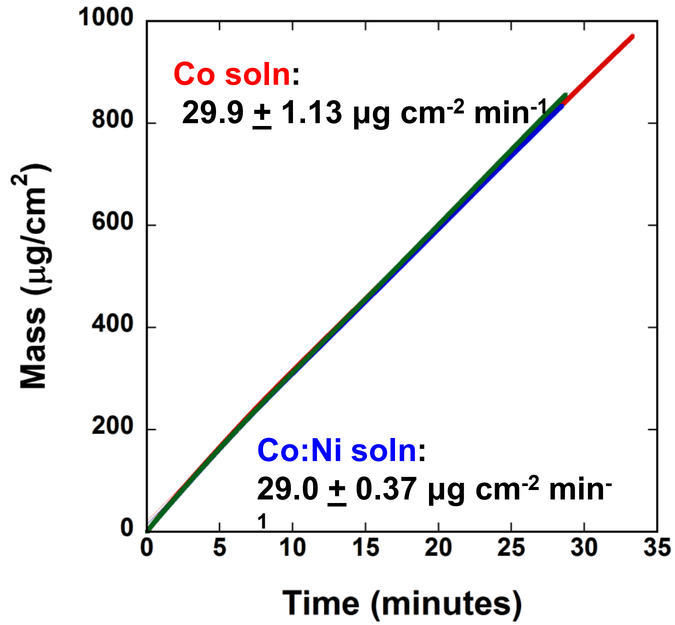
$\log[Co^{2+}] = 12.60 - 2pH$
$\log[HCoO_2^-] = -19.10 + pH$
$\log[Ni^{2+}] = 12.18 - 2pH$
$\log[HNiO_2^-] = -18.22 + pH$

M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, Pergamon Press, Oxford, 1966.

Acid Digestion/ ICP Analysis

Co: Ni Ratio		Stoichiometry
1:0.5	=	$Ni_{0.6}Co_{2.4}O_4$

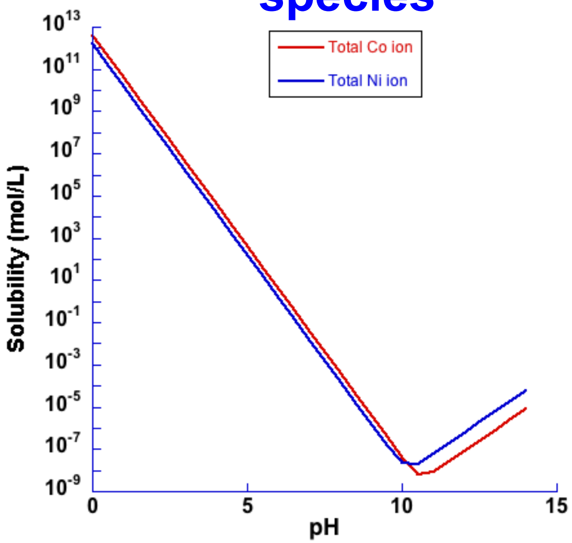
QCM & TGA



Synthesis of $Ni_xCo_{3-x}O_4$ Spinel Films

$$Co(NO_3)_2 + Ni(NO_3)_2 \xrightarrow{e^-} Co_{1-z}Ni_z(OH)_{2-x}(NO_3)_x \bullet y(H_2O) \xrightarrow{\Delta} Ni_xCo_{3-x}O_4$$

Calculated Solubility vs. pH for Co^{2+} and Ni^{2+} species



$\log[Co^{2+}] = 12.60 - 2pH$
$\log[HCoO_2^-] = -19.10 + pH$
$\log[Ni^{2+}] = 12.18 - 2pH$
$\log[HNiO_2^-] = -18.22 + pH$

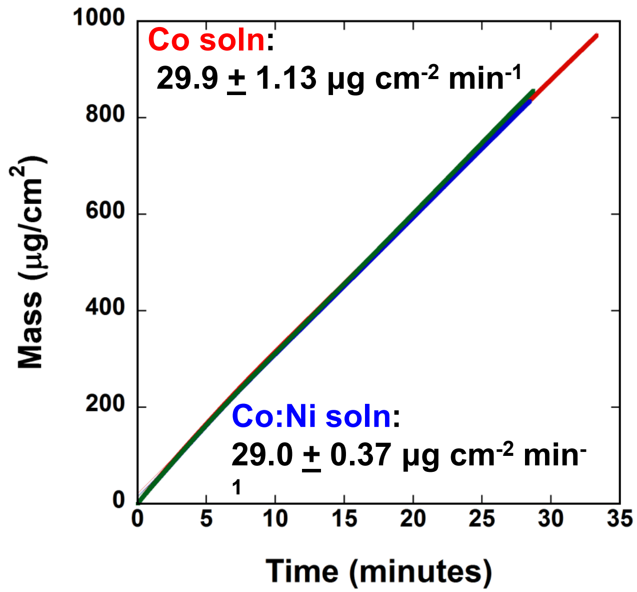
M. Pourbaix, *Atlas of electrochemical equilibria in aqueous solutions*, Pergamon Press, Oxford, 1966.

Acid Digestion/ ICP Analysis

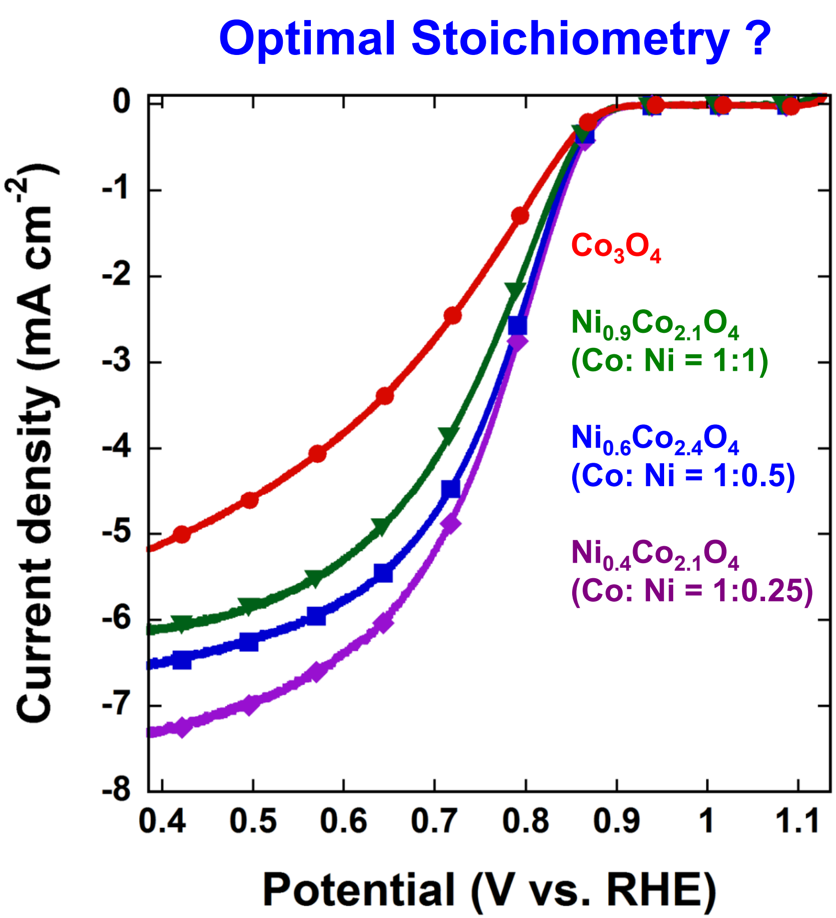
59% incorporation

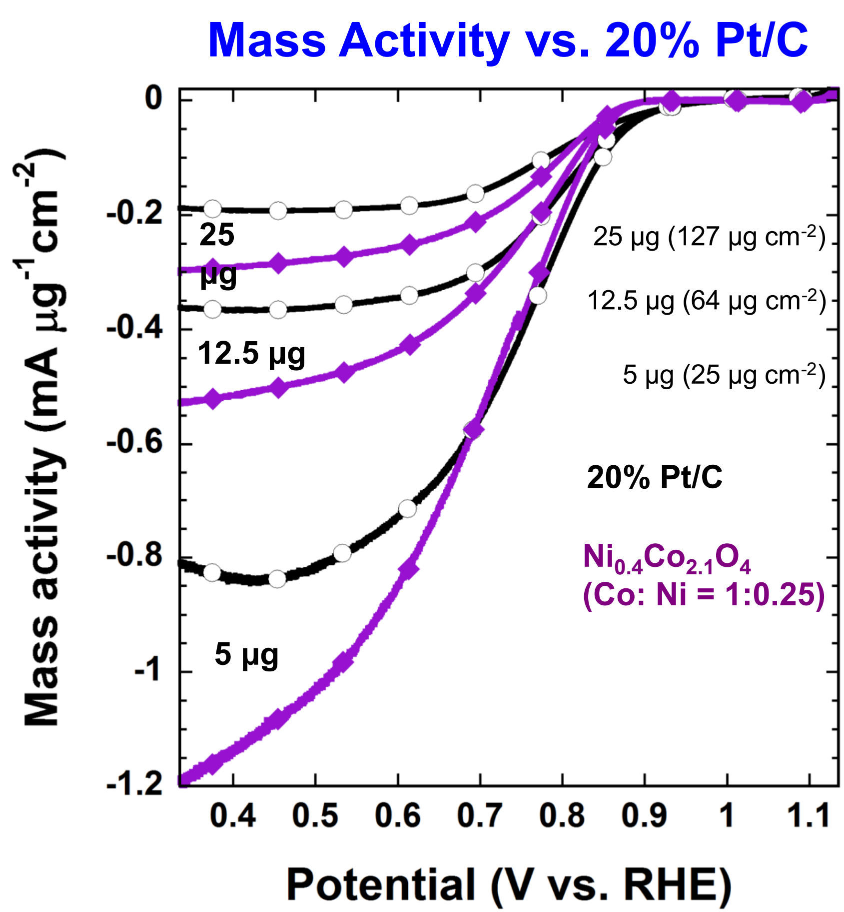
Co: Ni Ratio		Stoichiometry
1:0.25	=	$Ni_{0.4}Co_{2.56}O_4$
1:0.5	=	$Ni_{0.6}Co_{2.4}O_4$
1:1	=	$Ni_{0.9}Co_{2.1}O_4$

QCM



$Ni_xCo_{3-x}O_4$ Stoichiometry & Loadings





ORR/OER Activity: $Ni_{0.4}Co_{2.56}O_4$ > $Ni_{0.6}Co_{2.4}O_4$ > $Ni_{0.9}Co_{2.1}O_4$ > Co_3O_4

Most Active films has the least amount of Ni – Geometric or Electronic ?

T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

$Ni_xCo_{3-x}O_4$ Analysis

Is the larger crystallite size of $Ni_{0.4}Co_{2.6}O_4$ leading to more conductive sample ?

How does the surface area change ?

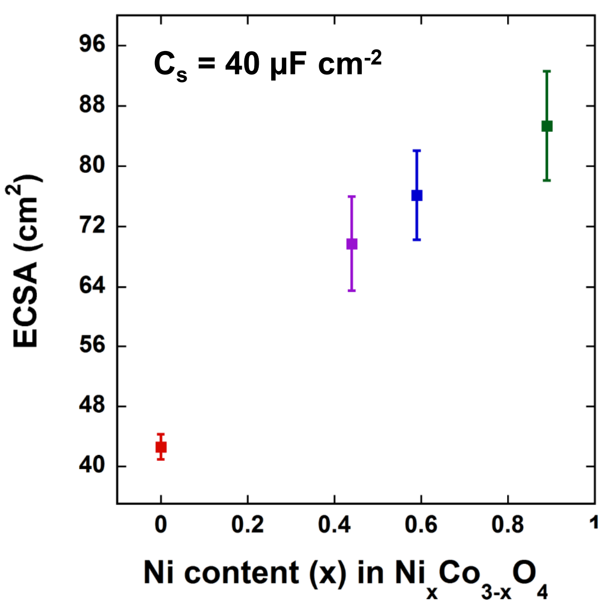
Charge transfer resistance

$Ni_{0.4}Co_{2.6}O_4$ (0.44 kΩ)
$Ni_{0.6}Co_{2.4}O_4$ (0.52 kΩ)
$Ni_{0.9}Co_{2.1}O_4$ (0.47 kΩ)
Co_3O_4 (0.62 kΩ)

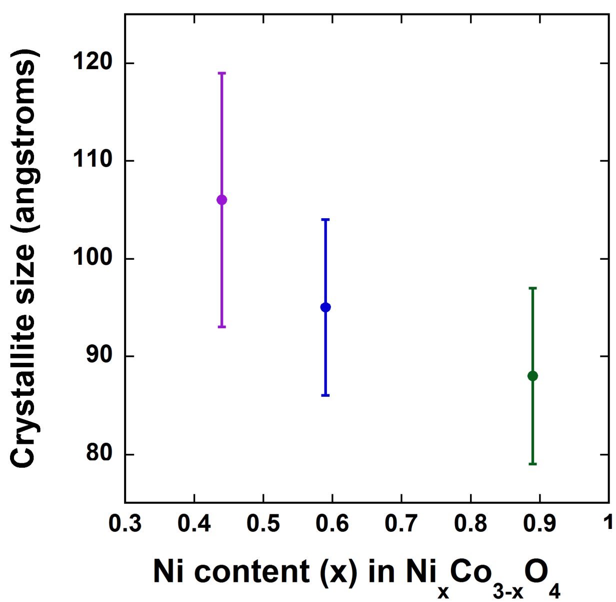
(BET) Surface Area

$Ni_{0.4}Co_{2.6}O_4$ (99.8 $m^2\ g^{-1}$)
$Ni_{0.6}Co_{2.4}O_4$ (94.2 $m^2\ g^{-1}$)
$Ni_{0.9}Co_{2.1}O_4$ (101.4 $m^2\ g^{-1}$)
Co_3O_4 (88.7 $m^2\ g^{-1}$)

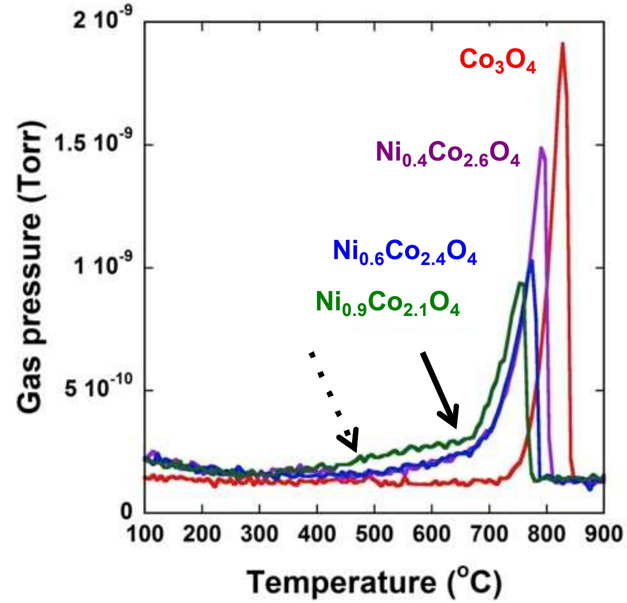
ECSA



Scherrer (XRD)



TGA/MS



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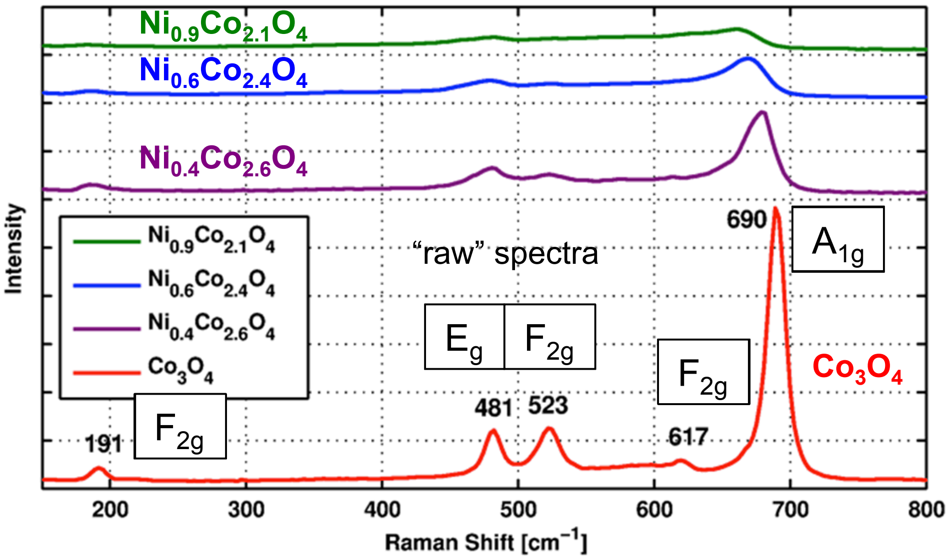
Spectral (Electronic) Analysis

Raman spectroscopy

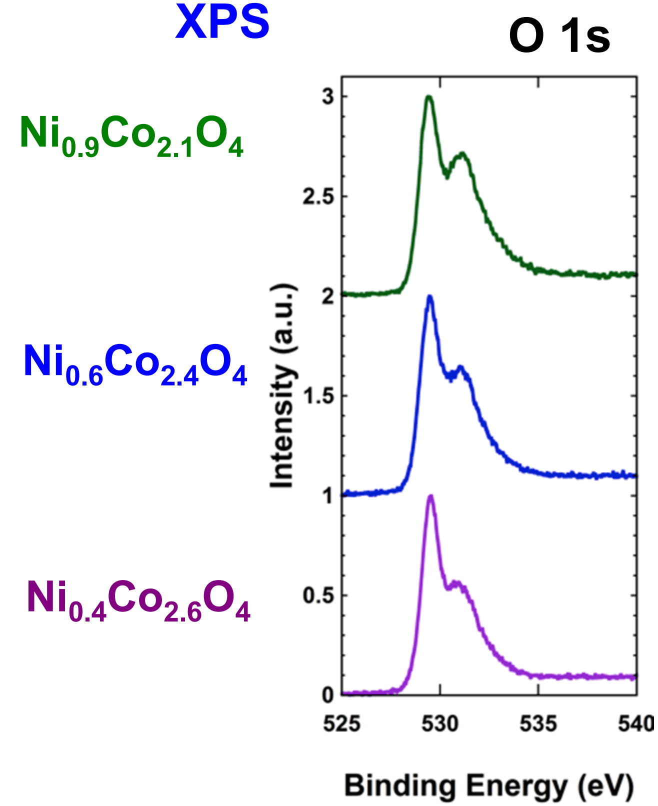


Co_3O_4 within 3 cm^{-1} of literature

Broad line widths = crystalline disorder (increases with Ni)

Raman could not Find NiO (fcc)

XPS



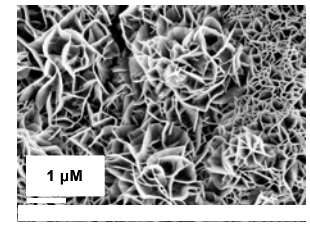
XPS did not show any difference in Ni valence

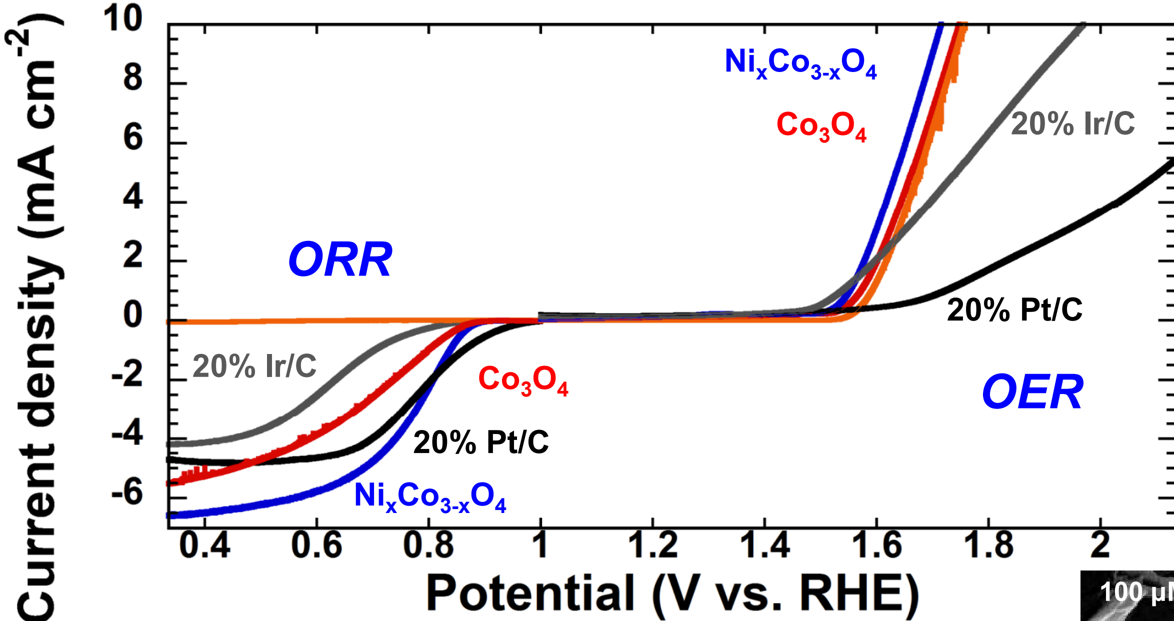
XPS shows ↑ Ni = ↑ hydroxyl

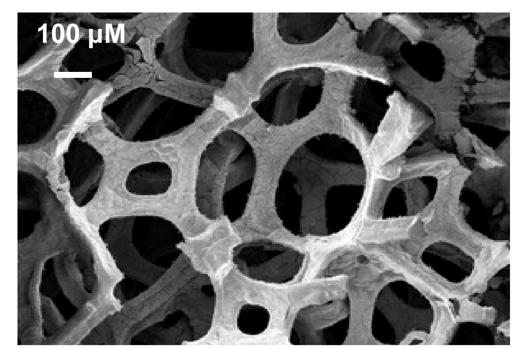
T. N. Lambert *et al. Chem. Commun.* **2015**, *51*, 9511-9514.

Summary

$$Co(NO_3)_2 + Ni(NO_3)_2 \xrightarrow{e^-} Co_{1-z}Ni_z(OH)_{2-x}(NO_3)_x \bullet y(H_2O) \xrightarrow{\Delta} Ni_xCo_{3-x}O_4$$

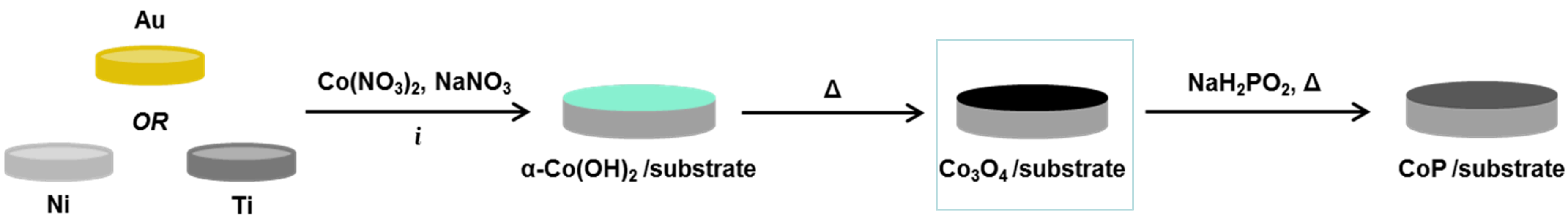






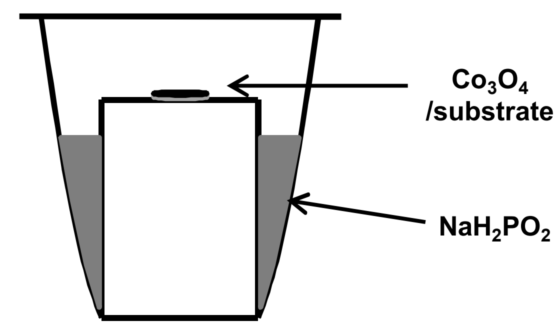
- *Activity $Ni_{0.4}Co_{2.56}O_4$* > *$Ni_{0.6}Co_{2.4}O_4$* > *$Ni_{0.9}Co_{2.1}O_4$* > *Co_3O_4*
  (Conductivity or increased presence of NiO)
- **Δ(OER-ORR) = 0.96, competitive with other *$Ni_xCo_{3-x}O_4$***

Bifunctional CoP-based nanostructured films for the HER and OER



$$2NaH_2PO_{2\,(s)} \longrightarrow PH_{3\,(g)} + Na_2HPO_{4\,(s)}$$

$$vPH_{3\,(g)} + wCo_3O_{4\,(s)} \longrightarrow xCoP_{(s)} + P_{(s)} + zH_2O_{(g)}$$



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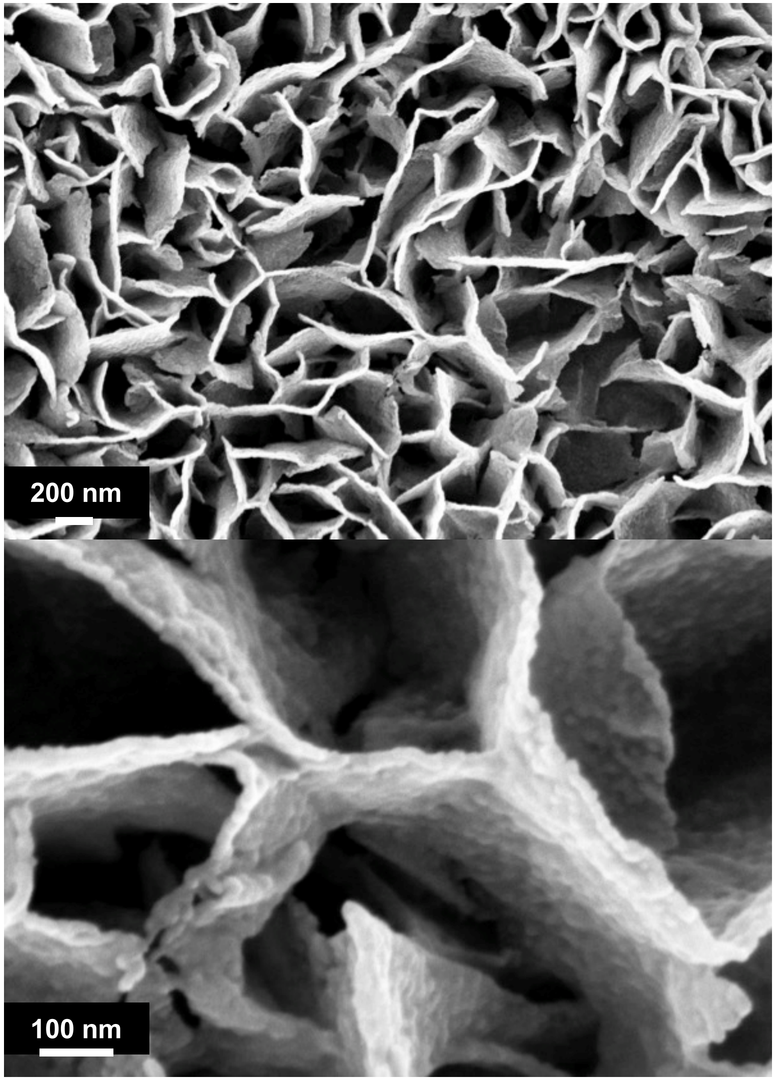
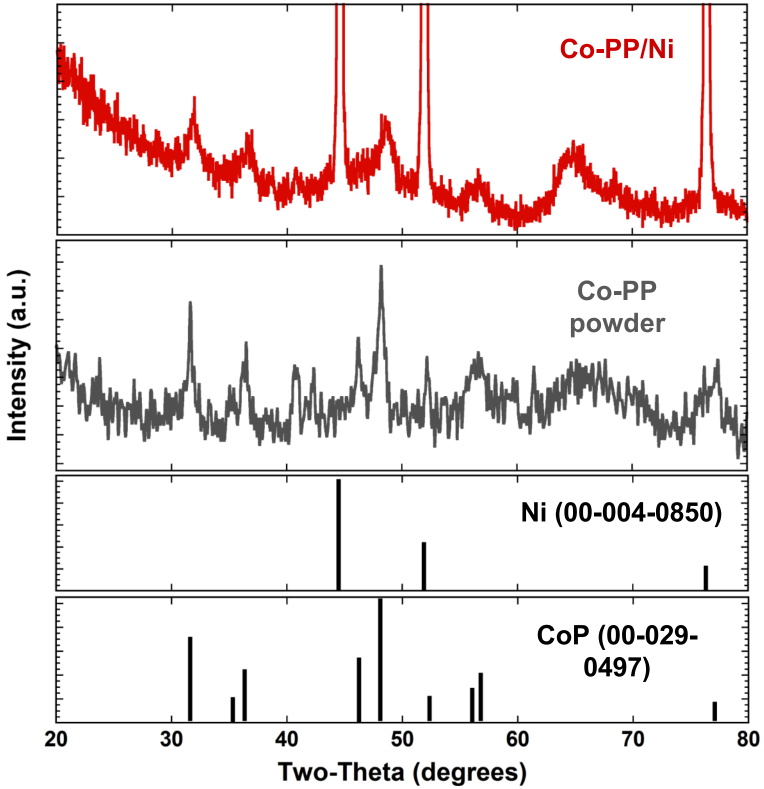
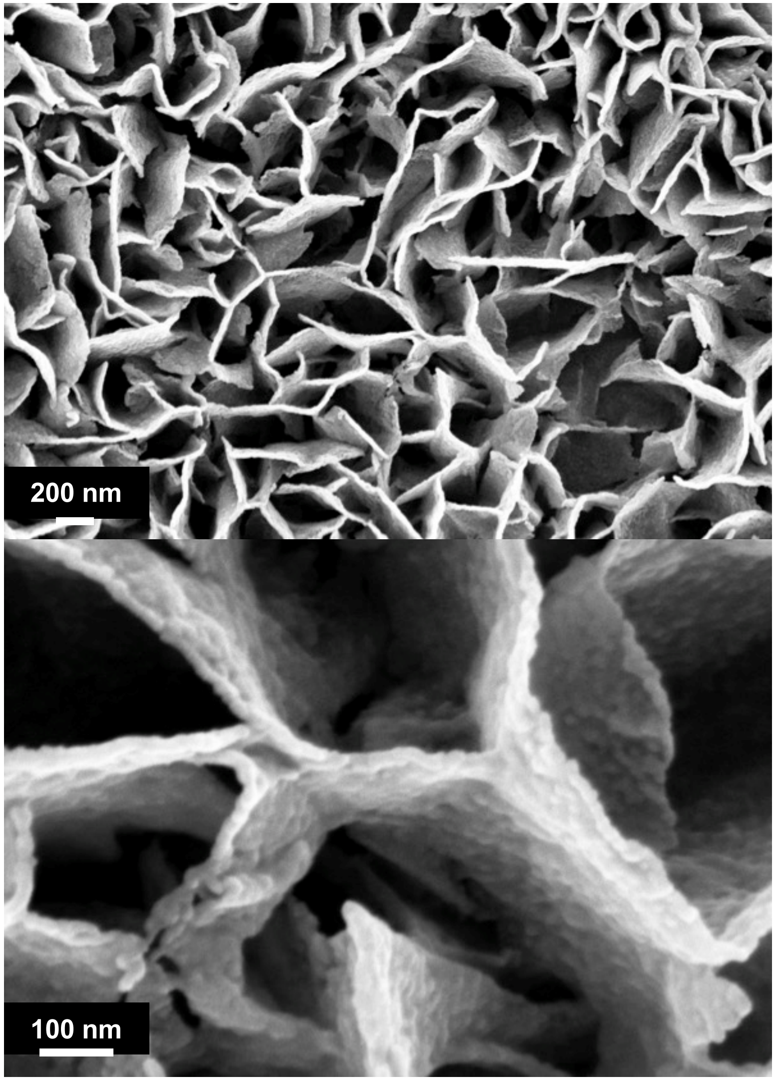
Bifunctional CoP-based nanostructured films for the HER and OER

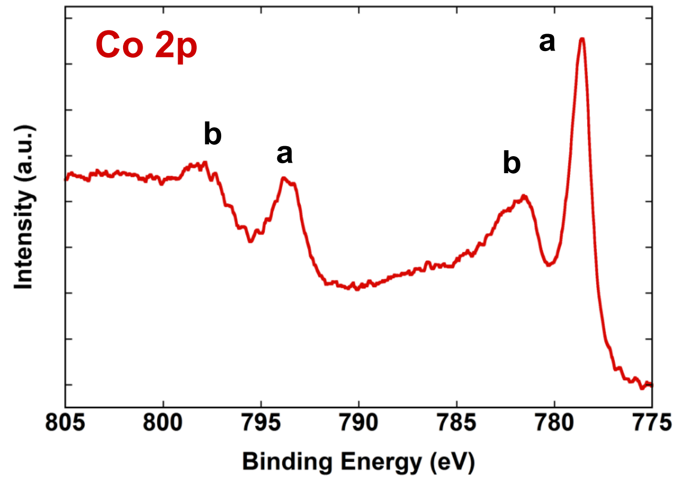




Mostly CoP (some oxide possible)

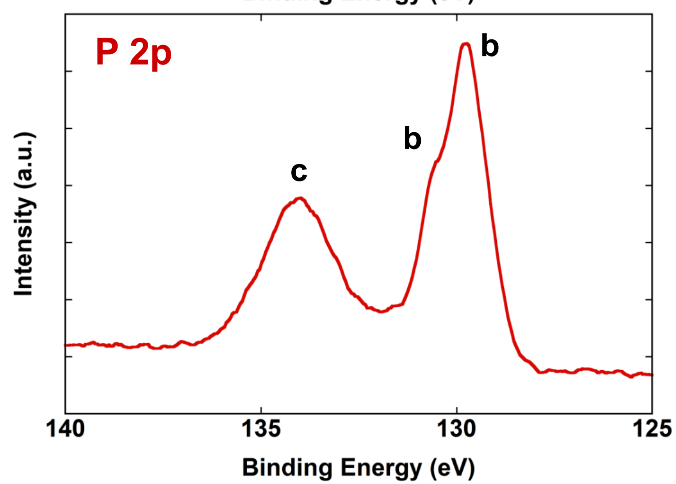
Bifunctional CoP-based nanostructured films for the HER and OER





a: CoP (Co°)

b: Co-phosphate/oxide



c: Phosphate

b: Phosphide ($2p_{1/2}$ & $2p_{3/2}$)

Cobalt phosphide and phosphate (surface oxidation of nano)

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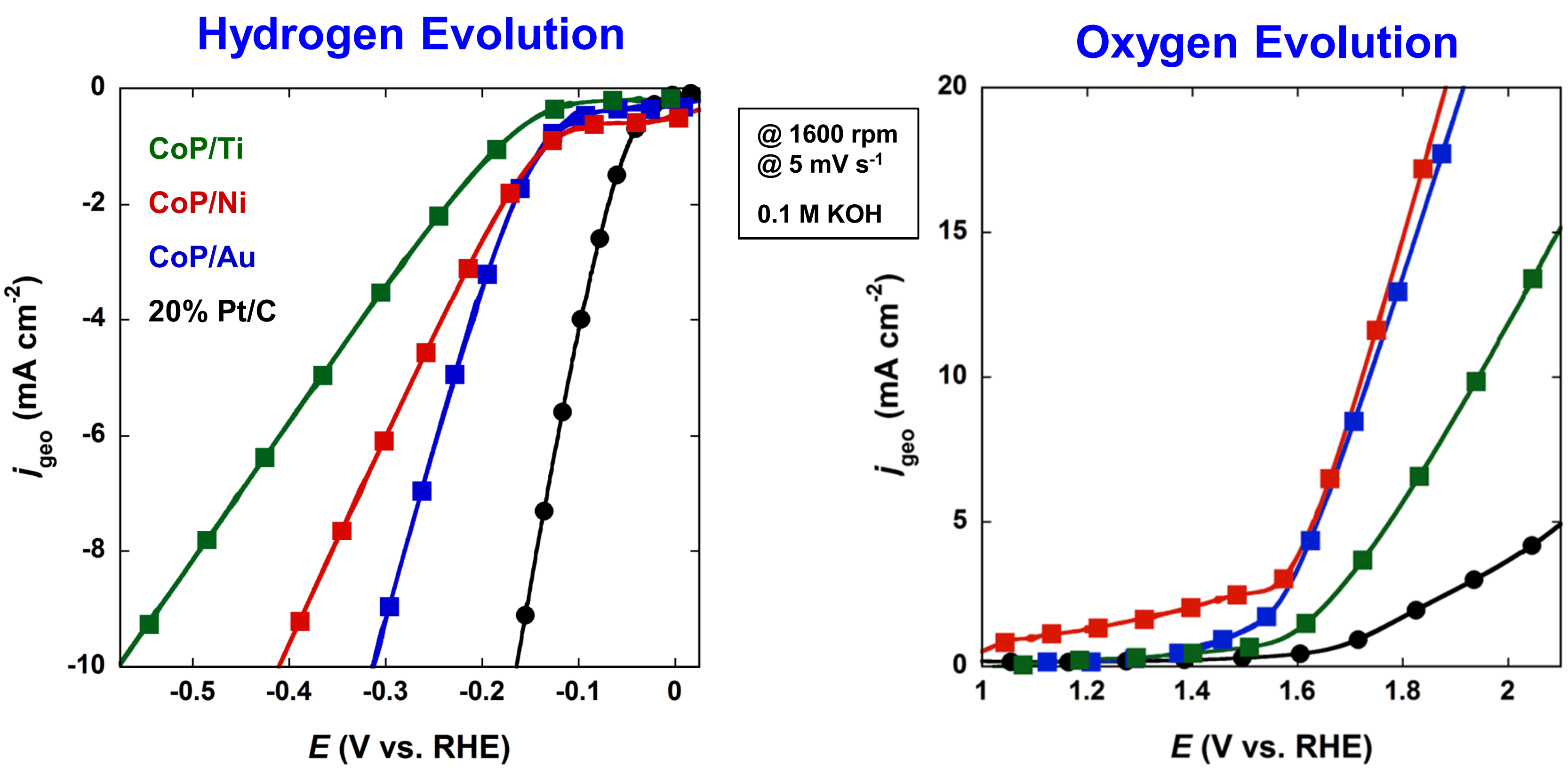
Bifunctional CoP-based nanostructured films for the HER and OER

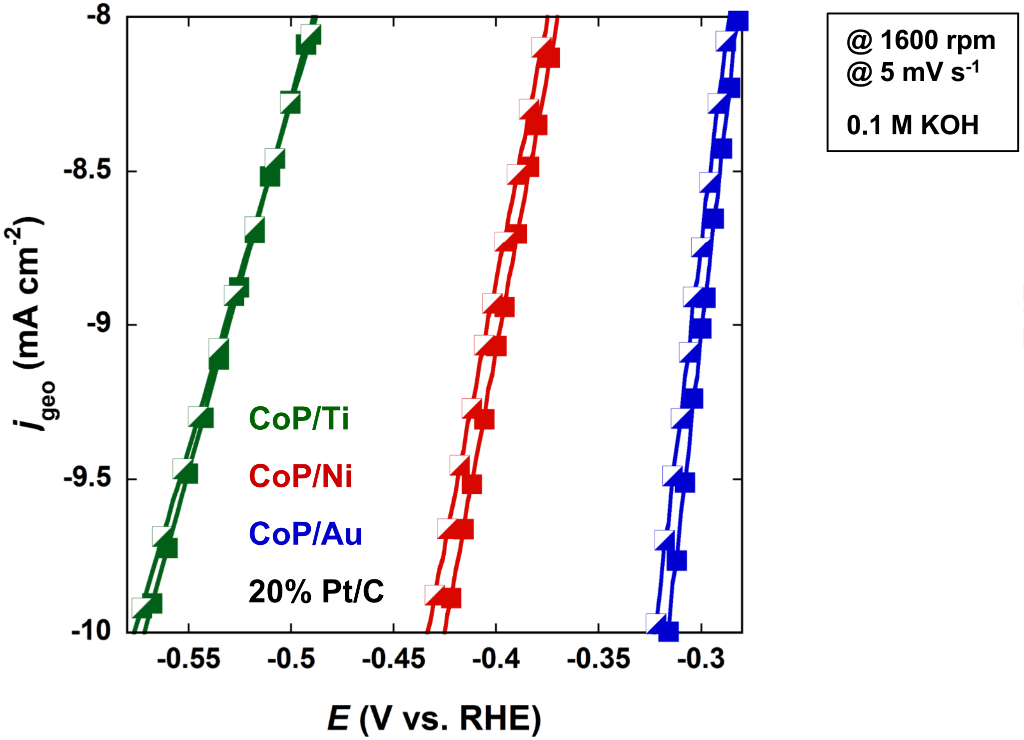


HER (HO^-): CoP/Au > CoP/Ni > CoP/Ti

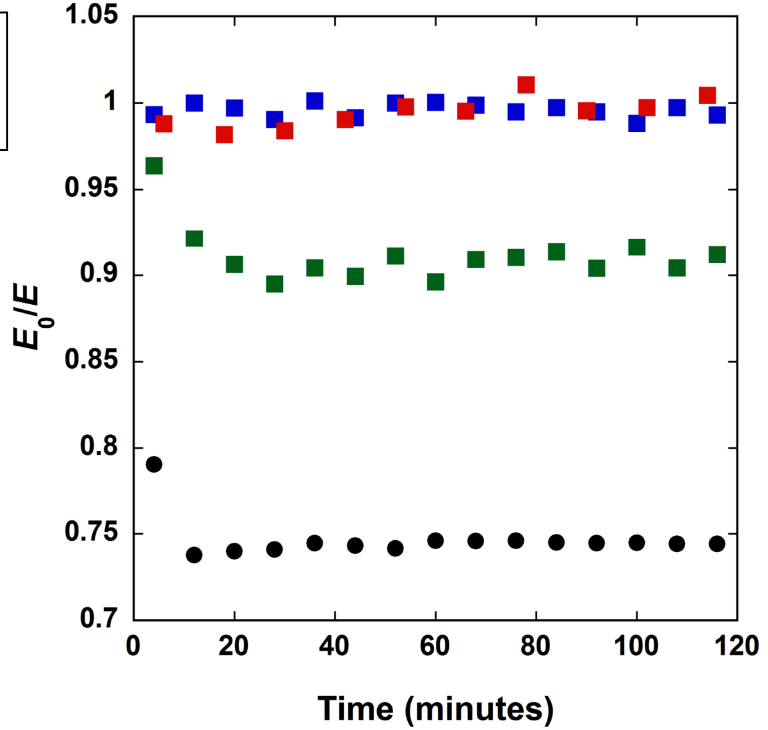
OER (HO^-): CoP/Au ~ CoP/Ni > CoP/Ti

Bifunctional CoP-based nanostructured films for the HER and OER

HER: Stability testing

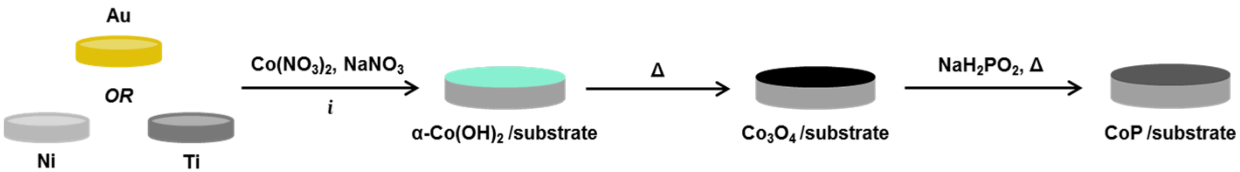


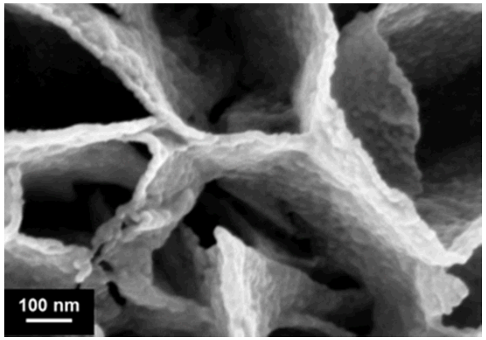
OER: Stability testing

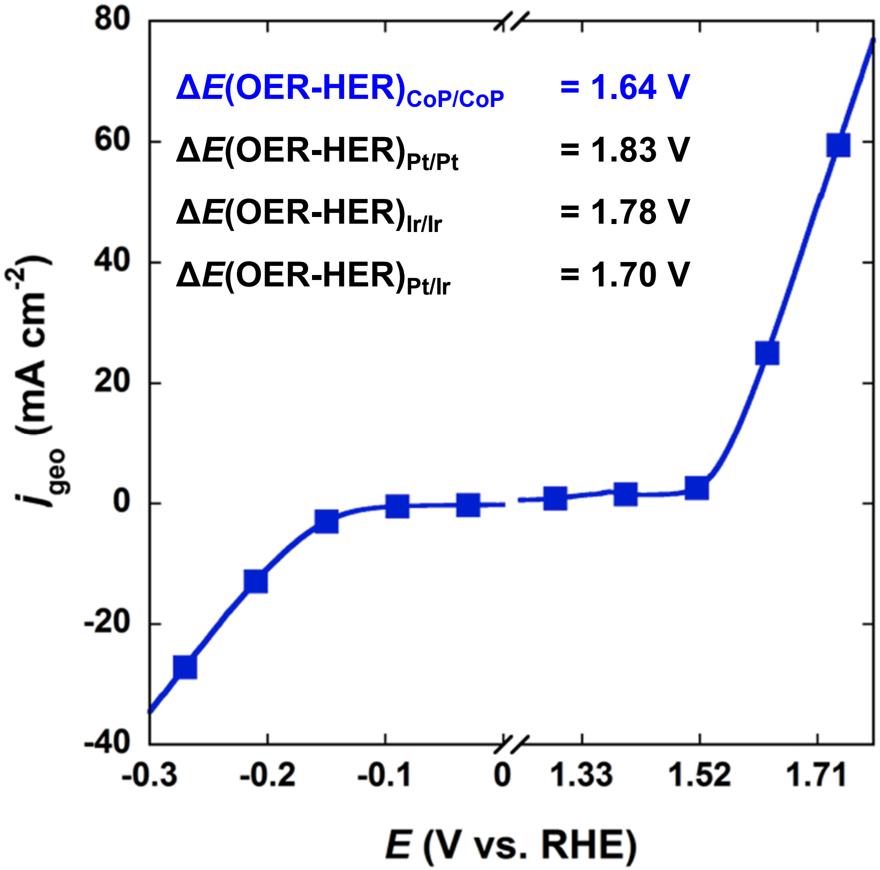


HER (HO^-): CoP/Au > CoP/Ni > CoP/Ti

Bifunctional CoP-based nanostructured films for the HER and OER

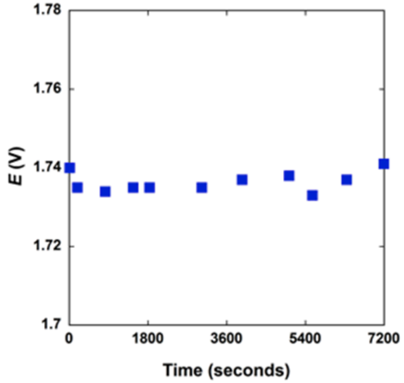


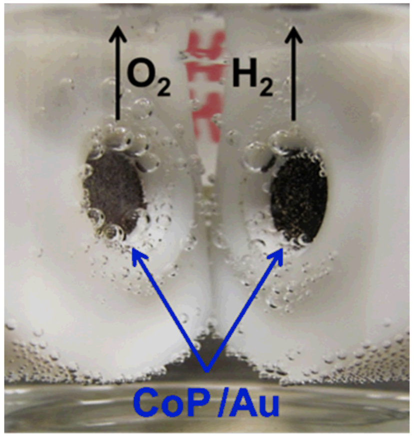




HER: $4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^-$

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





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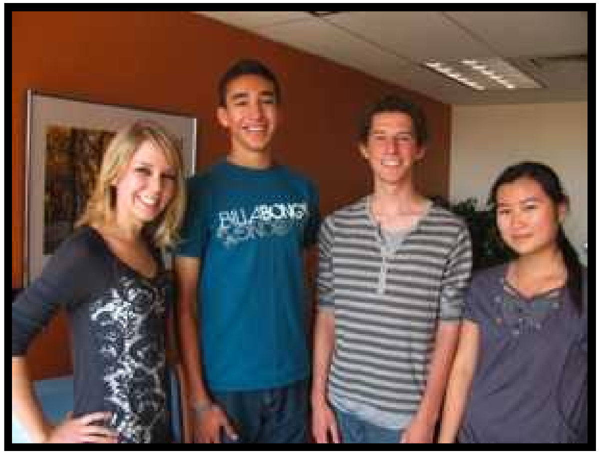
- Sandia National Laboratories (LDRD)
- Department of Energy
- SNL STAR Program
- Lambert Group

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



Suzanne White
High School Student

- Additional SNL/CINT collaborators:

  Mark Rodriguez (XRD)

  Mike Brumbach (XPS)

  Eric Coker (TGA/MS)

  Paul Kotula (TEM/EELS)

  Bonnie McKenzie (SEM)

Patrick Burton, Ph.D.

Steven Limmer, Ph.D

Seeking Postdoc

Job #652439: Postdoctoral Appointee – Electrochemistry

Application Window: 2/08/2016 – 3/09/2016

Primary Responsibility:
Reversible Zn/MnO_2 batteries for grid energy storage

Other:
Electrocatalysis – Materials and Testing

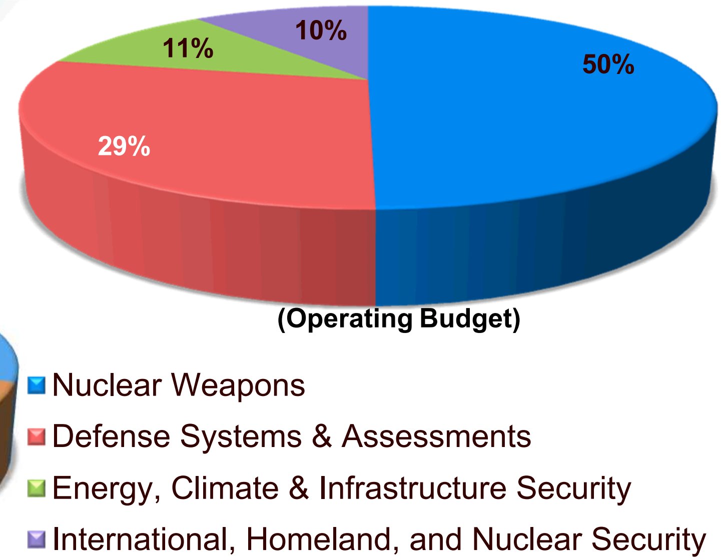
Thank you

People and Budget

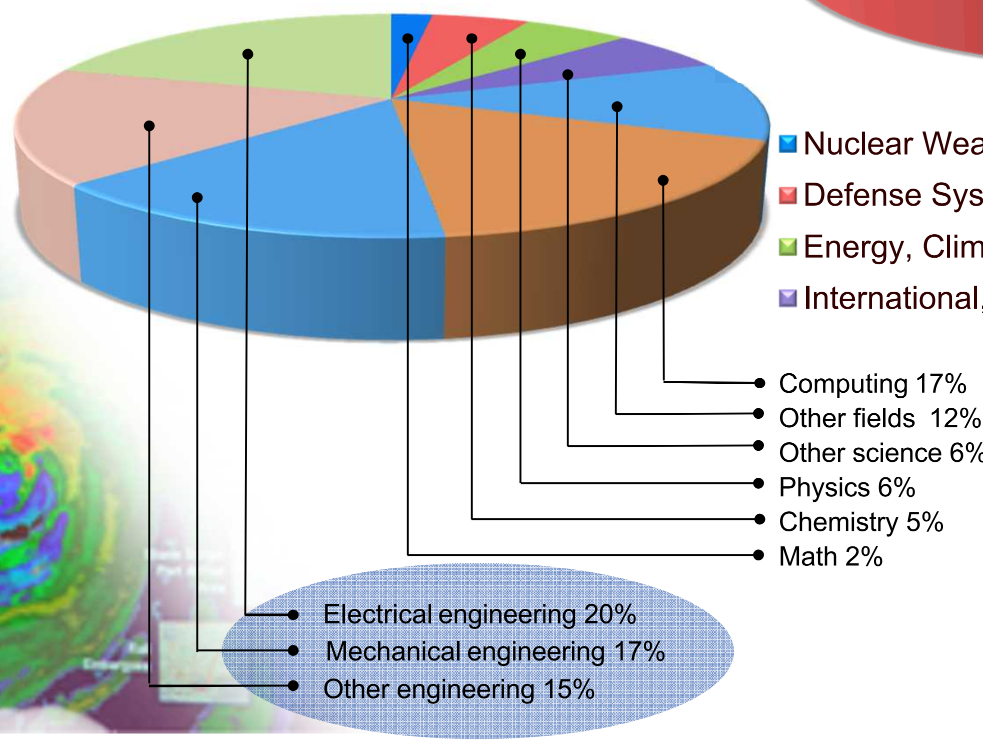
(As of October 11, 2011)

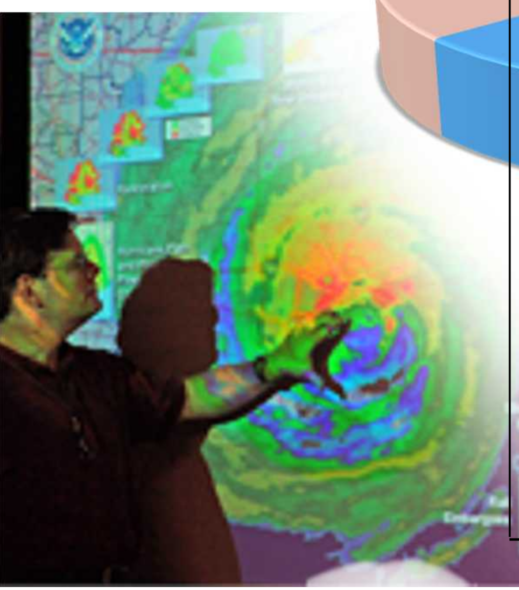
- On-site workforce: 11,876
- Regular employees: 9,122
- Gross payroll: ~$943 million

FY11 Operating Revenue $2.4 billion



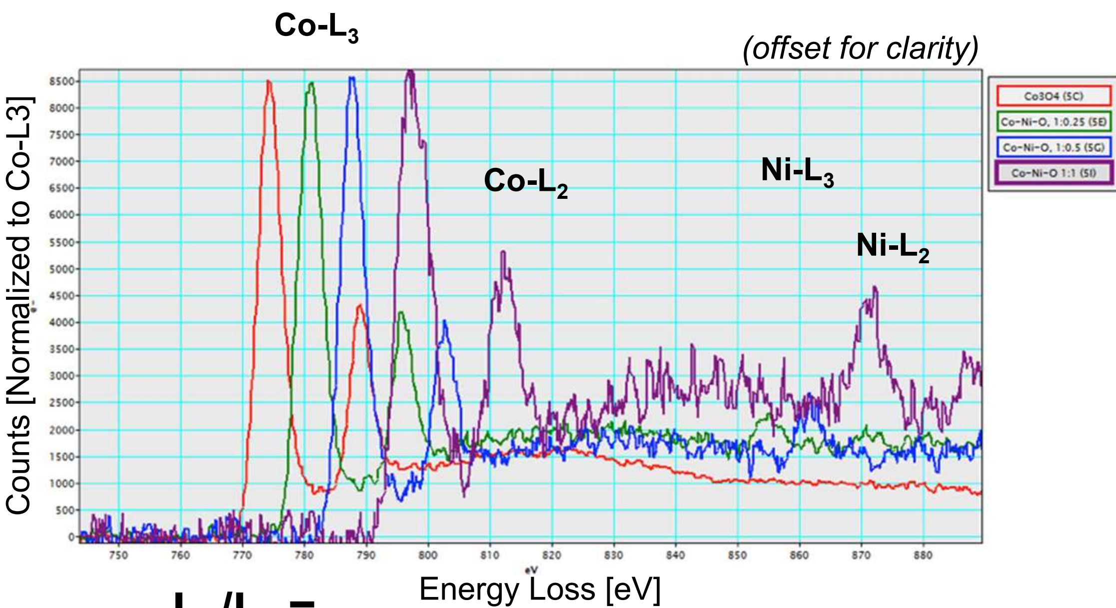
Technical staff (4,557) by discipline





Spectral Analysis

TEM EELS



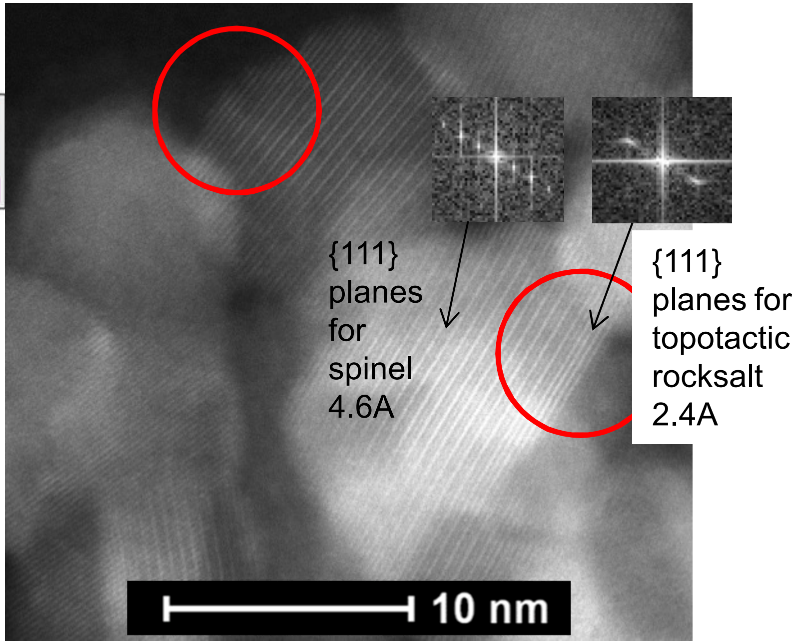
L_3/L_2 =

Co_3O_4	**2.9 ± 0.17**
$Ni_{0.4}Co_{2.6}O_4$	**3.0 ± 0.15**
$Ni_{0.6}Co_{2.4}O_4$	**3.0 ± 0.19**
$Ni_{0.9}Co_{2.1}O_4$	**2.7 ± 0.21** ← Higher Co^{3+} content?

L_3/L_2 is sensitive to the valence state of the corresponding element

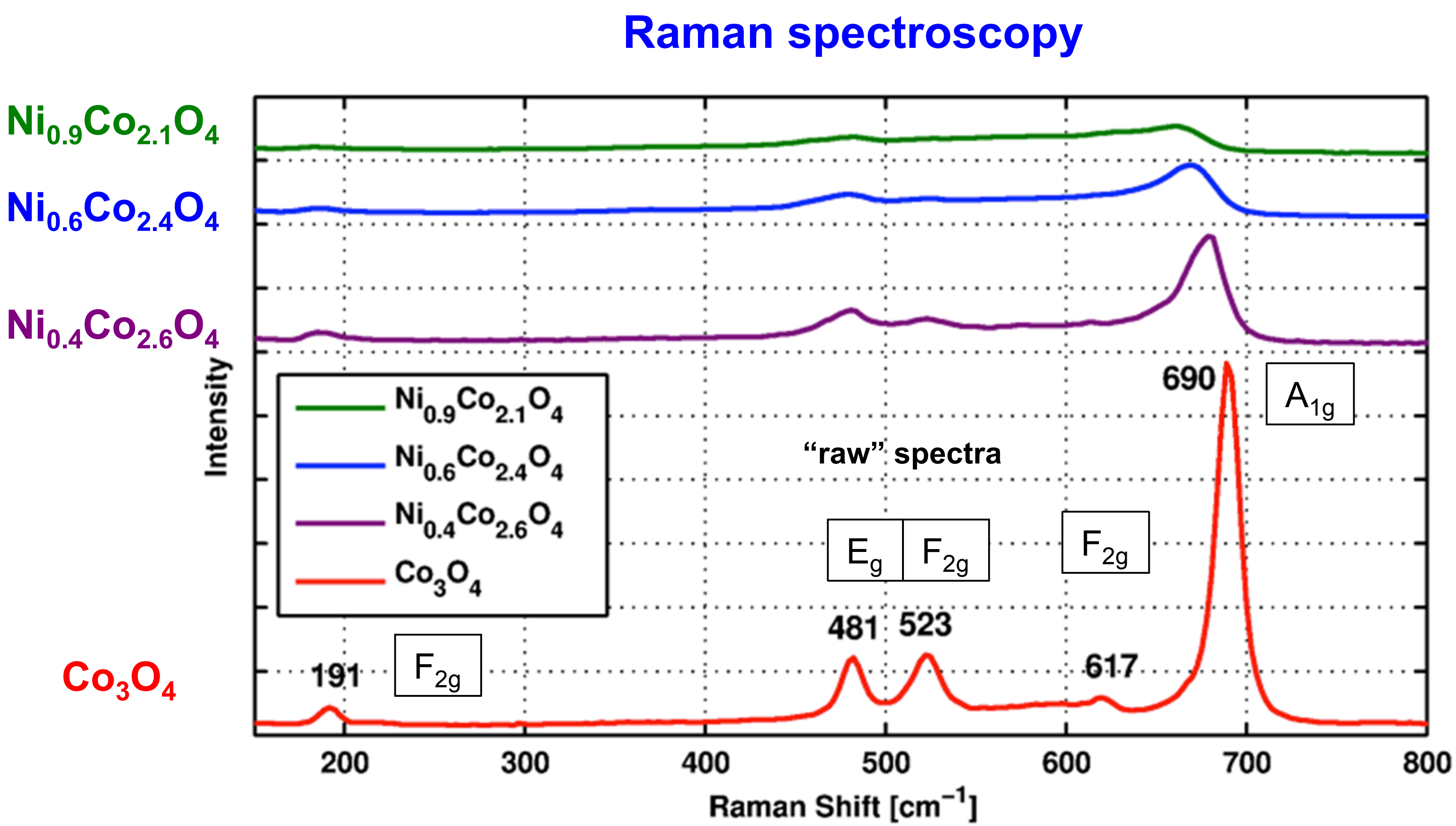
Z. L. Wang, *et al. Micron* **31** (2000) 571-580.

TEM SAED



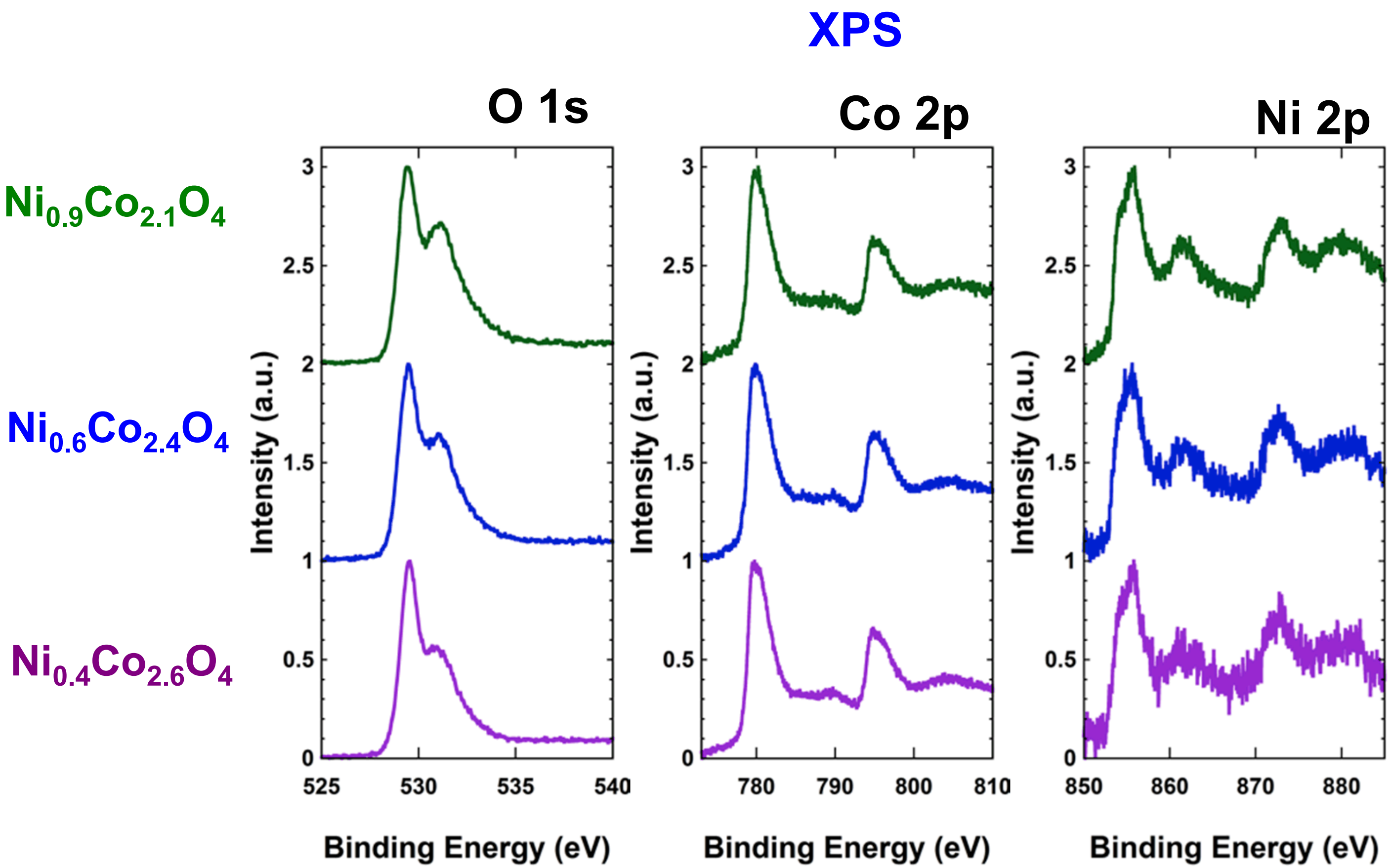
- Evidence from diffraction that rocksalt may be present in low quantities for all samples
- Direct imaging evidence for rocksalt found for $Ni_{0.9}Co_{2.1}O_4$
- Unexpected peak at ~ 1.61-1.65Å for all samples

Spectral (Electronic) Analysis



Raman could not Find NiO (fcc)

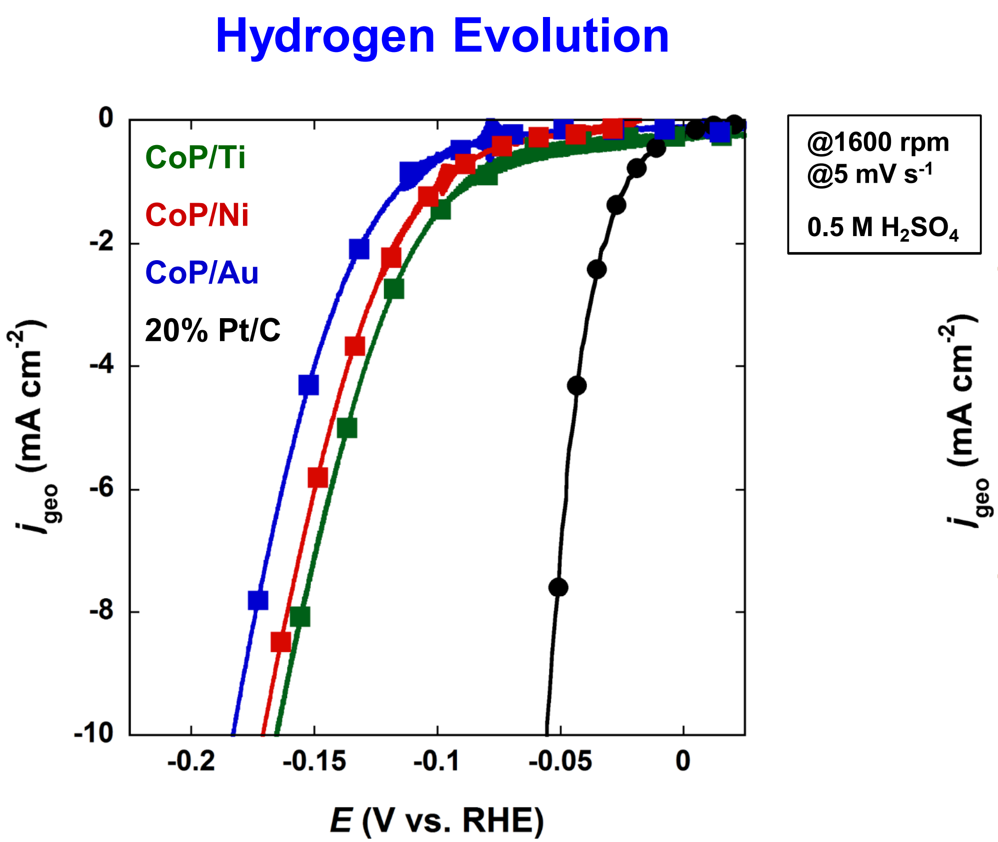
Spectral (Electronic) Analysis

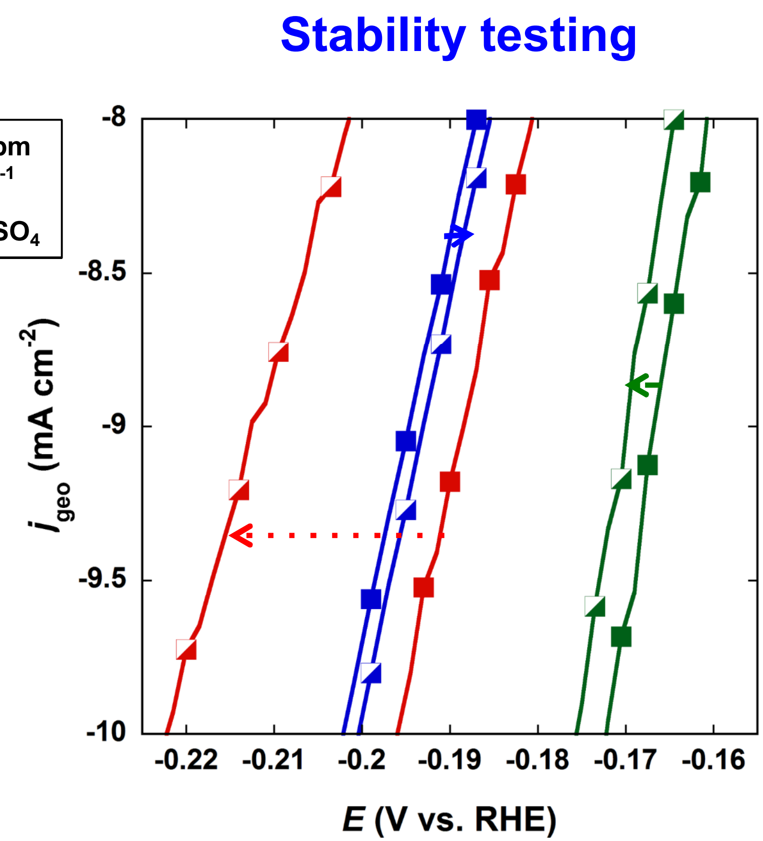


XPS did not show any difference in Ni valence

XPS shows ↑ Ni = ↑ hydroxyl

Bifunctional CoP-based nanostructured films for the HER and OER

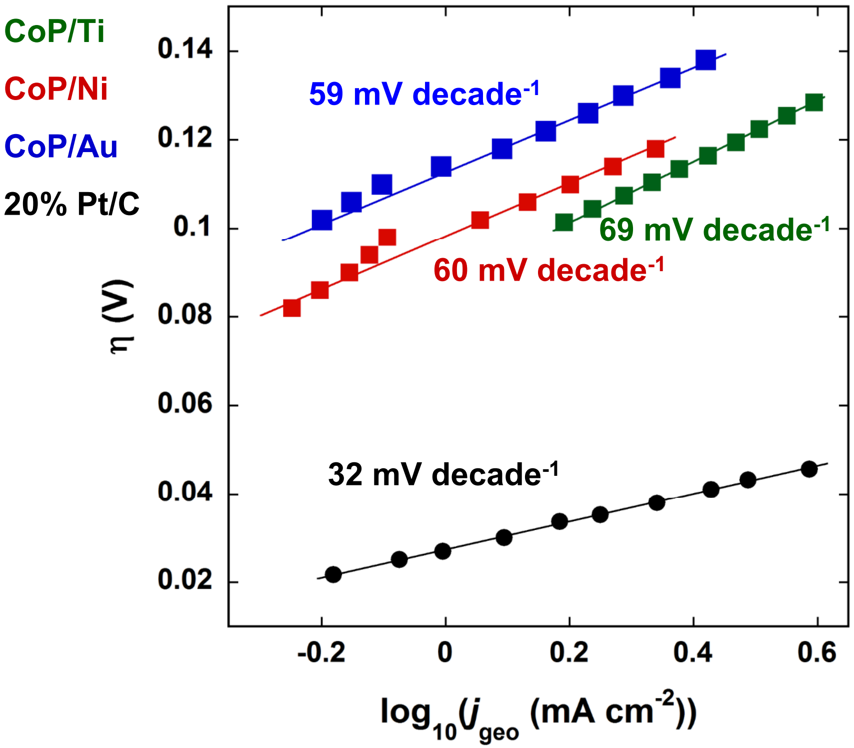




HER (H^+): CoP/Ti > CoPAu > CoP/Ni

Bifunctional CoP-based nanostructured films for the HER and OER

HER: $2H^+ + 2e^- \rightarrow H_2$



1. Volmer Reaction (Primary Discharge Step):

$H_3O^+ + e^- \rightarrow H_{ads} + H_2O$ $b = 2.3\,RT/\alpha F \approx 120$ mV

2a. Heyrovsky reaction (Electrochemical Desorption Step):

$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O$ $b = 2.3\,RT/(1+\alpha)F \approx 40$ mV

OR

2b. Tafel Reaction (Recombination Step):

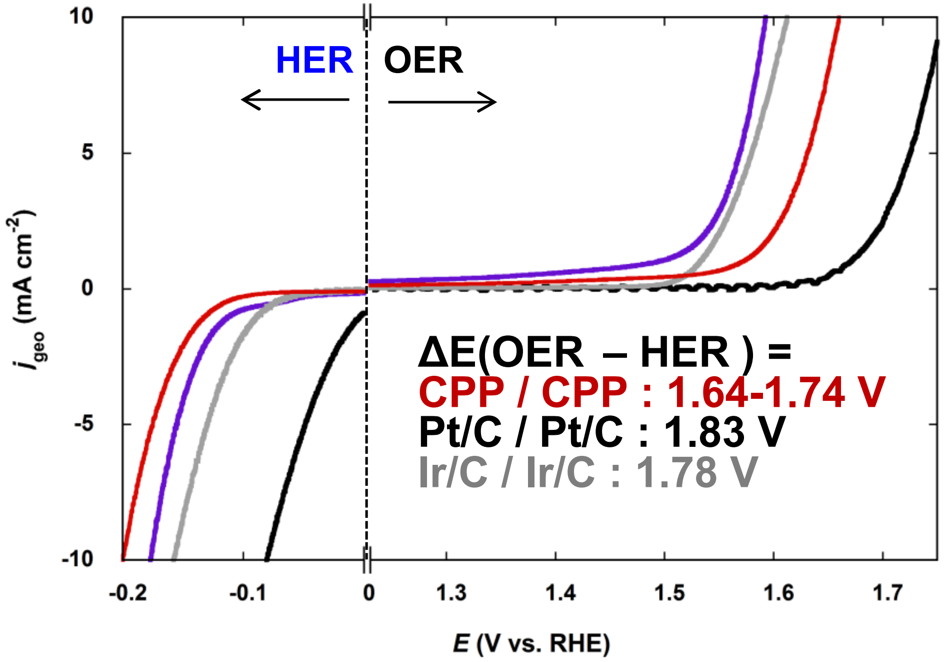
$H_{ads} + H_{ads} \rightarrow H_2$ $b = 2.3\,RT/2F \approx 30$ mV

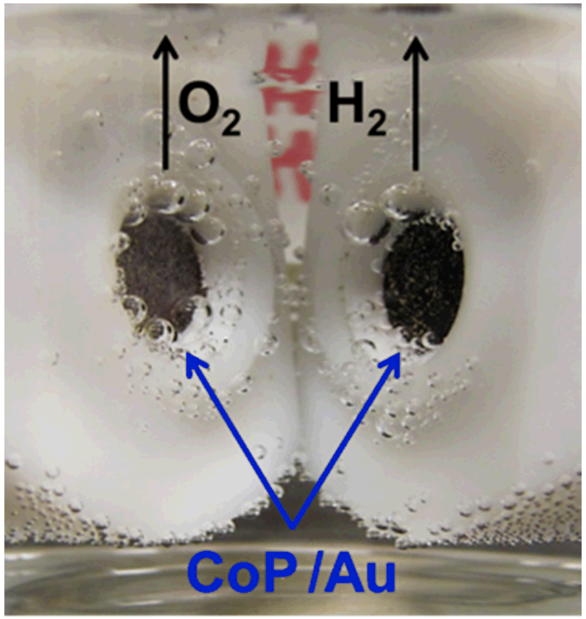
J. A. Vigil *et al. RSC Advances* **2015**, *5*, 105814-105819.

Bifunctional CoP-based nanostructured films for the HER and OER

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

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





J. A. Vigil *et al.* *RSC Advances* **2015**, *5*, 105814-105819.

The Pathways of ORR

Alkaline Media

(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:

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

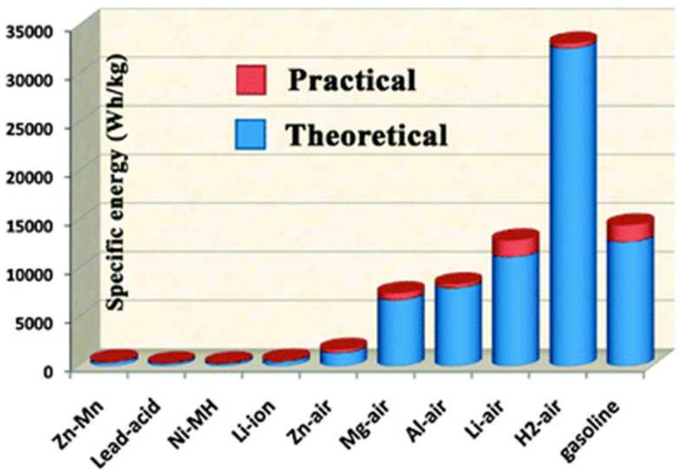
or (b) the catalytic peroxide decomposition:

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

Importance of O_2 Electrochemistry

Electrical Energy Storage

Gravimetric Energy Densities



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

Multi-electron ceramic/air batteries (Primary)

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

Practical volumetric capacities:

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

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

Sodium/air batteries (Secondary)

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

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

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

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

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

Solar Fuels Synthesis

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

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

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

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