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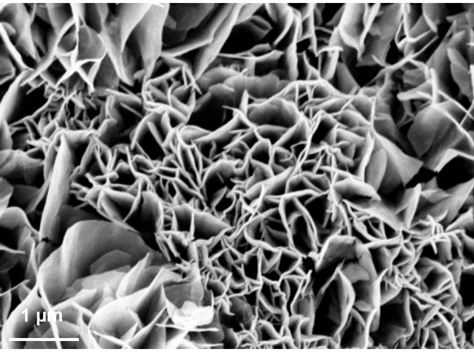

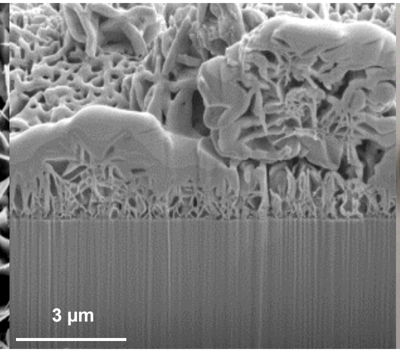

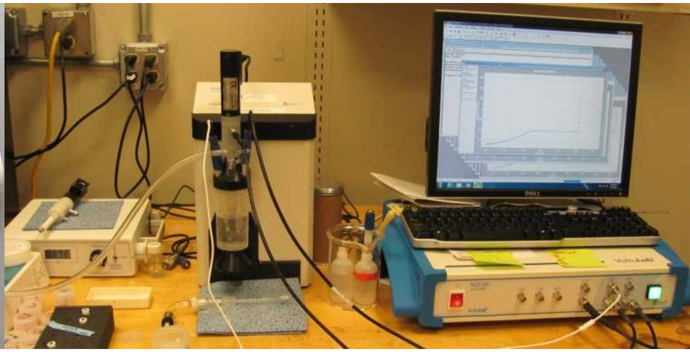

Nanostructured Nickel-Cobalt Oxide Spinel Films as Bi-Functional Electrocatalysts in Alkaline Media

Julian A. Vigil*, Timothy N. Lambert, Danae J. Davis, Suzanne E. White, Steven J. Limmer
Sandia National Laboratories; Materials, Devices, and Energy Technologies

U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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The Importance of Oxygen Electrocatalysis

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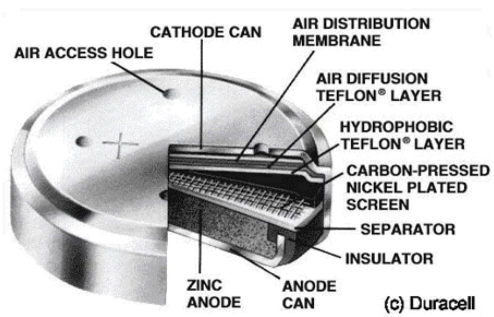
Devices that use water electrolysis for energy conversion and storage:

- Metal-Air Batteries
- Fuel Cells
- Electrolyzers

Practical Volumetric capacities:

Li-ion = 0.5 kWh L^{-1}
Zn-air = 1.75 kWh L^{-1}
Gasoline = 2.7 kWh L^{-1}
VP-air = 4.81 kWh L^{-1}

T. Lambert, D. Davis *et al.*, *Chem. Commun.*, **2011**, 47, pp 9597-9599.

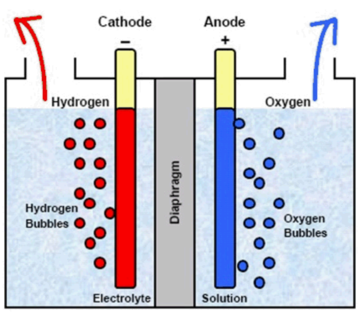


Zinc-Air Battery (Alkaline) –

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

Cathode Reaction: $O_2 + H_2O + 4e^- \longrightarrow 4OH^-$

Oxygen Reduction Reaction



Standard Electrolysis

Fuel Cell Electrolysis (Alkaline) –

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

Oxygen Evolution Reaction

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

Catalysis of the Oxygen Reduction and Oxygen Evolution Reactions

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Oxygen Reduction Reaction (ORR)

$O_2 + H_2O + 4e^- \longrightarrow 4OH^-$ ***OR*** $O_2 + H_2O + 2e^- \longrightarrow HO_2^- + OH^-$

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

Oxygen Evolution Reaction (OER)

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

Efficient, Economically Viable Electrocatalysts:

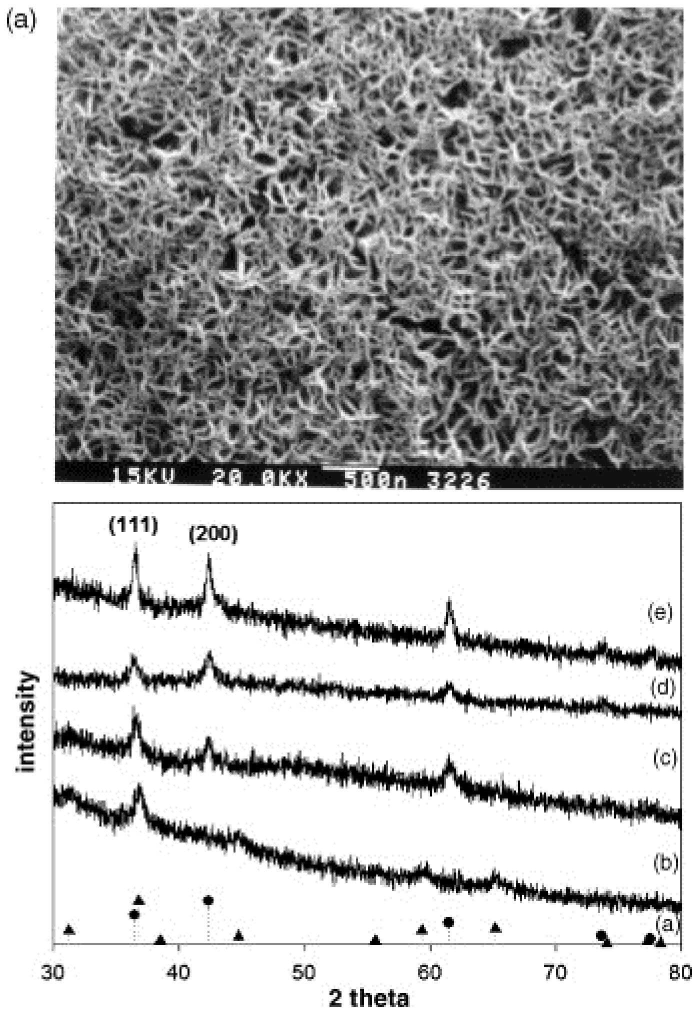
Nano-size particles → High Surface Area → Non-Precious Metal → Easily Prepared → Catalyzes ORR → Catalyzes OER

- Allows more sites for electrolyte and oxygen to interact with catalyst surface.

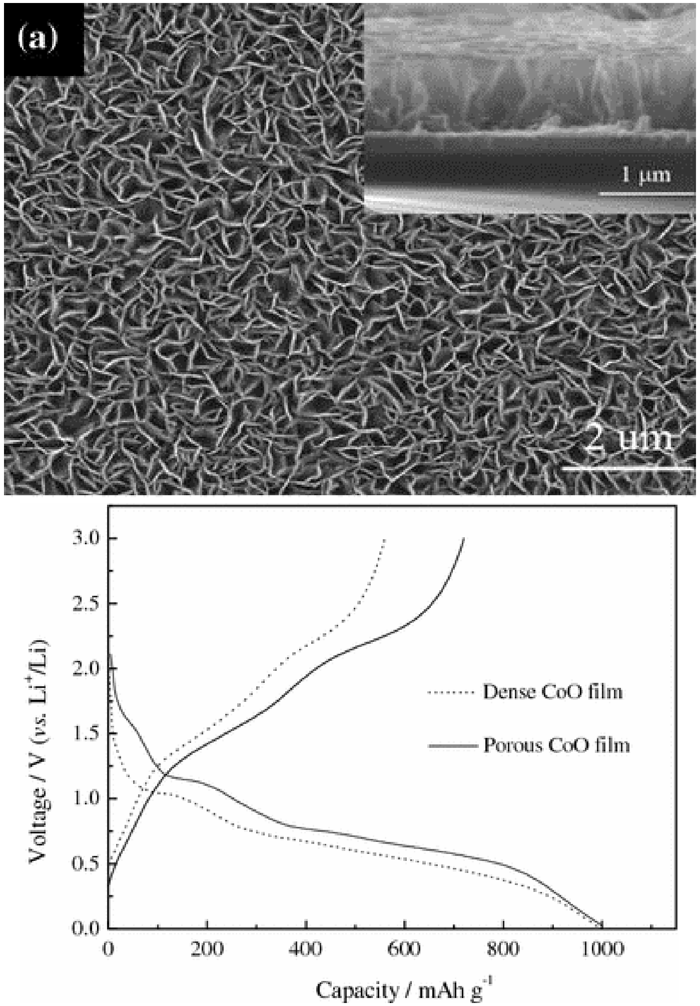
- Economically viable.
- Simple preparation.
- Scalable for large-scale production/ consumption.

- **Bi-Fuctionality**
- Allows for use in multiple kinds of devices, as an anode or a cathode material.
- Allows batteries to be re-chargeable.

Cobalt Oxide Films and Catalysts – Recent Studies



J. Do, R. Dai, *Journal of Power Sources* 189 **2009**, p 204-210.



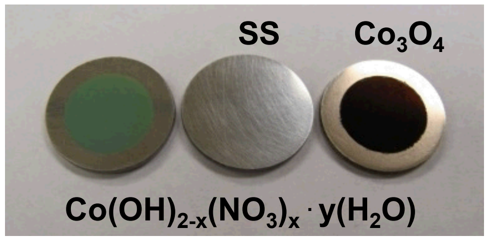
A. Xiao, J. Yan *et al., J. Porous Mater* **2010**, 17, p 583-588.

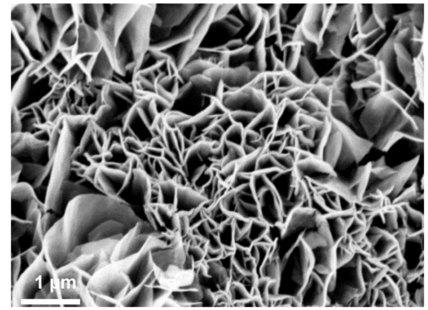
Cobalt Oxide Nanostructured Spinel Film Synthesis

Sandia National Laboratories

Preliminary, un-doped cobalt oxide films

$$Co(NO_3)_2 \bullet 6H_2O_{(aq)} + NaNO_{3(aq)} \xrightarrow{i} \alpha - Co(OH)_2 \xrightarrow{\Delta} \mathbf{Co_3O_4}$$





Ni-doped cobalt oxide films

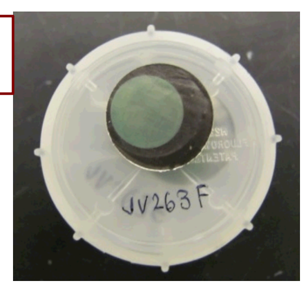
$\boxed{1}$ $Ni(NO_3)_2 \bullet 6H_2O_{(aq)} + Co(NO_3)_2 \bullet 6H_2O_{(aq)} + NaNO_{3(aq)} \xrightarrow{i}$

$\boxed{2}$ $Ni - \alpha - Co(OH)_2 \xrightarrow{\Delta}$

$\boxed{3}$ $\mathbf{Ni_xCo_{3-x}O_4}$

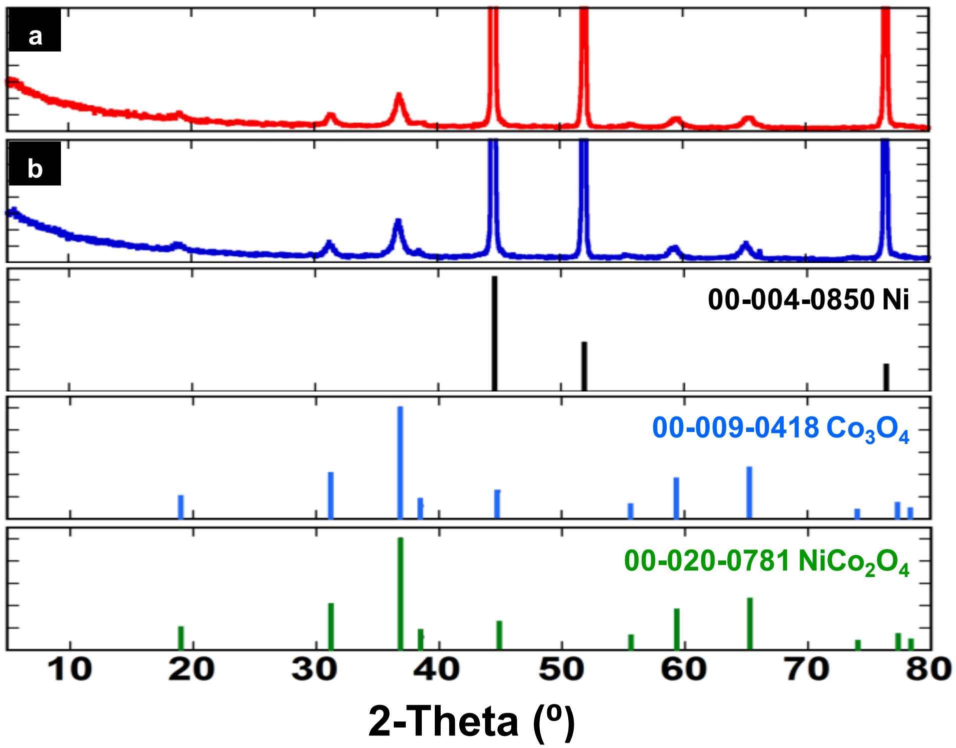
1

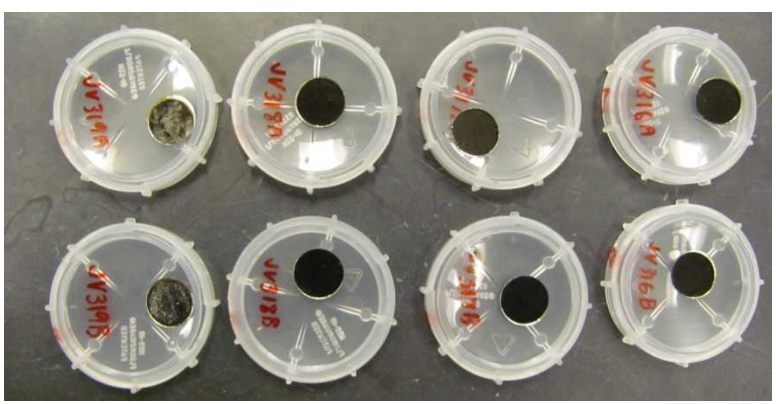
2

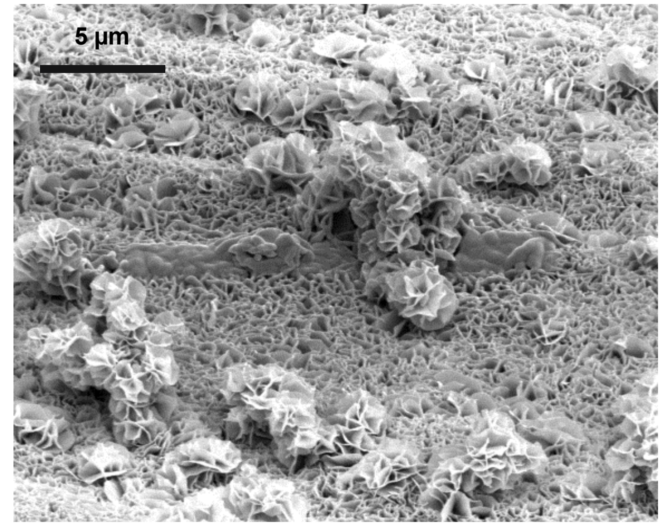


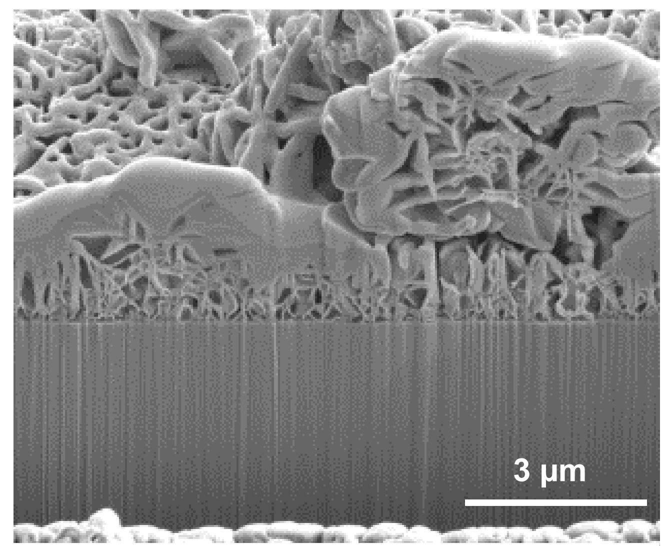
3

Characterization of Nickel-Cobalt Oxide Films







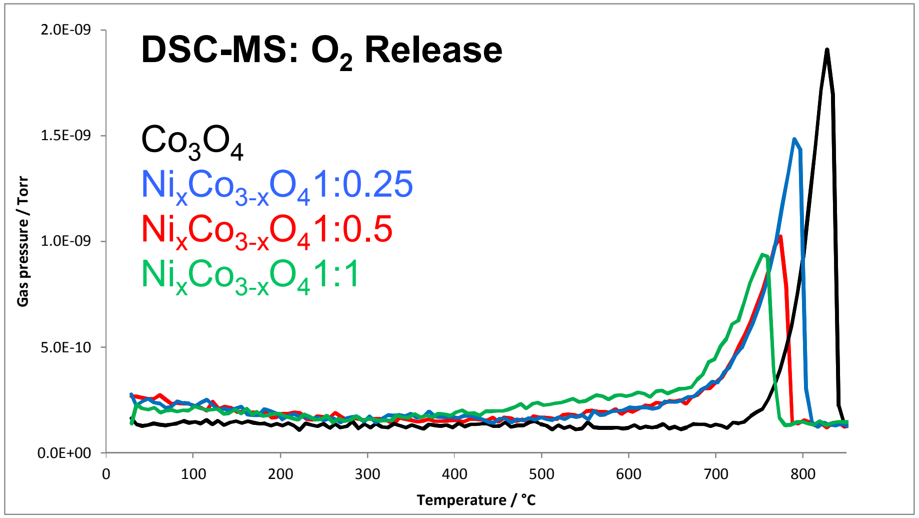


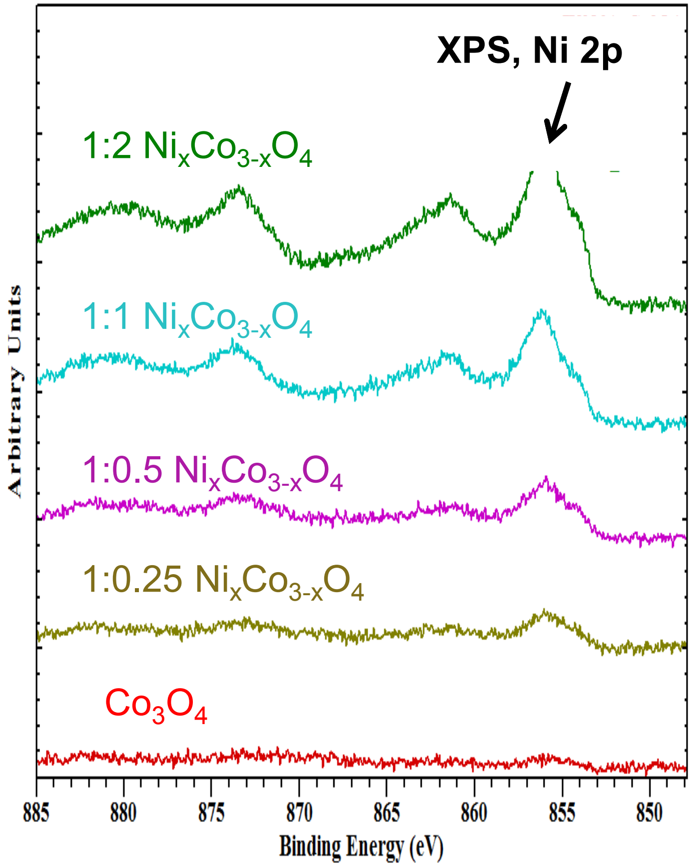
Varying Ni-doping levels in $Ni_xCo_{3-x}O_4$ (changing x)

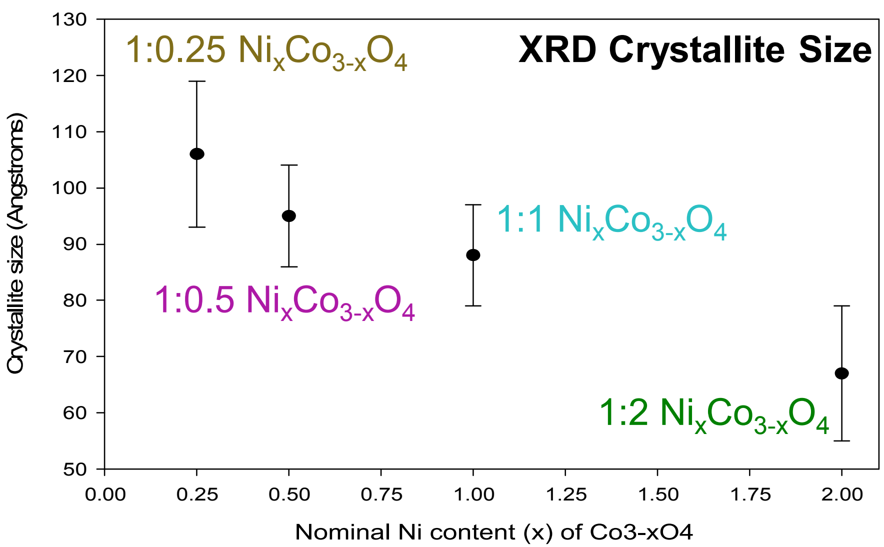
	Precursor Solution Co:Ni Ratio	Co:Ni Ratio by ICP-MS	Stoichiometry by ICP-MS	Co:Ni Ratio by XPS	Stoichiometry by XPS
Co_3O_4	1:0	297:1	Co_3O_4	1:0	Co_3O_4
$Ni_xCo_{3-x}O_4$ 1:0.25	1:0.25	5.77:1	$Ni_{0.44}Co_{2.56}O_4$	9:1	$Ni_{0.3}Co_{2.7}O_4$
$Ni_xCo_{3-x}O_4$ 1:0.5	1:0.5	4.08:1	$Ni_{0.59}Co_{2.41}O_4$	4:1	$Ni_{0.6}Co_{2.4}O_4$
$Ni_xCo_{3-x}O_4$ 1:1	1:1	2.39:1	$Ni_{0.89}Co_{2.11}O_4$	1.75:1	$Ni_{1.09}Co_{1.91}O_4$
$Ni_xCo_{3-x}O_4$ 1:2	1:2	N/A	N/A	1.33:1	$Ni_{1.29}Co_{1.71}O_4$

	Co_3O_4	1:0.25 $Ni_xCo_{3-x}O_4$	1:0.5 $Ni_xCo_{3-x}O_4$	1:1 $Ni_xCo_{3-x}O_4$
BET Surface Area (m^2/g)	**88.7277**	**99.8345**	**94.1476**	**101.3587**
Pore Size – Adsorption (nm)	**16.44493**	**7.7317**	**10.117**	**7.8381**
Pore Volume – Adsorption (cm^3/g)	**0.39868**	**0.23734**	**0.238123**	**0.24089**

Varying Ni-doping levels in $Ni_xCo_{3-x}O_4$ (changing x)

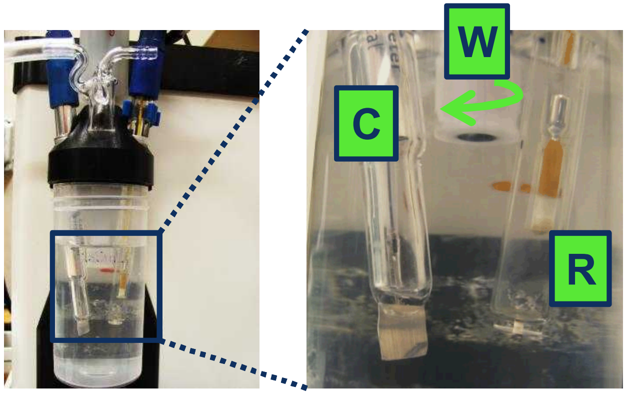






Electrochemical Characterization of Cobalt Oxide Films

Rotating Disk Electrode (RDE) Set-up



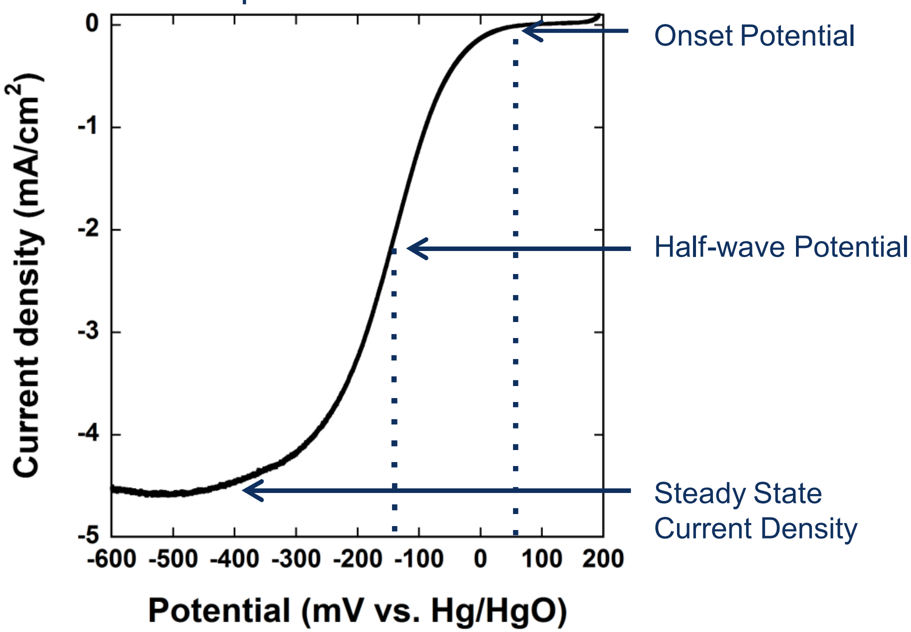
W (Working): Film in PTFE holder
C (Counter): Pt Foil
R (Reference): Hg/HgO

Koutecky-Levich & Tafel provide:

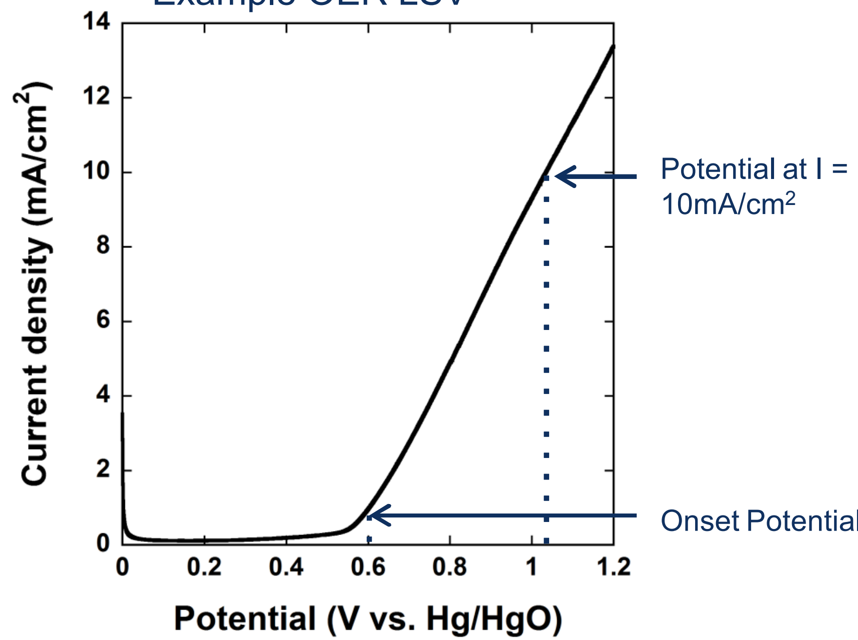
- Rates
- n-values
- Charge Transfer Resistances

etc. given defined catalyst surface area.

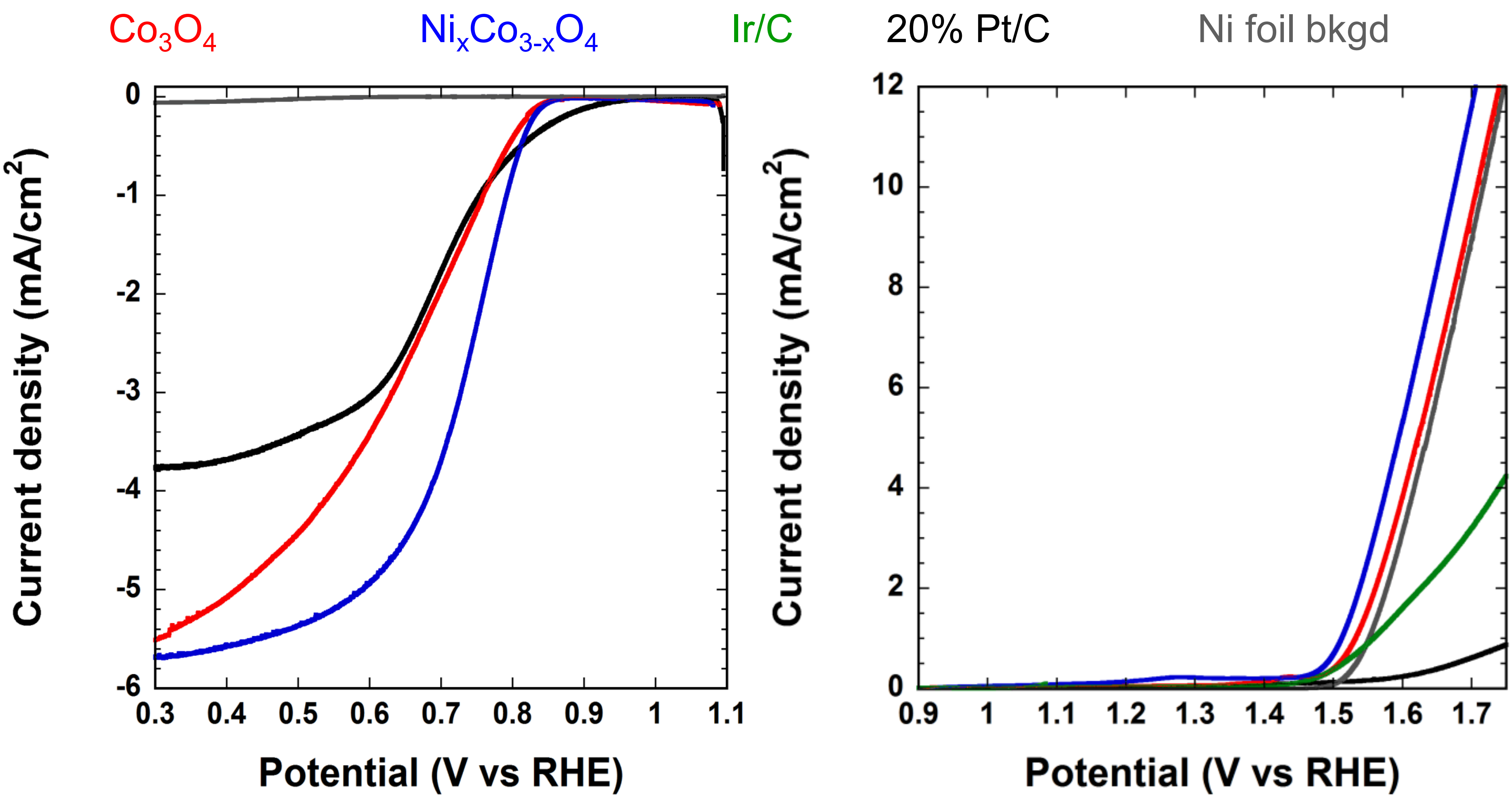
Example ORR LSV



Example OER LSV

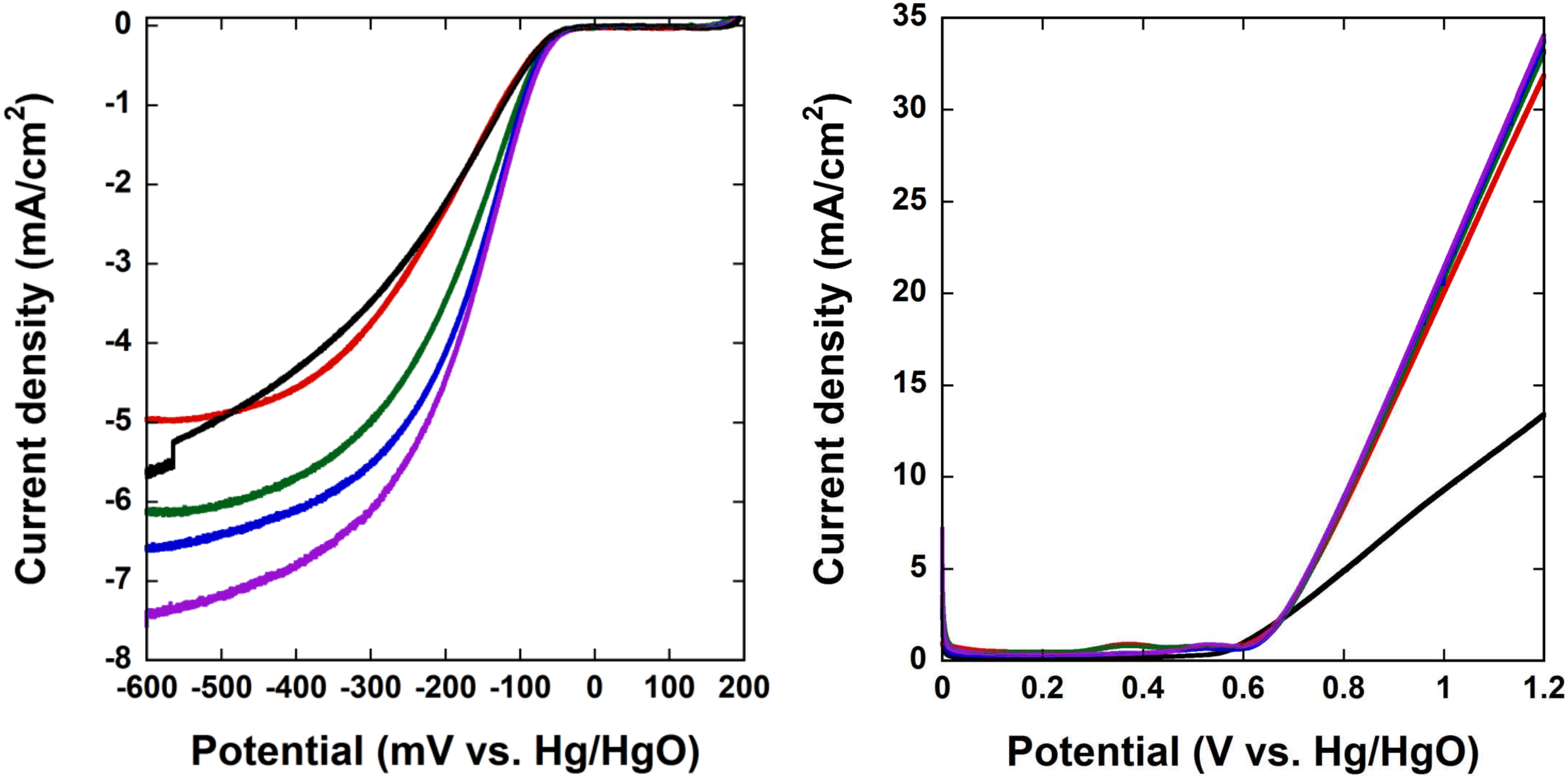


Preliminary $Ni_xCo_{3-x}O_4$ Film Studies

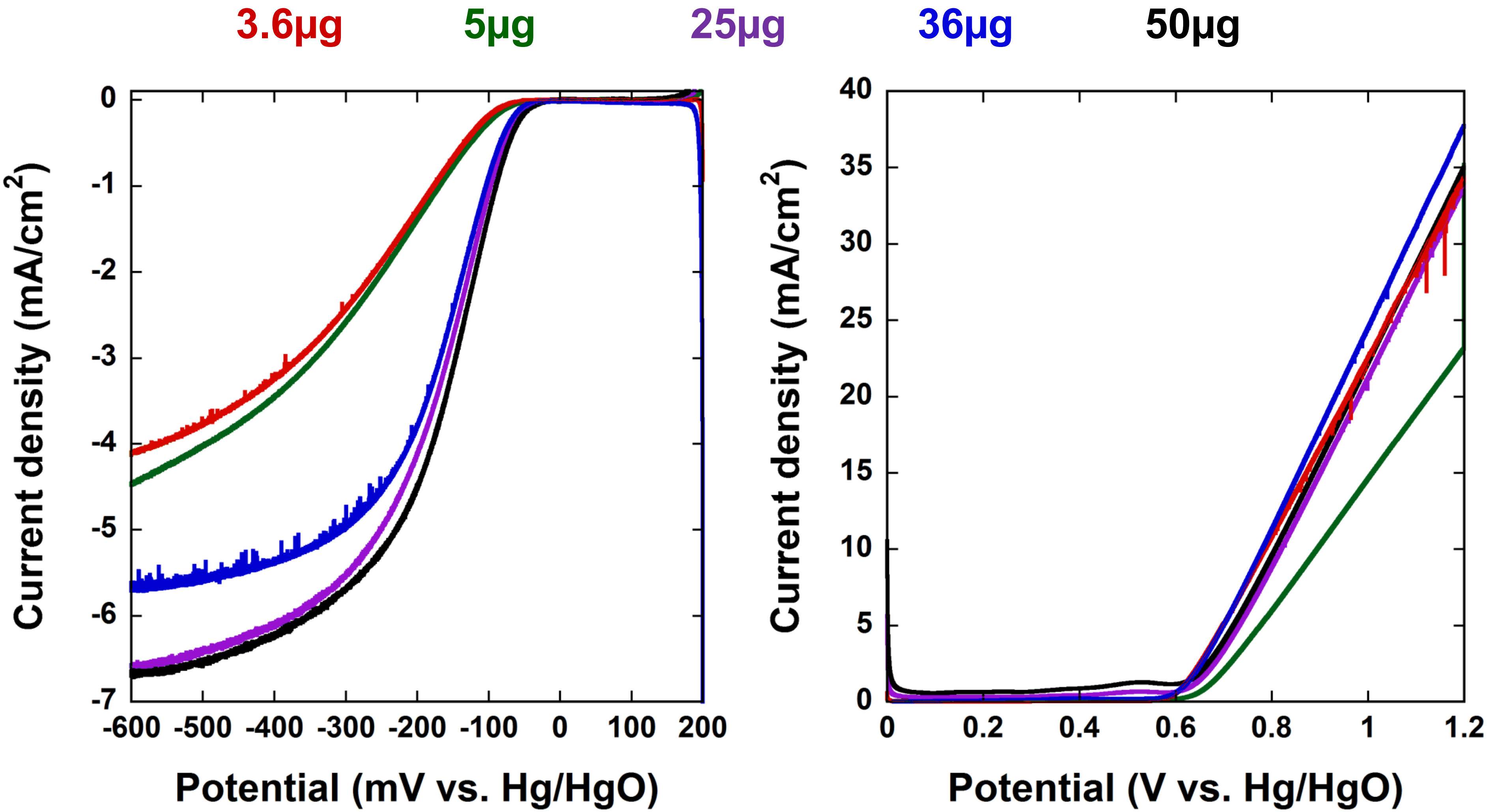


Electrochemical Characterization $Ni_xCo_{3-x}O_4$: Ni-doping Variation

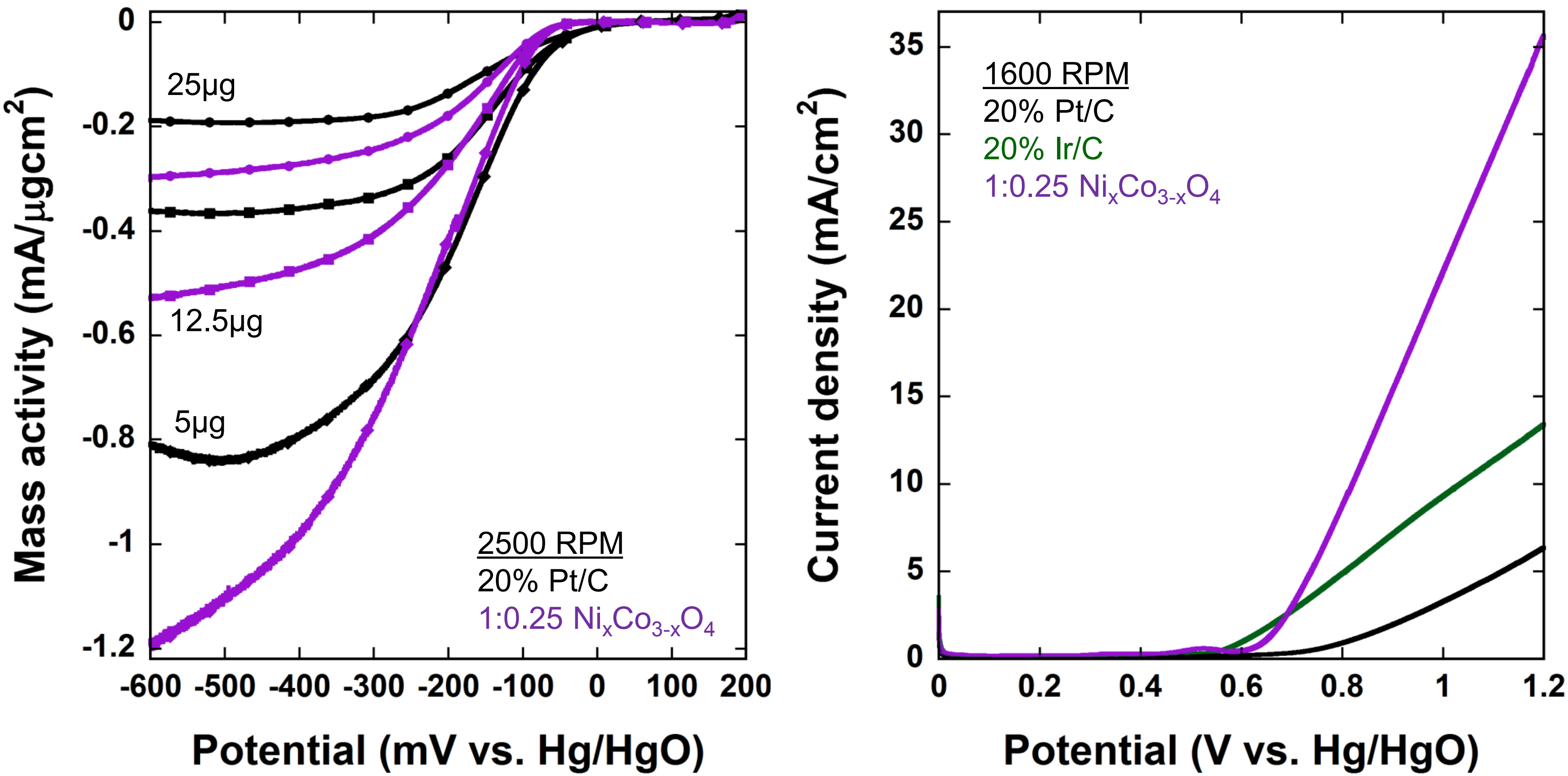
Co_3O_4 1 Co : 2 Ni 1 Co : 1 Ni 1 Co : 0.5 Ni 1 Co : 0.25 Ni



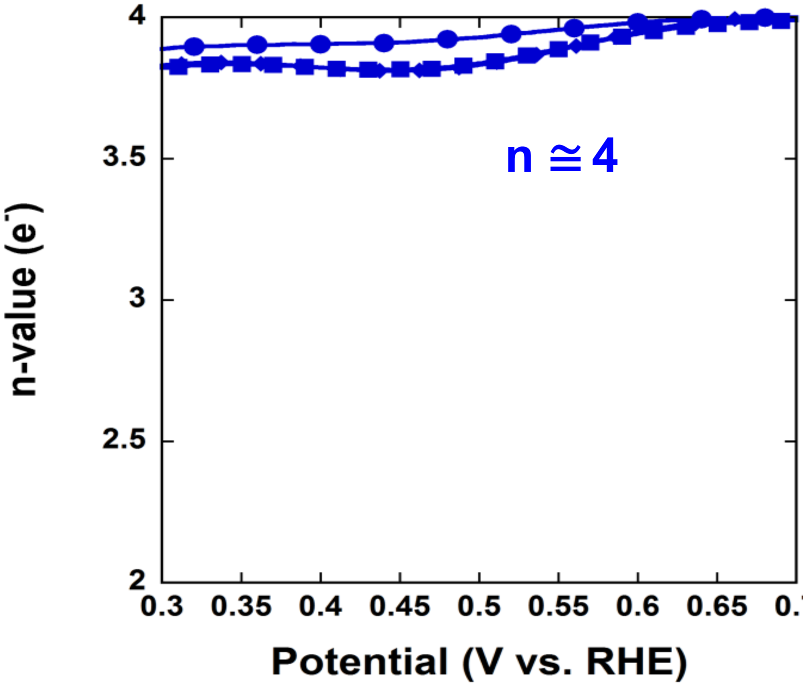
Electrochemical Characterization $Ni_xCo_{3-x}O_4$: Mass Deposition Variation

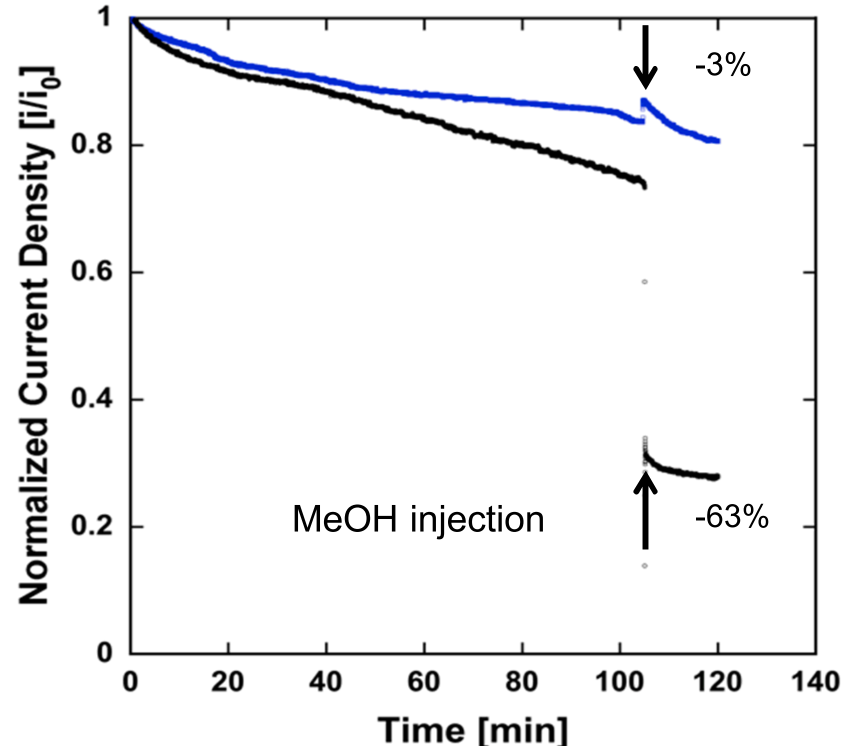


Electrochemical Characterization $Ni_xCo_{3-x}O_4$: Comparison to Commercial Benchmarks



Electrochemical Characterization $Ni_xCo_{3-x}O_4$: Reaction Mechanism and Stability





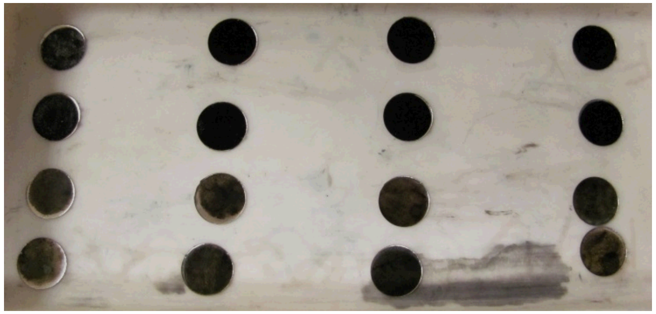
$Ni_xCo_{3-x}O_4$
20% Pt/C

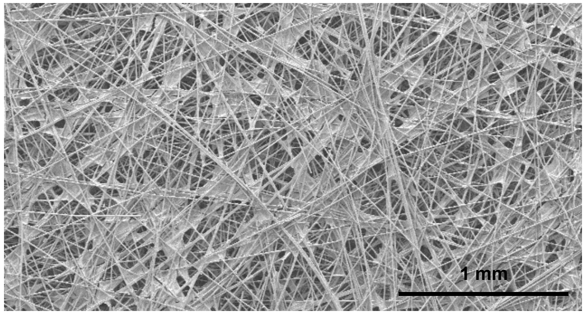
Nickel Cobalt Oxide catalyst performs direct, 4-electron ORR mechanism. (Data from powders)

Nickel Cobalt Oxide catalyst suffers significantly less degradation from methanol poisoning than commercial Pt/C.

Conclusions and Future Work

- Demonstrated ability to dope Co_3O_4 spinel film with Ni.
- $Ni_xCo_{3-x}O_4$ films showed improvement upon Co_3O_4 films, which were already outperforming commercial ORR and OER catalysts.
- $Ni_xCo_{3-x}O_4$ films are more stable and more active than the commercial Pt/C and Ir/C catalysts AND exhibit exemplary bi-functionality for ORR and OER.





- Further studies are warranted to explain trends in higher activity with less Nickel in the structure.
- Deposition on three-dimensional substrates such as gas diffusion electrodes and meshes will also be investigated.

Acknowledgements

- **Sandia National Laboratories**
- **Department of Energy**
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- **Other Collaborators**
  - Dr. Erik N. Coker, SNL/AML
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  - Dr. Mark A. Rodriguez, SNL

Questions?

Thank you!