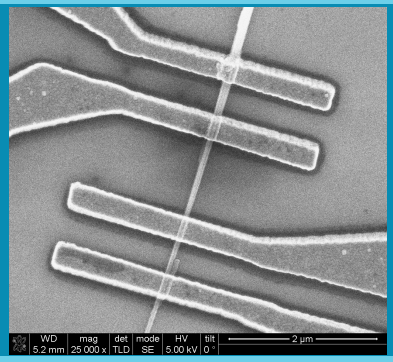
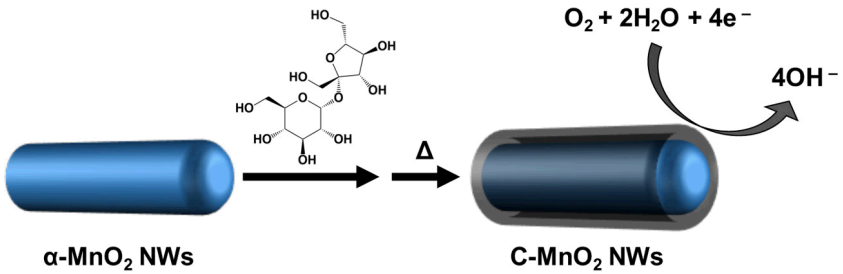
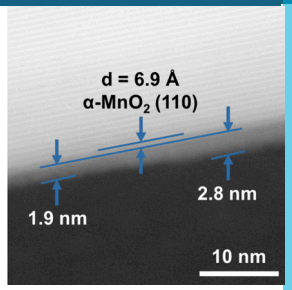
SAND2018-7792C

Nanoscale Hybrid Carbon Coated MnO_2 Nanomaterials for ORR Electrocatalysis







PRESENTED BY

Timothy Lambert, Julian Vigil, and Jonathon Duay

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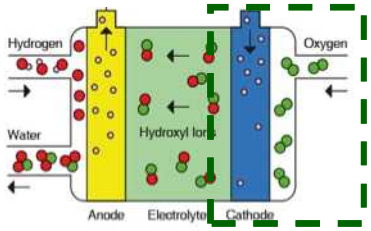
ORR in energy devices



Fuel cell schematic

Alkaline fuel cell:

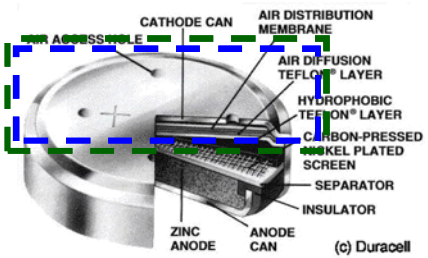
Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

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

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

Oxygen Reduction Reaction (ORR)

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



Zn-air battery schematic

Discharge

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

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

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

ORR

Charge

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

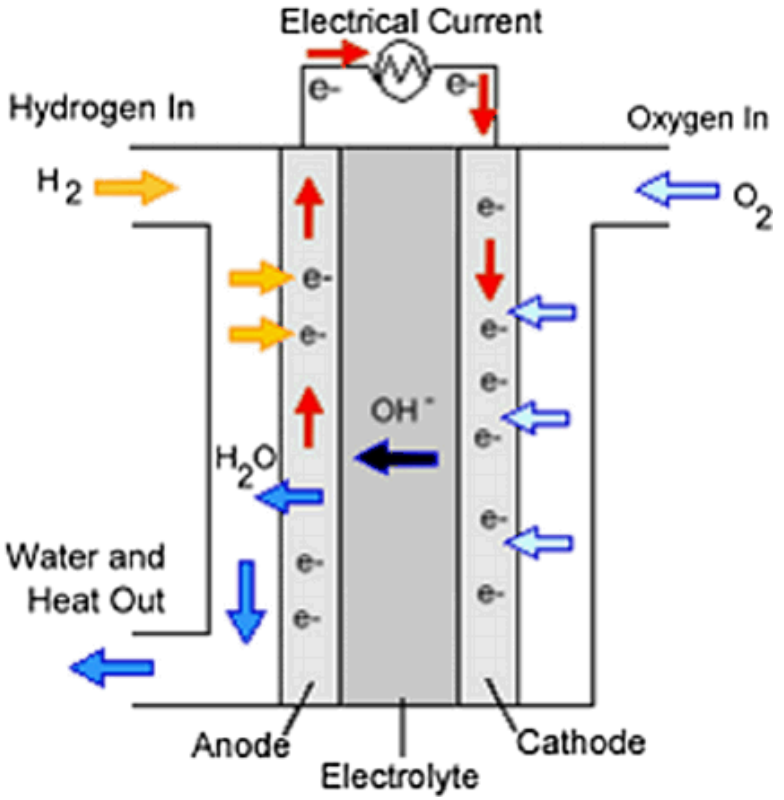
Cathode: $4OH^- \longrightarrow O_2 + 2H_2O + 4e^-$

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

Oxygen Evolution Reaction (OER)

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

Our interest has been Alkaline Systems



Problem:

1.) Cathode: kinetics, high overpotentials, poor reversibility ~ 60% of energy losses due to cathode

2.) Leading Catalysts are <u>expensive and rare</u> metals/oxides

(e.g. Pt, Ir, IrO_x) – Also – poor stability and electrochemical selectivity.

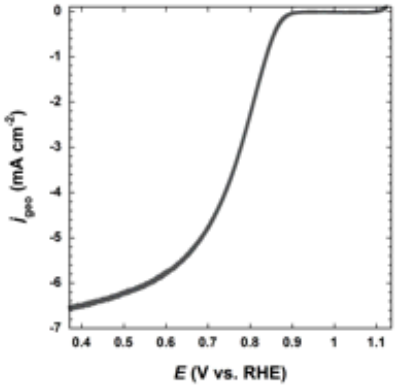
Solution: Develop new non-Pt catalysts = durable, active, economically viable

Catalyst Material Selection

ORR

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

- E_0 = 1.23 V vs. RHE
- commercial benchmark catalysts: Pt, Pt/C
- e.g.



Abundant, economically viable materials

- Non-precious metals and non-metals
- Easily prepared and scalable

Oxygen/hydrogen catalytic activity

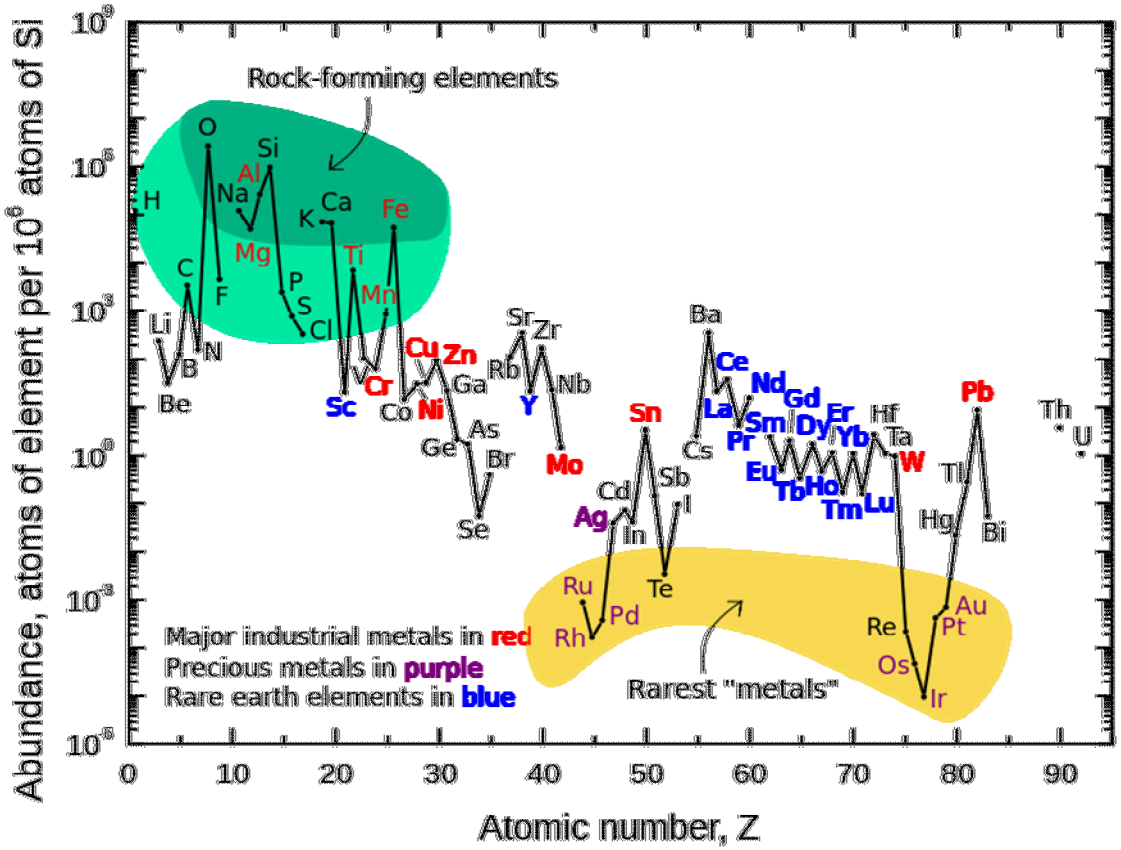
- Oxides/hydroxides for ORR/OER
- Phosphides/sulfides for HER
- Bifunctionality

Nanoscale and high surface area structures

- More active catalytic sites
- High mass efficiency

Manganese Oxide(s)

Cheap and Abundant



ORR Catalyst Activity

$MnO_2 \approx MnOOH > Mn_2O_3 > Mn_3O_4$

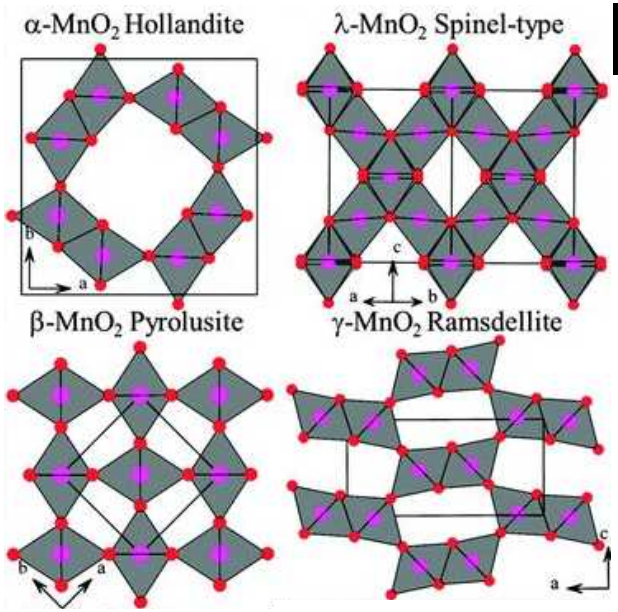
$MnO_2 > Mn_3O_4 > MnO$

Tang, Q.; Jiang, L.; Liu, J.; Wang, S.; Sun, G. ACS Catal. 2014, 4 (2) 457– 463

Lima, F. H. B.; Calegaro, M. L.; Ticianelli, E. A. Electrochim. Acta 2007, 52 (11) 3732– 3738

Manganese Oxide (MnO_2) Nanowires

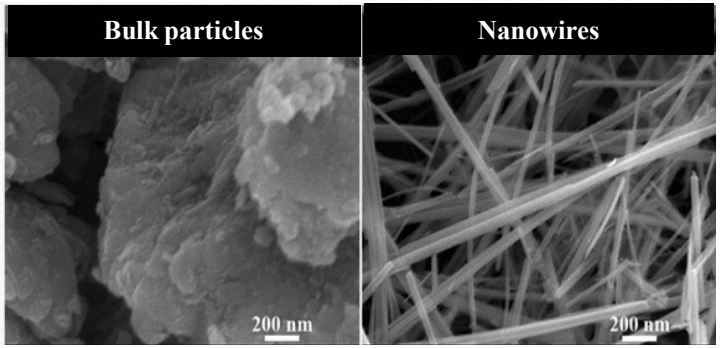
Phase



α-MnO_2 > β-MnO_2 > γ-MnO_2 > λ-MnO_2

Increased ORR Activity

Size



nm MnO_2 > μm MnO_2 > mm MnO_2

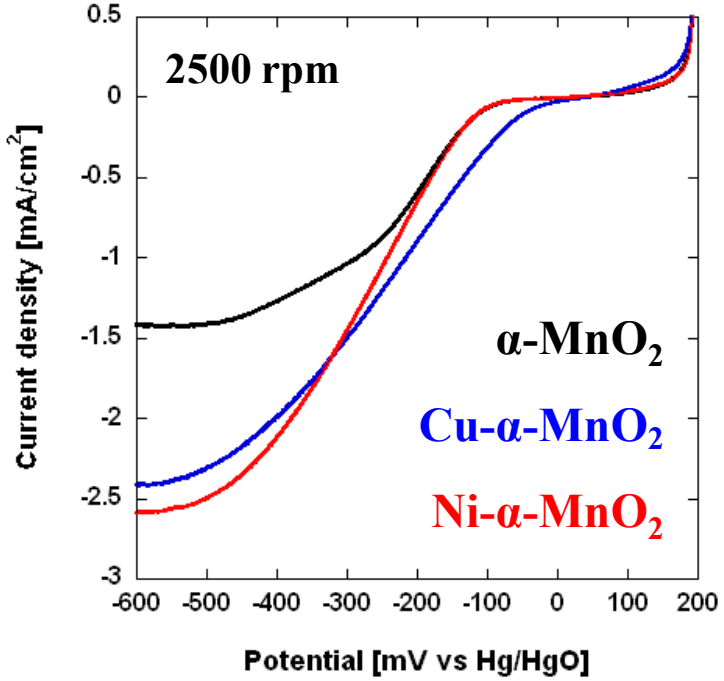
Increased ORR Activity

Increased ORR Activity

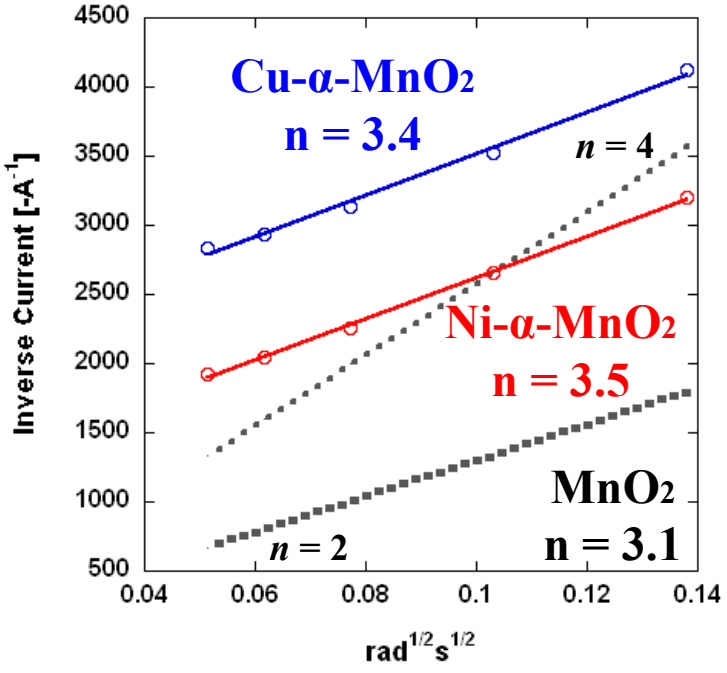
F. Cheng, *et al. Chem. Mater.* **2010**, *22*, 898–905

Intrinsically Doped Ni- and Cu-α-MnO_2 Nanowires

Increased Electrocatalysis



ORR n-values are improved with doping

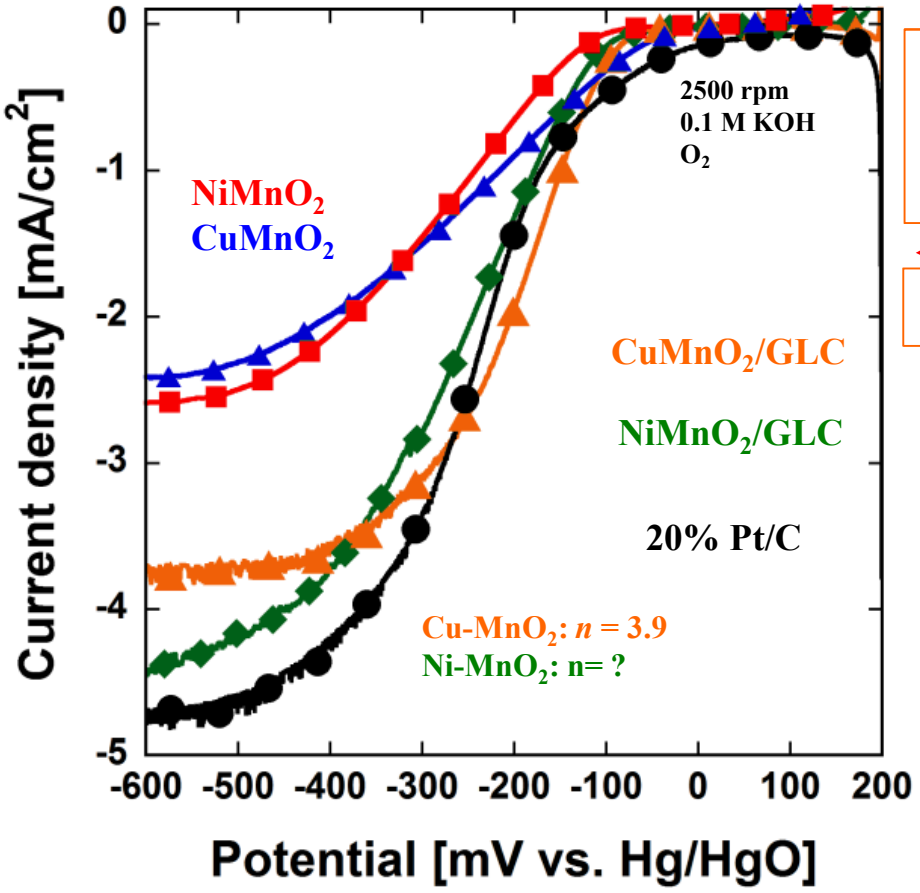


- Peroxide production is < 5% for all catalysts; this corresponds to a fast peroxide disproportionation reaction.
- Reaction rates also improved:

MnO_2: 3.98 x 10^{-3} cm/s $CuMnO_2$: 6.70 x 10^{-3} cm/s $NiMnO_2$: 1.53 x 10^{-2} cm/s

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

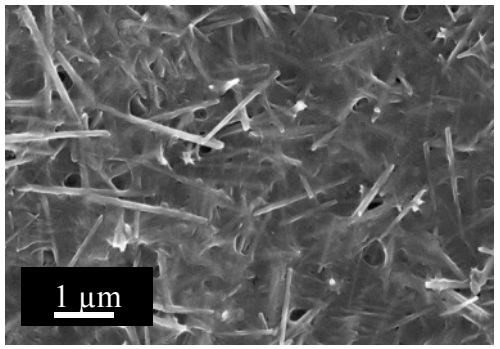
Increased Electrocatalysis with Carbon



Good dispersion of catalyst

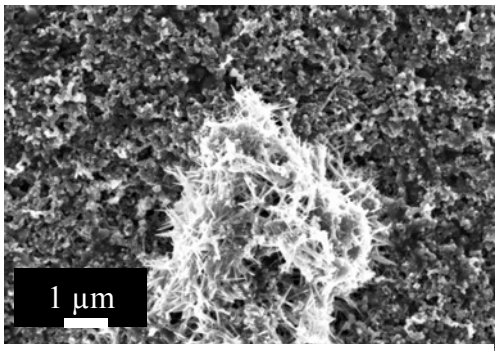
Conductivity

Cu-a-MnO_2 NWs / GLC / Nafion



GLC:
Excellent Dispersion of NWs

Cu-a-MnO_2 NWs / Vulcan XC-72 / Nafion

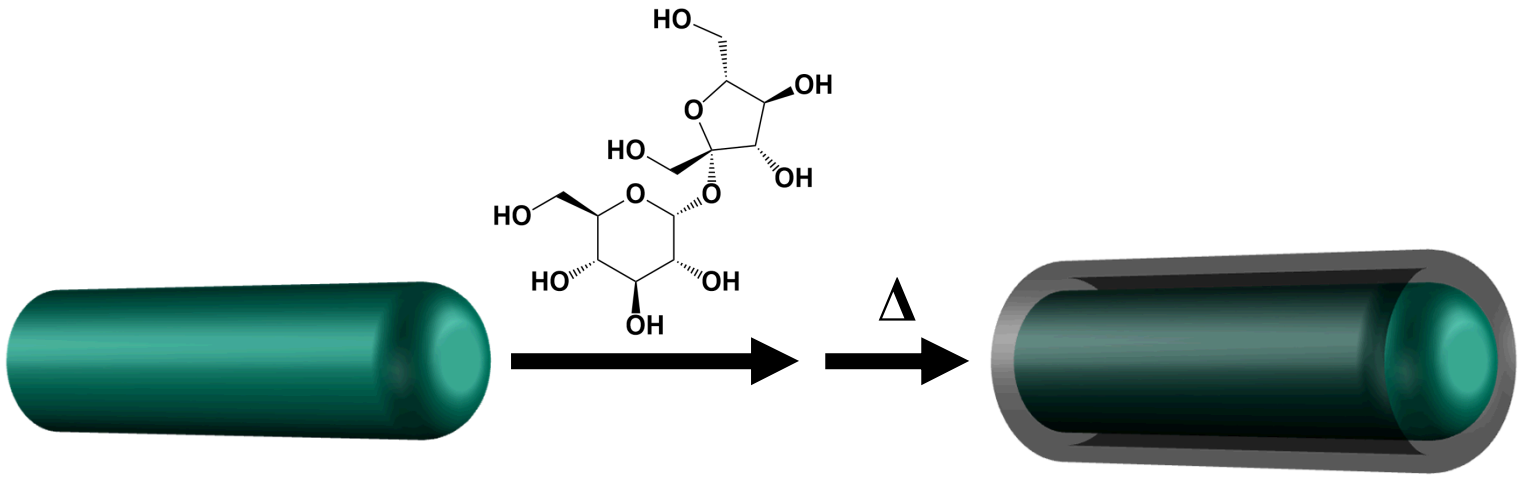


Vulcan:
Poor dispersion of NWs

-Poor Batch to Batch Reproducibility

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

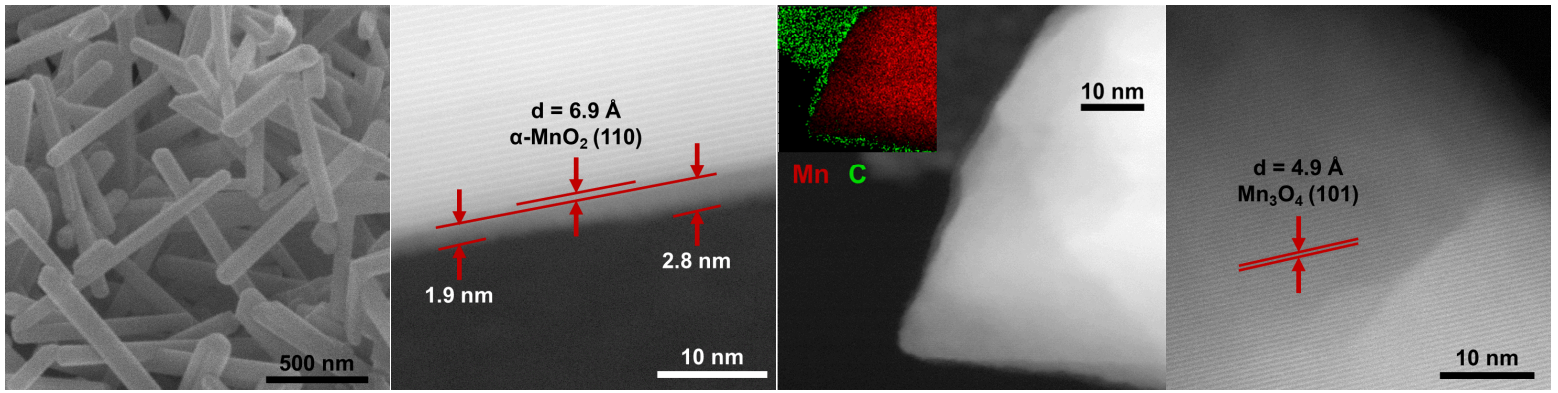
Synthesis of Carbon Coated α-MnO_2



α-MnO_2 NWs

C-MnO_2 NWs

Electron Microscopy and EDS Characterization



Carbon Coating <3nm Thick

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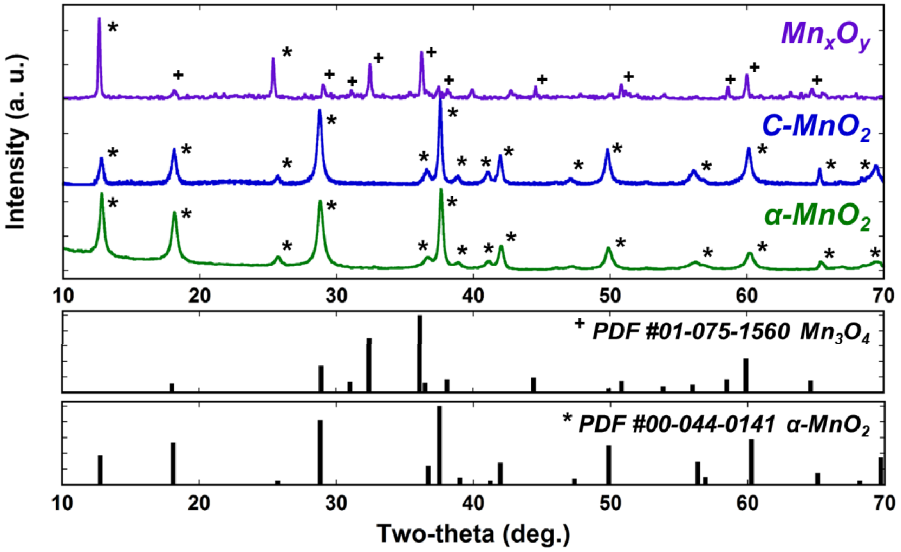
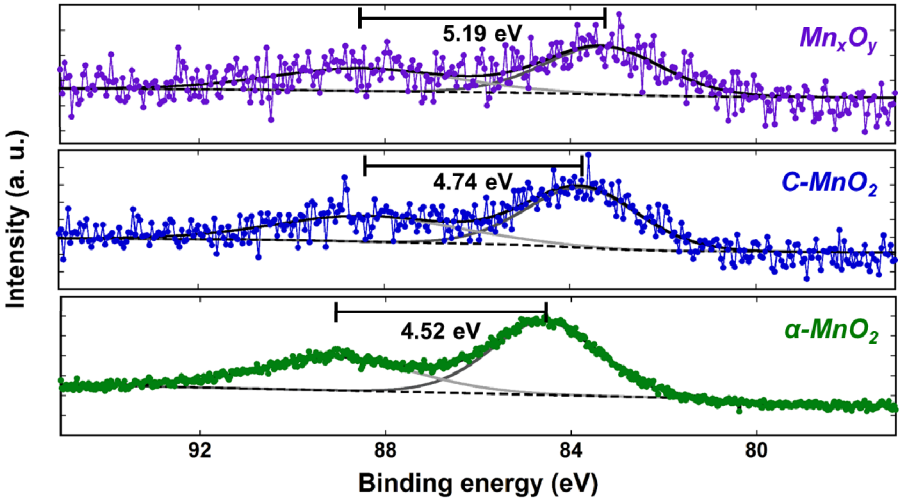
Characterization of Carbon Coated α-MnO_2

XRD



XPS



-Surface Increases Mn^{3+} character

-MnO_2 maintains α polymorph after coating

	XPS surface ΔE(Mn 3s) (eV)	XPS surface Mn AOS[a]	bulk Mn^{3+}(%)	bulk Mn AOS[a]
α-MnO_2NWs	4.51 ± 0.02	3.98 ± 0.02	12	3.88 ± 0.05
C-MnO_2NWs	4.74 ± 0.08	3.73 ± 0.09	34	3.66 ± 0.03

[a]AOS = Average Oxidation State

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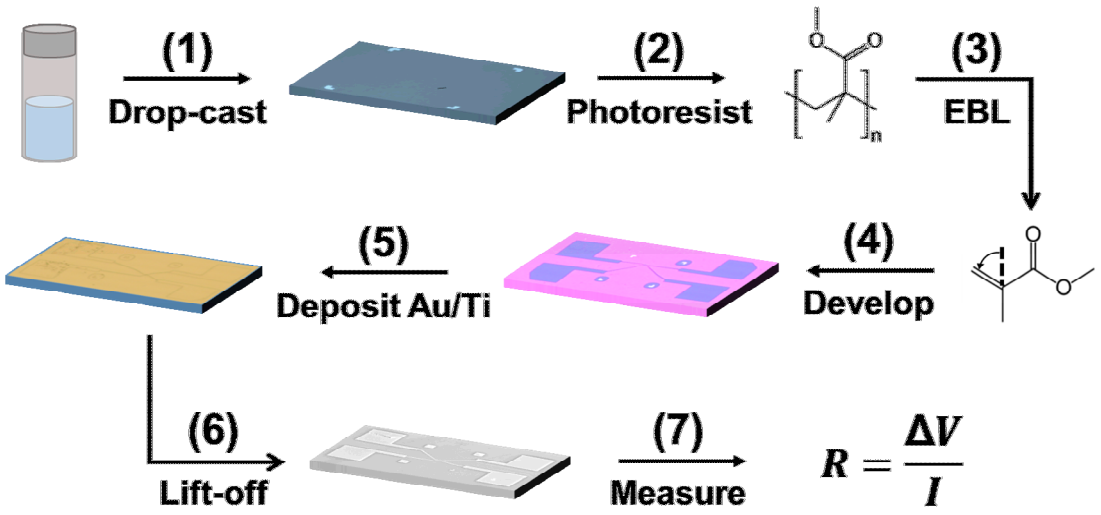
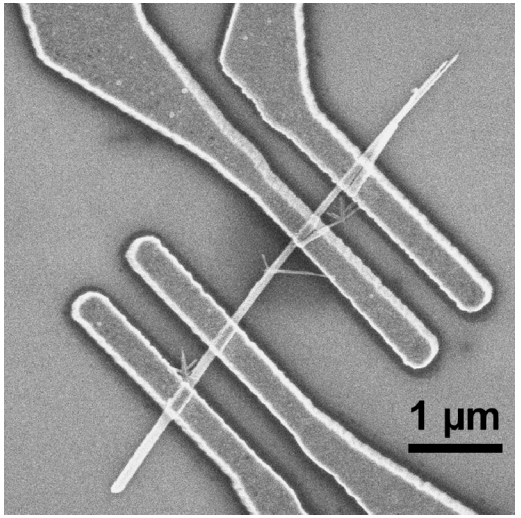
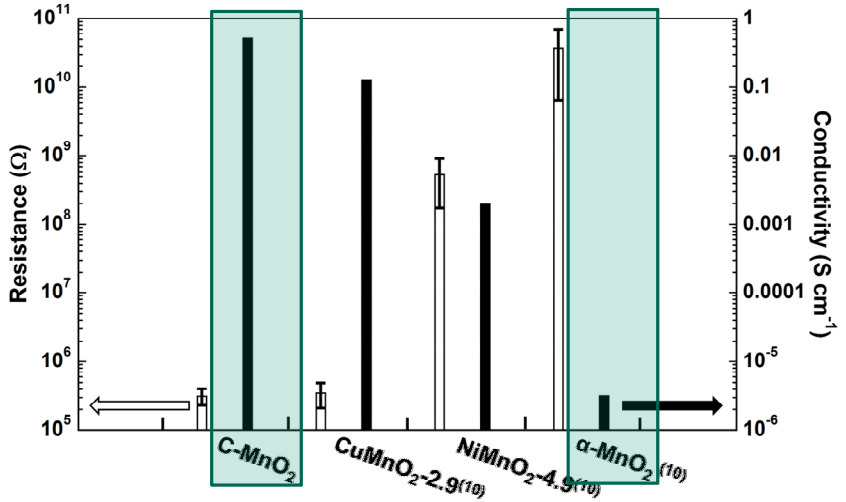
Single Nanowire Conductivity Studies







Carbon-coated MnO_2
-5 order of magnitude increase in Conductivity

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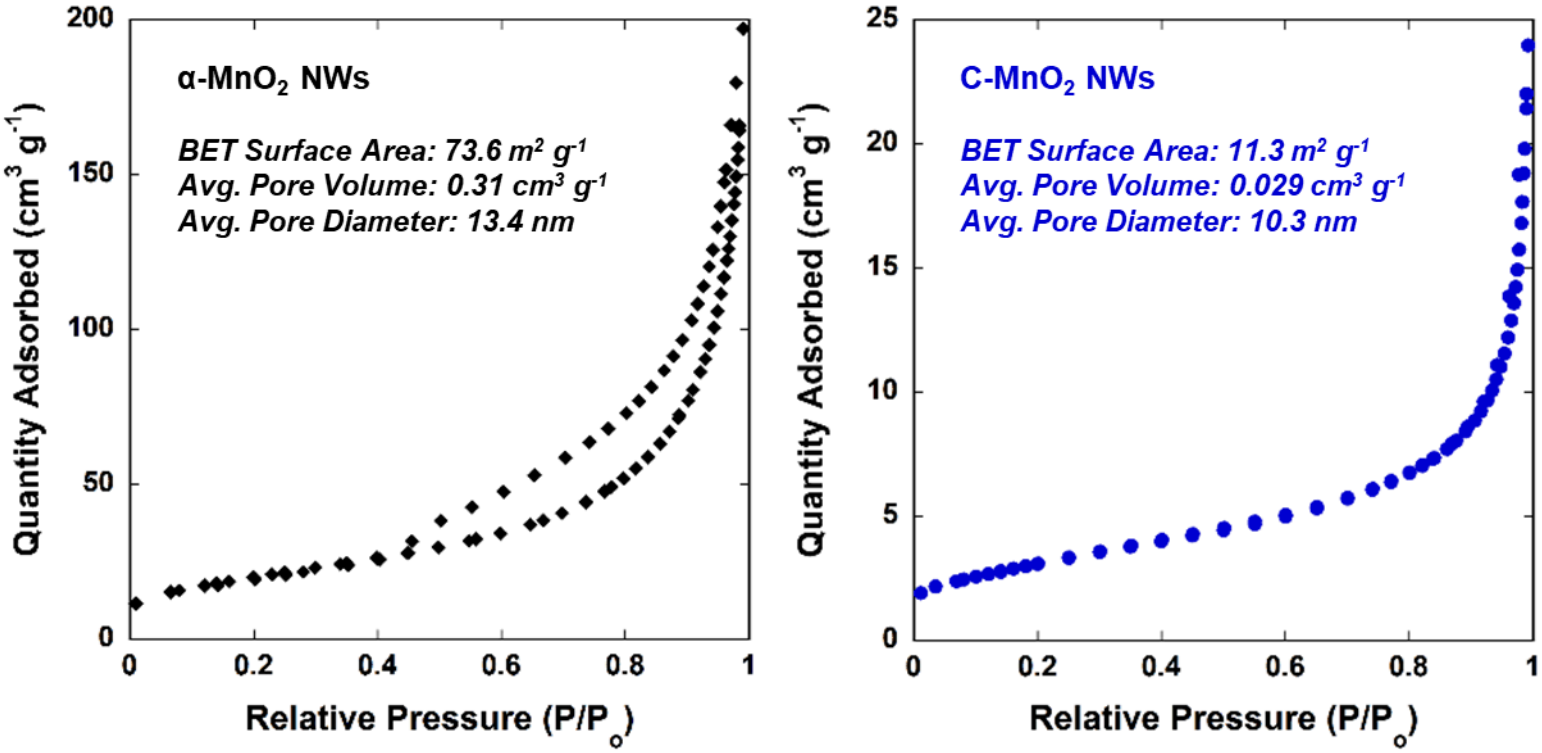
BET Surface Area/Porosimetry



Surface Area Decrease

Type IV (mesoporous) to Type II (macroporous) Isotherm

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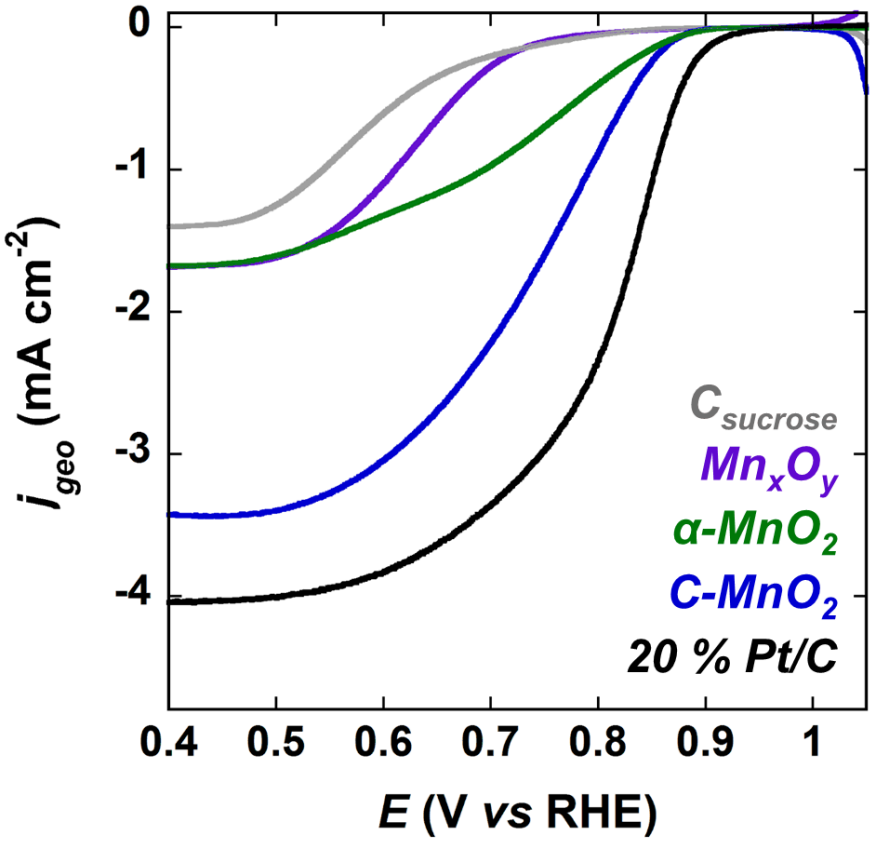
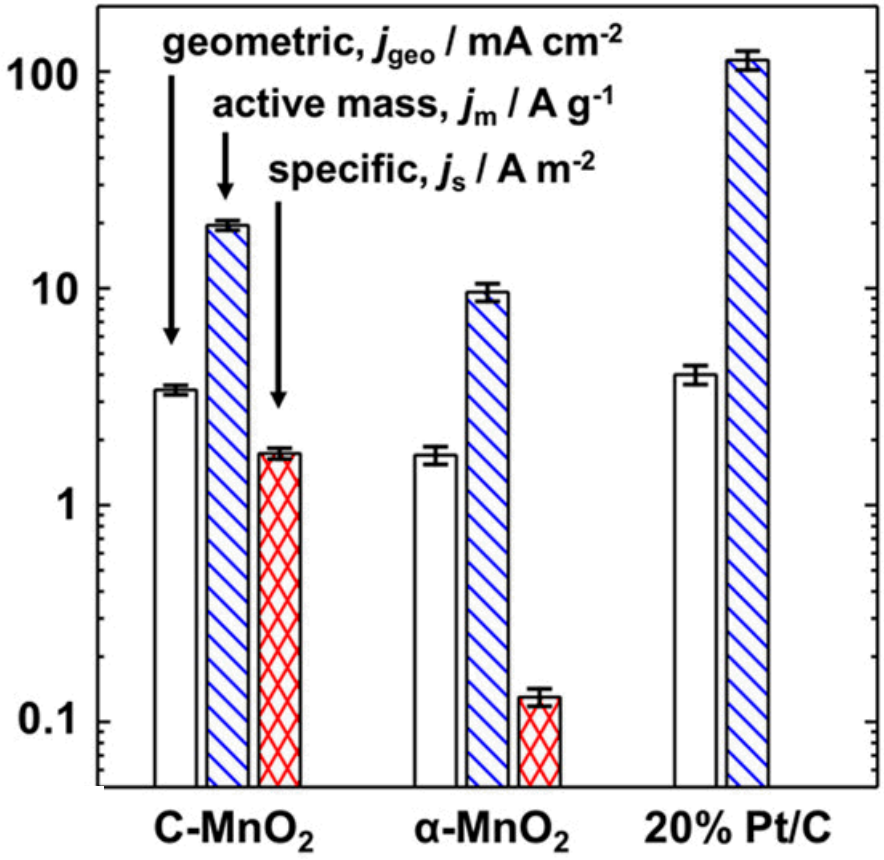
ORR Reactivity

Linear Sweep Voltammetry



Normalized Currents



-13 times Increase in specific activity after Carbon Coating
-C-MnO_2 Performance Metrics near that of 20% Pt/C

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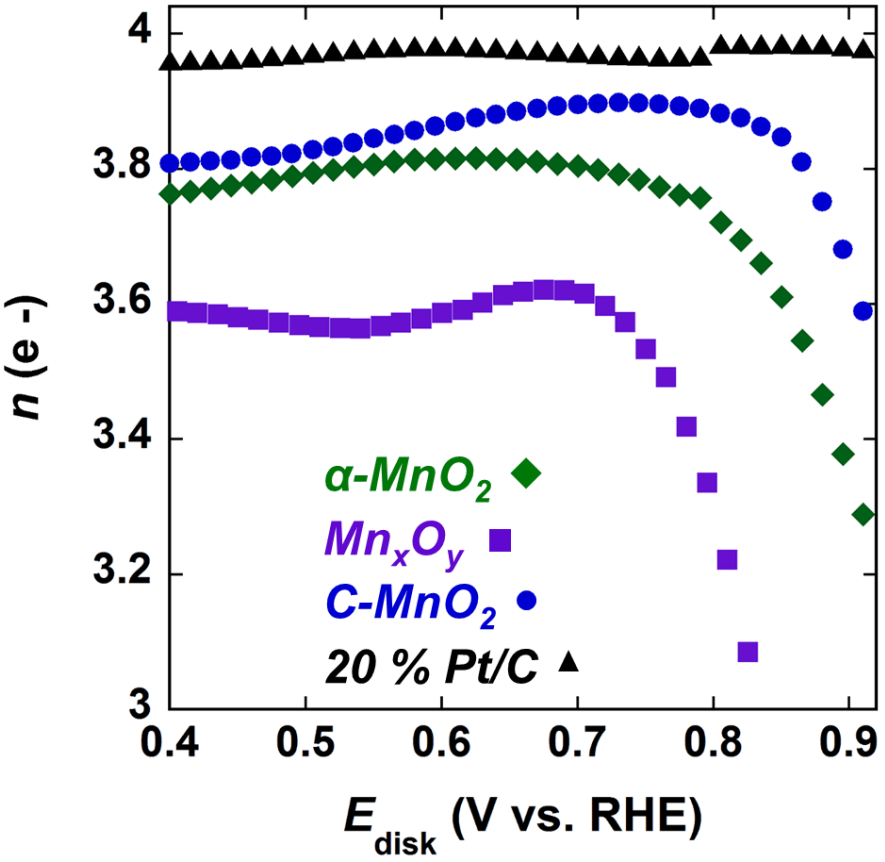
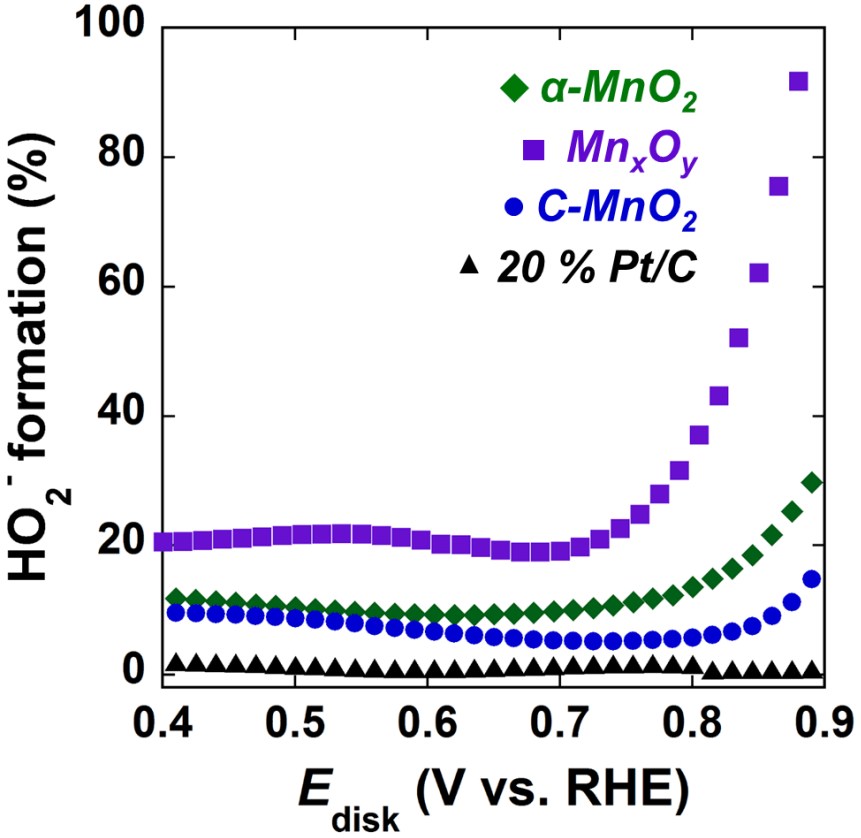
Rotating Ring-Disk Electrode (RRDE)

RRDE *n* values



-Higher n-value are obtained after carbon coating

RRDE Peroxide Generation



-Lower peroxide is generated after carbon coating

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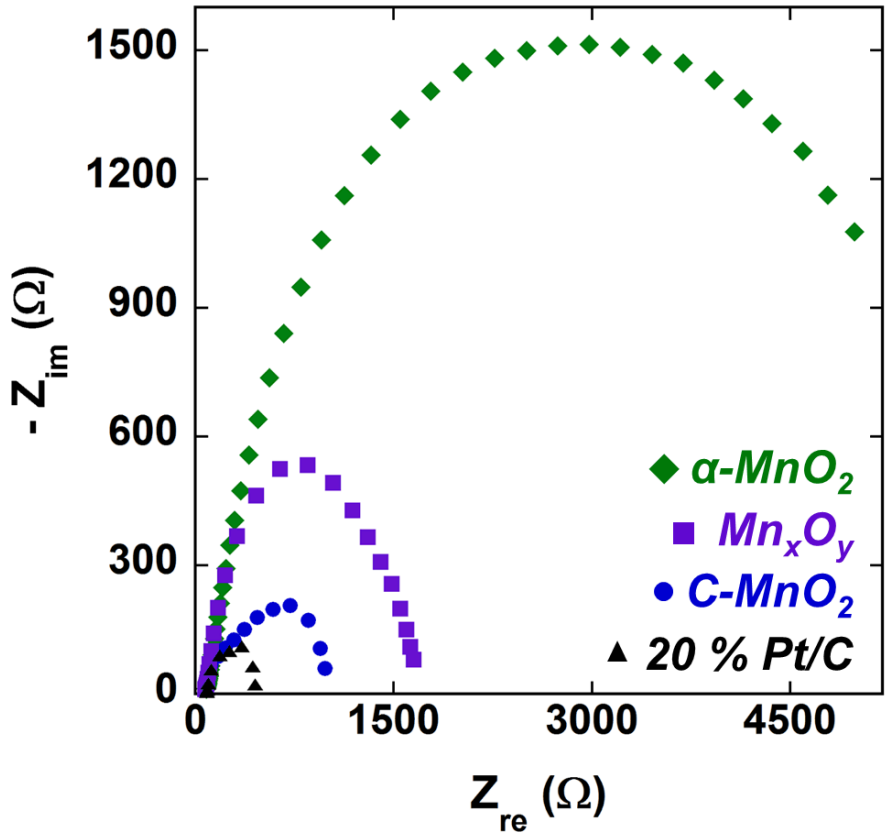
Charge Transfer Resistance



R_{CT} decreases in the order of: 6200 (α-MnO_2) 1780 (Mn_xO_y) 920 (C-MnO_2) 310 Ω (20% Pt/C)

-the carbon coating leads to a less resistive electrocatalyst at low overpotential

Comparison to Literature Materials

Catalyst	Ref.	Mass loading (mg cm^{-2})	C comp. (wt. %)	Conditions	Onset potential (V *vs* RHE)	Half-wave potential (V *vs* RHE)	Diffusion-limited geometric current density (mA cm^{-2})	*n* (e-)
Carbon-coated oxides								
C-MnO_2 NWs	this work	0.177	≤ 1.2	0.1 M KOH/ 2500 RPM	0.88 **	0.75	3.4	3.84
$BaMnO_3$@5%C	6	NR	NR	0.1 M KOH/ 1600 RPM	0.71	0.61	5.5	3.8
Mn_3O_4@CN_x	7	0.59 – 0.66	28.5	0.1 M KOH/ 1600 RPM	0.86	0.79	1.1	4 *
ND-Fe_3O_4@mC-2 /CB	8	0.1	65 ***	0.1 M KOH/ 1600 RPM	0.77	0.69	5.25	3.72
Carbon-coated metals, sulfides, phosphides								
PdCo@NPNCs	9	0.202	NR	0.1 M KOH/ 1600 RPM	0.95	0.91	5	>3.75
PC-$CoS_{1.097}$	10	0.566	24.8	0.1 M KOH/ 2400 RPM	0.89	0.84	3.7	>3.8
FeP@NPCs	11	0.2	88 ****	0.1 M KOH/ 1600 RPM	0.91	0.82	5.85	>3.75

NR = not reported; * reported *n* values calculated using the Koutecky-Levich method exceed the theoretical limit of 4 at some potentials; ** onset potential calculated using the tangential method, which may underestimate the value compared to the literature[2]; *** total C comp. = 60 wt % carbon black + 14.5 wt % of the remaining 40 wt % ND-Fe_3O_4@mC-2 catalyst = 65.8 wt % C; **** 88 at %.

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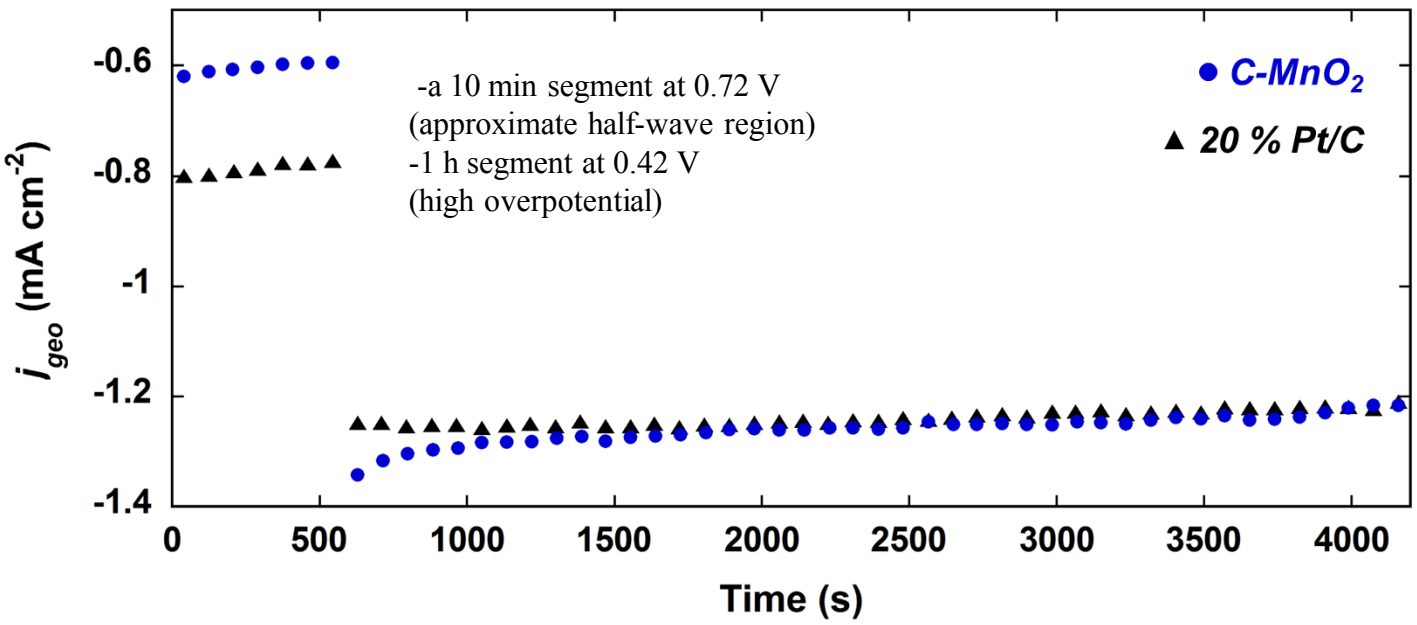
ORR Activity at Elevated Temps (60 °C)



-20% Pt/C outperforms C-MnO_2 at low overpotential
-both catalysts are stable and maintain currents of
≤ -1.2 mA cm^{-2} for 1 h at high overpotential

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Conclusions

-Carbon-coated α-MnO2 NWs were prepared by Sucrose/Pyrolysis Method

-C was found to be ≤1.2 wt%

-α-MnO_2 phase was preserved

-Surface Mn^{3+} increased

-Single NW conductivity increased 5 orders of magnitude

-13 times increase in Specific Activity (A/m^2)

-Catalyst performed better than 20 wt% Pt/C at 60°C

Acknowledgements

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Collin Delker
Thomas Beechem
Brian Swartzentruber

Questions?