Silver and Silver-Manganese Cathode Catalysts for Alkaline Fuel Cells

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Introduction

- Background
  - Alkaline fuel cell cathode catalysts
- Objectives
- Silver-manganese bi-metallic alloy
  - Linear sweep voltammetry
  - Cyclic sweep (Ag_2O reduction)
  - X-ray photoelectron spectroscopy (XPS)
- Nano-structured carbon nanofiber system
  - Image and composition analysis
  - Linear sweep voltammetry
- Conclusions

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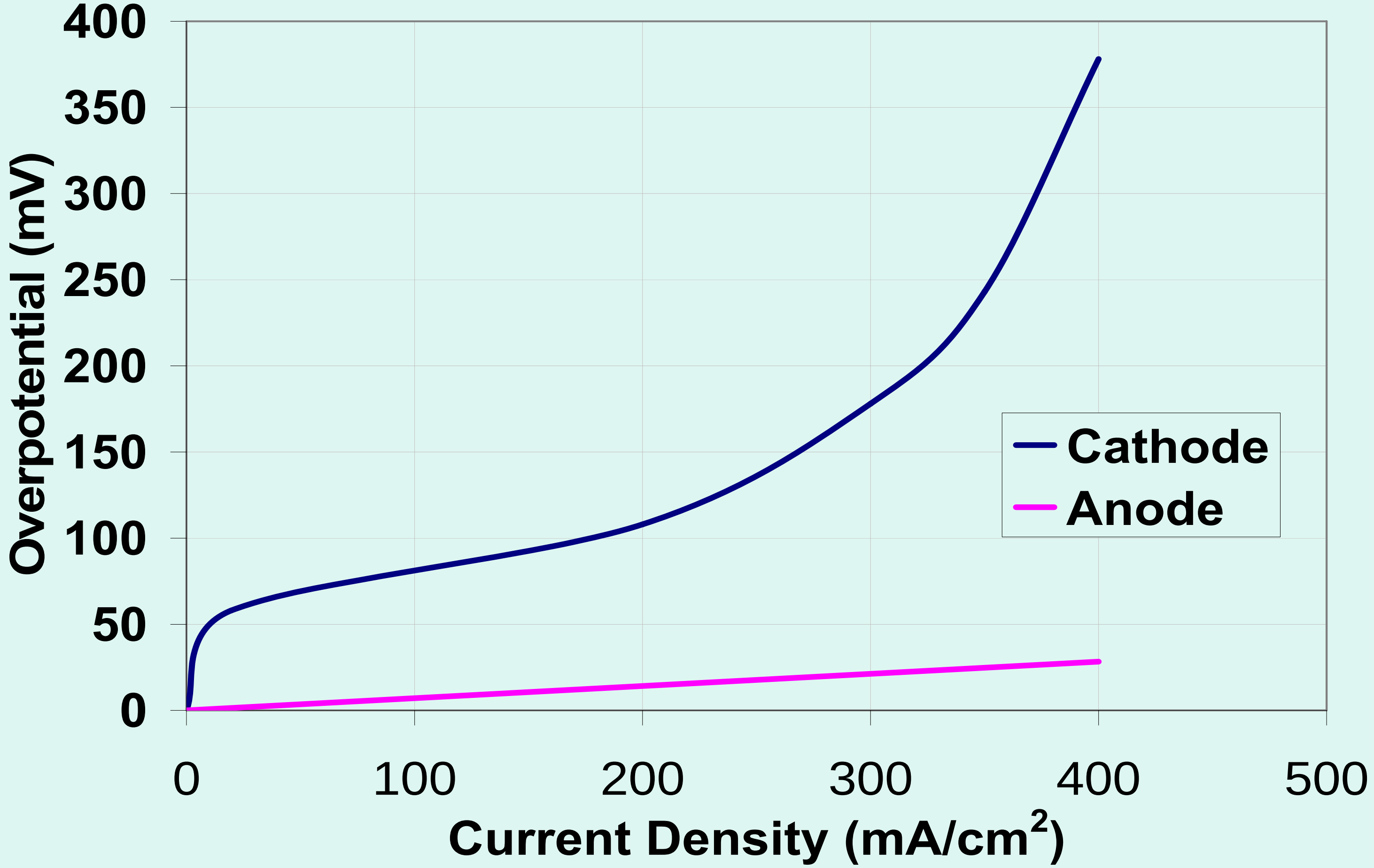
Background

In alkaline fuel cells (AFCs) the cathode electrode is the main contributor to losses in cell performance



1. K. Kordesch, et al., *Journal of Power Sources*, 86 (2000), 162-165

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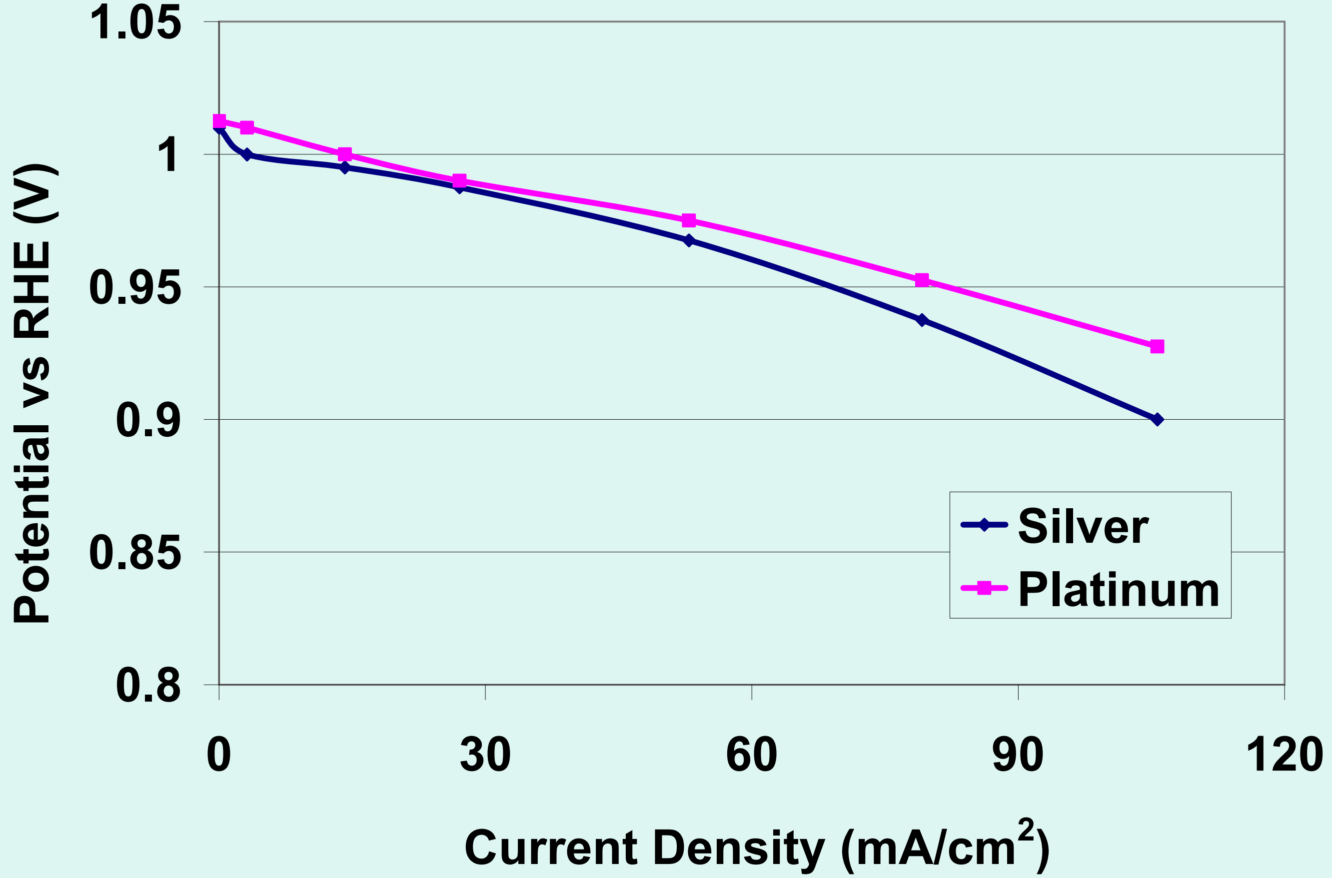
Background

Silver and manganese dioxide show comparable oxygen reduction catalytic activities to platinum in alkaline electrolyte



2. Hacker, et. al., *Electrochemistry Communications*, 7 (2005), 377–382

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Objectives

- Study two systems of silver and manganese to determine the synergistic effects of these two catalysts coupled together towards the kinetics and mechanism of the oxygen reduction reaction (ORR)
  - Silver-manganese bi-metallic alloy system
  - Nano-structured catalyst system of electrolessly deposited silver and manganese dioxide supported on carbon nanofibers

Ag-Mn Alloy Test Program

- 3 different alloy systems: 5, 10 and 15 wt% manganese in silver by vacuum arc melting
  - Characterized samples by SEM, EDX and XPS
- Electrochemical measurements of pure silver and silver-manganese alloys
  - Linear potential step and hold testing in oxygen reduction reaction region
  - Cyclic voltammetry
  - Obtain potential onset of ORR, maximum current density and Tafel data

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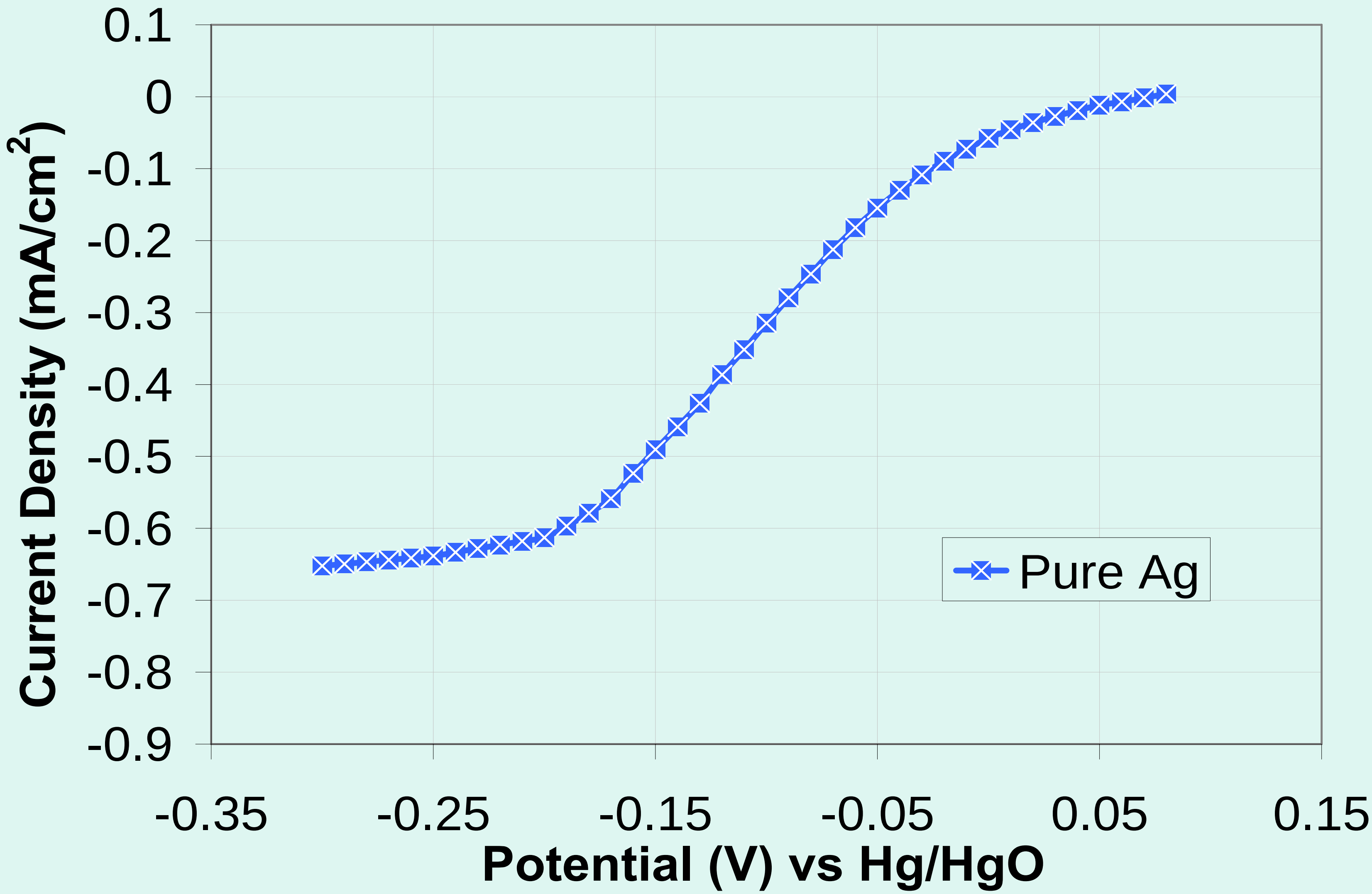
Pure Ag in 0.1 M KOH at 80˚C



Potential steps (10 mV increments): 0.10 V → - 0.3 V

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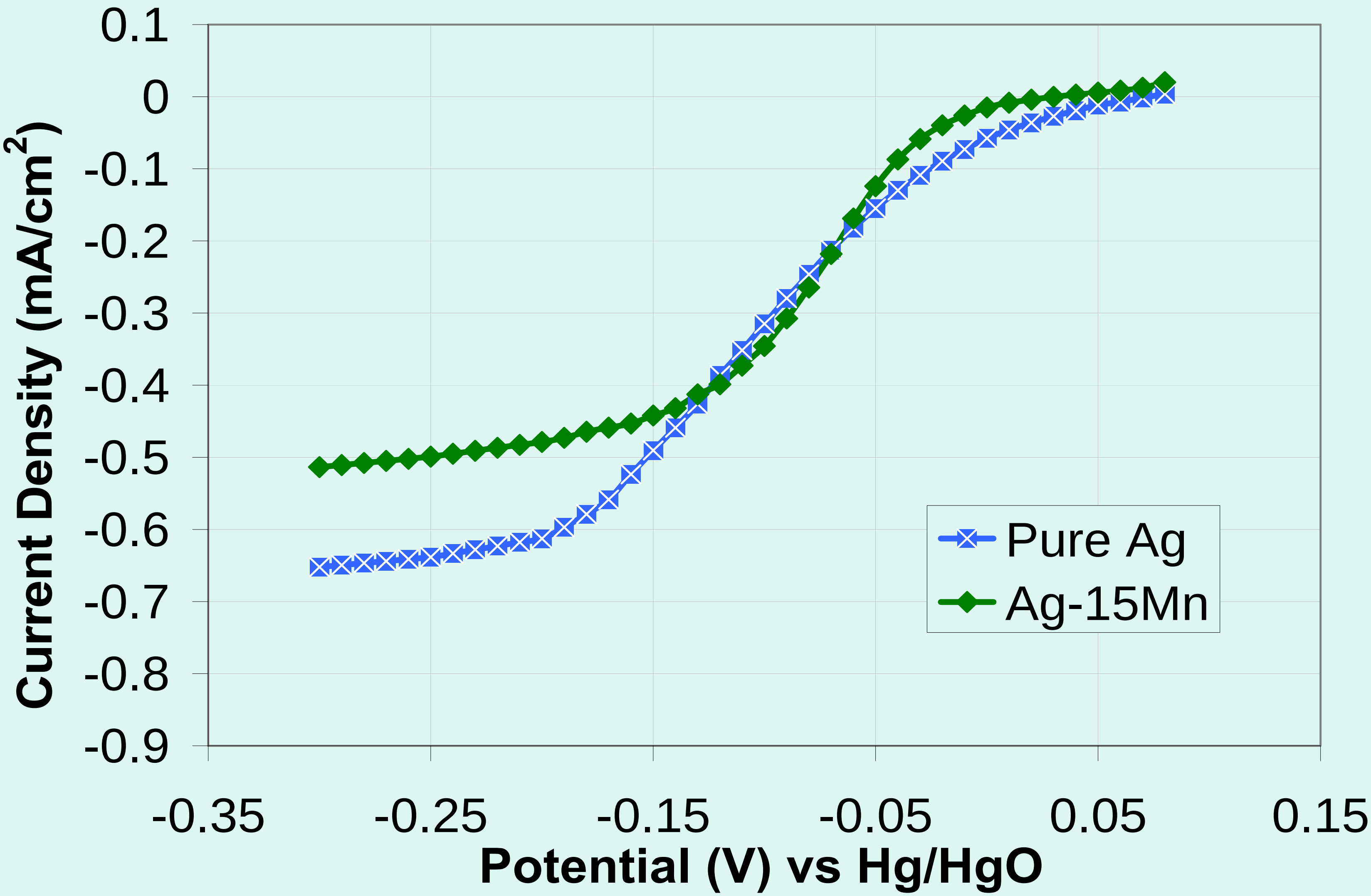
Ag-15wt%Mn in 0.1 M KOH at 80˚C



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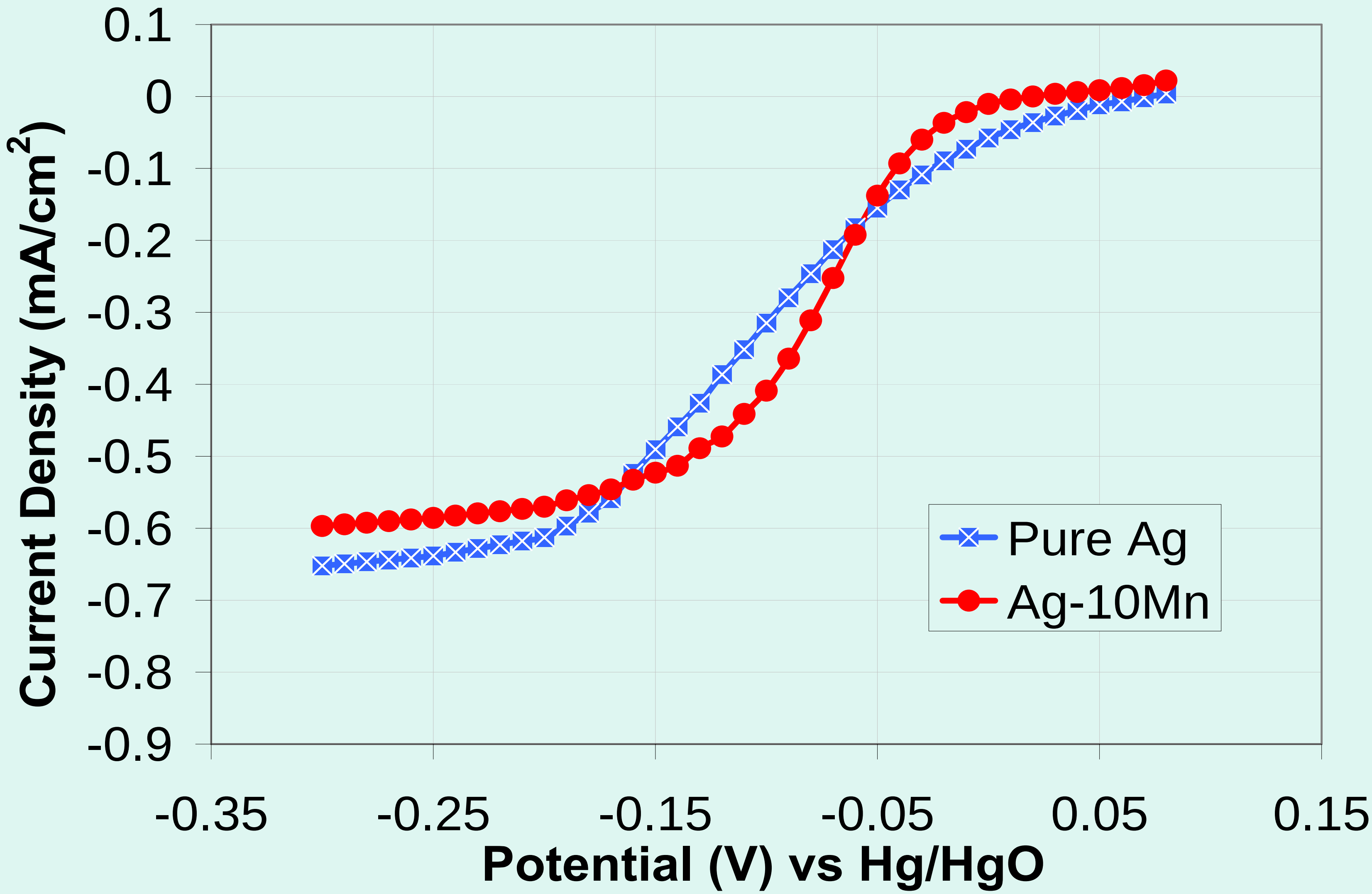
Ag-10wt%Mn in 0.1 M KOH at 80˚C



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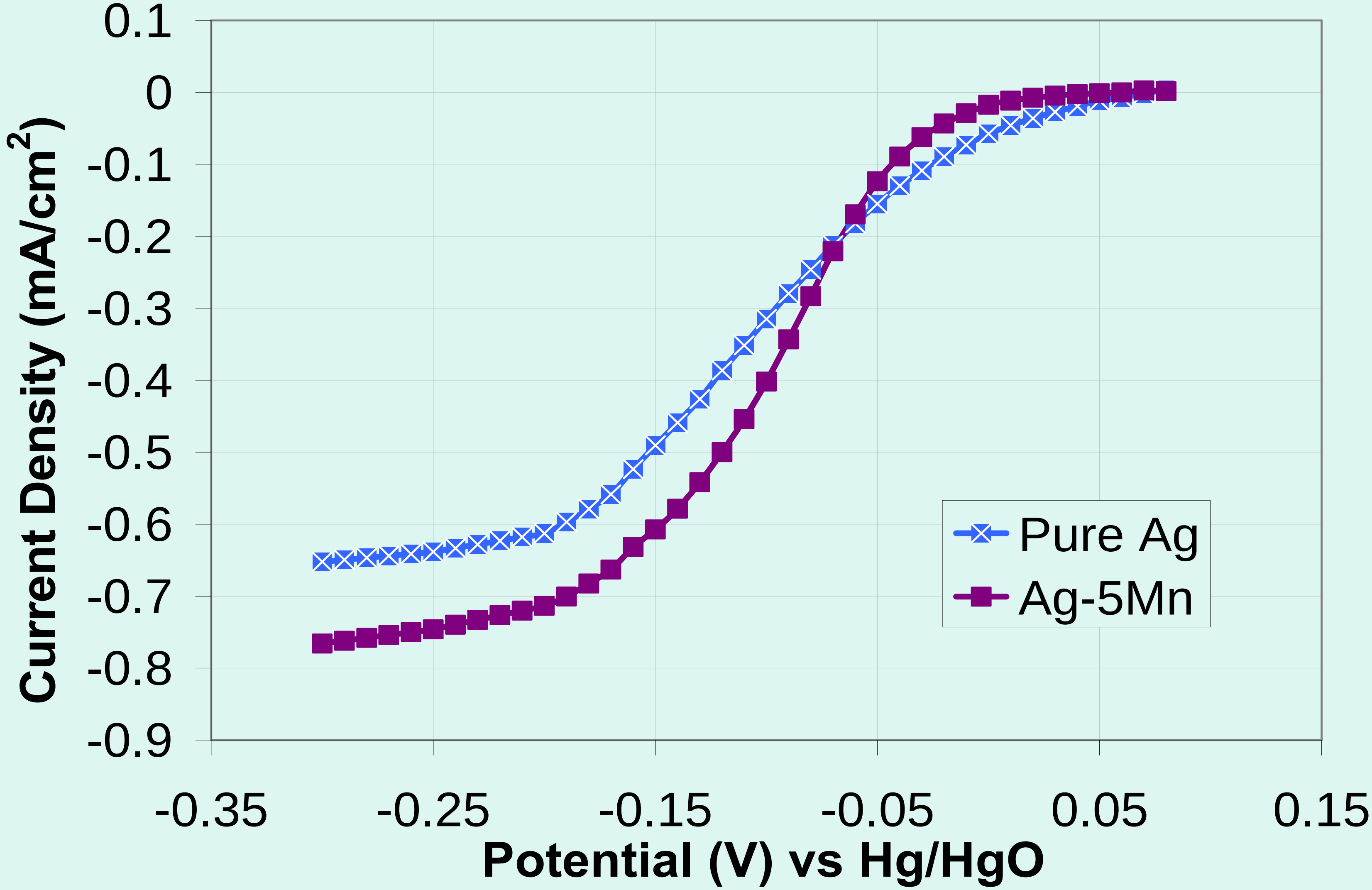
Ag-5wt%Mn in 0.1 M KOH at 80˚C



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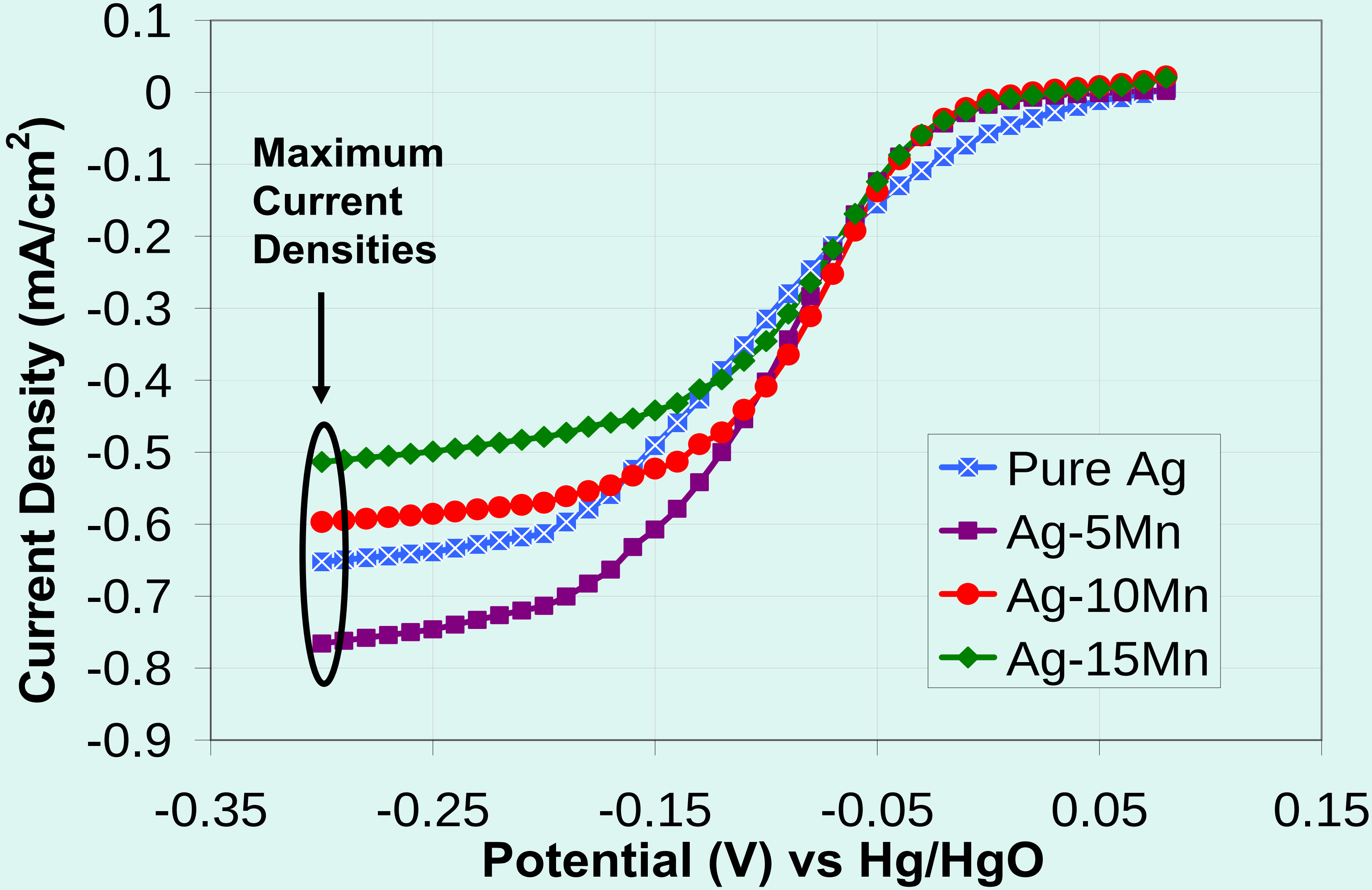
ORR Results - Comparison



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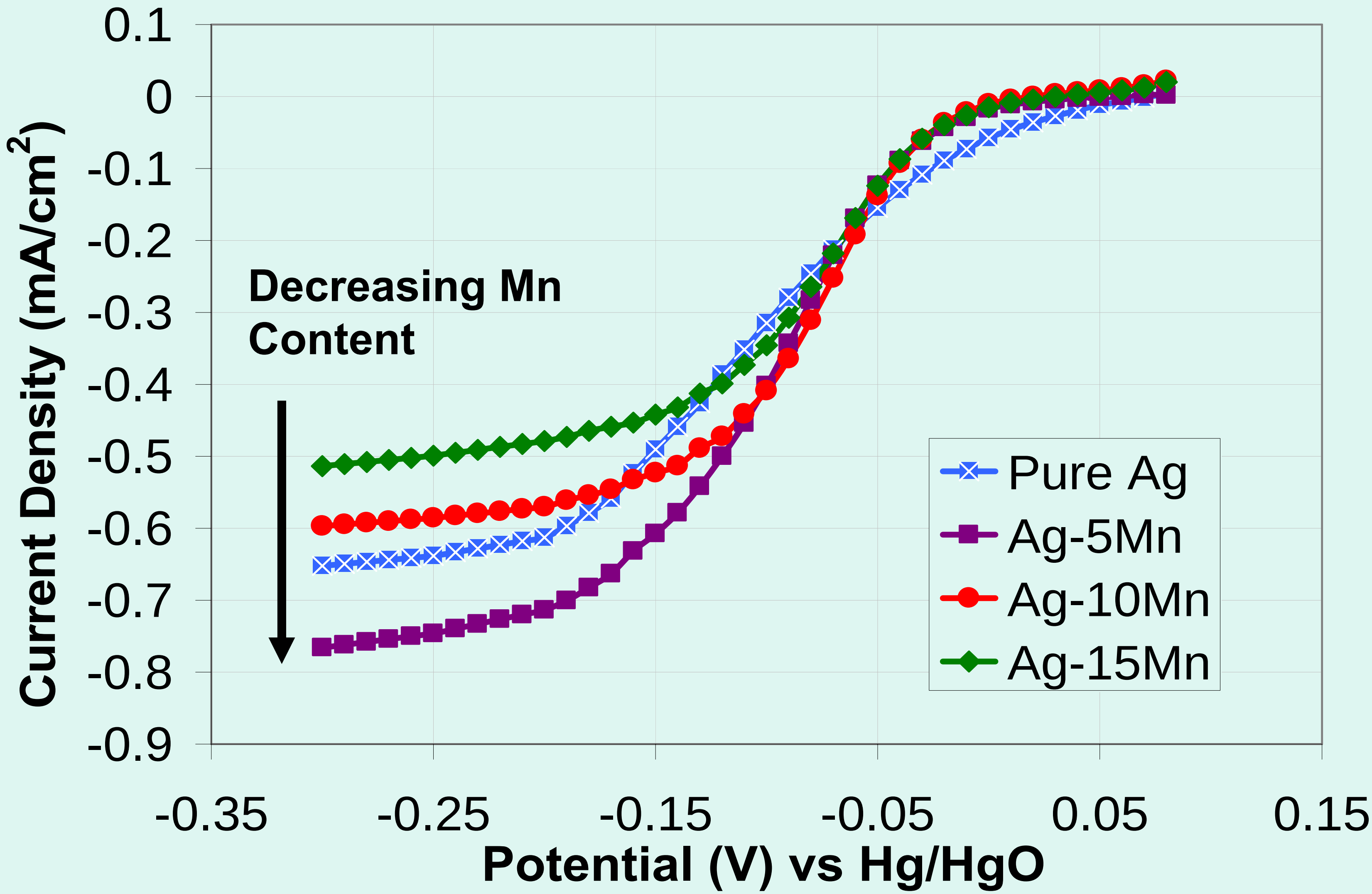
ORR Results - Comparison



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ORR Results - Summary

Alloy	Maximum Current (mA/cm^2)	Onset of ORR (V vs Hg/HgO)	Tafel Slope (mV/dec)	Cathodic Transfer Coefficient
Pure Silver	~ 65	~ + 0.075	70 (small η) & 140 (large η)	1 (small η) & 0.5 (large η)
Ag-15wt%Mn	~ 51	~ +0.030	60	~1.16
Ag-10wt%Mn	~ 60	~ +0.030	60	~1.16
Ag-5wt%Mn	~ 77	~ +0.050	60	~1.16

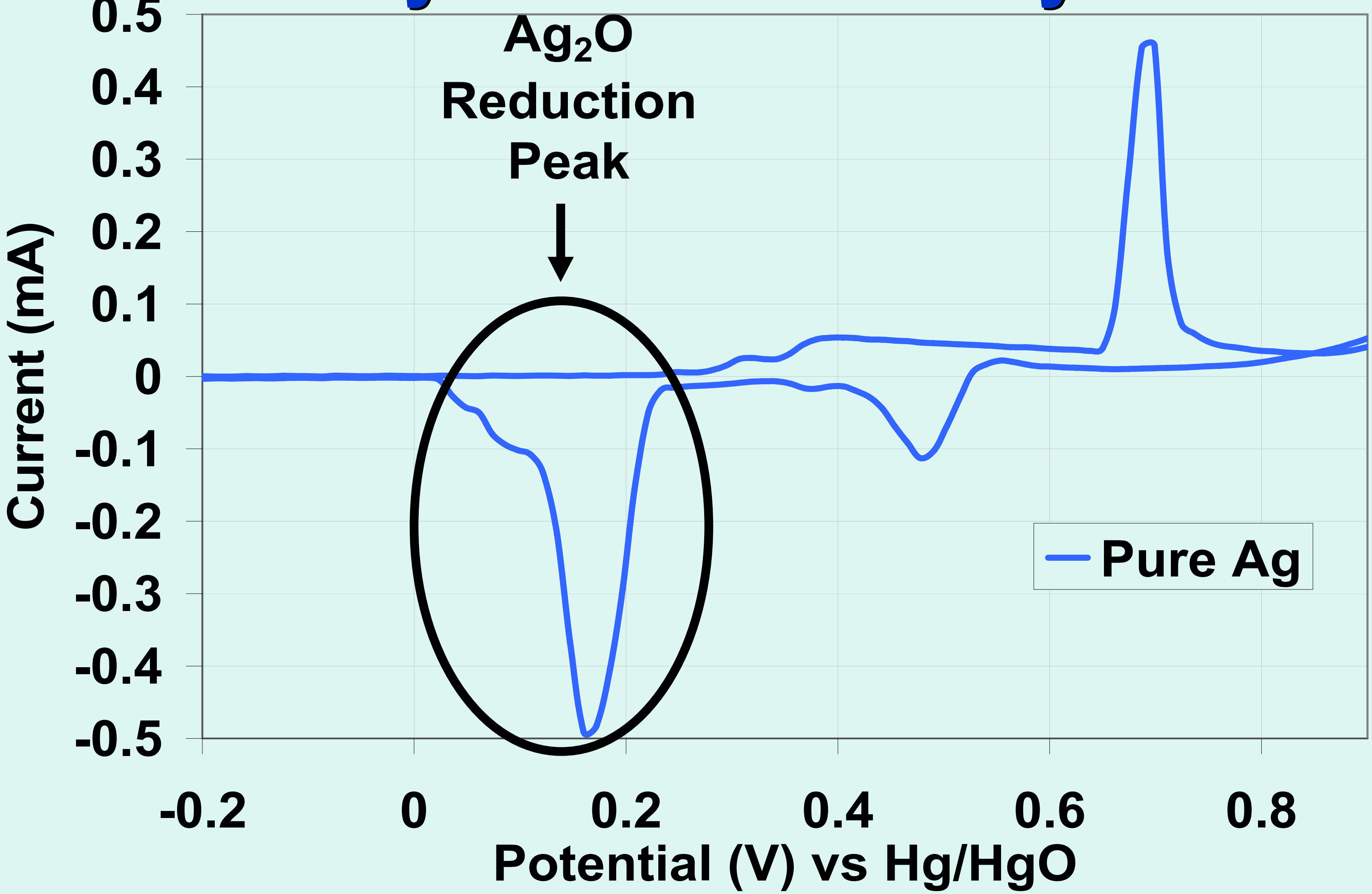
ORR Mechanism

- Silver shows two distinct Tafel regions
  - 4 e^- ORR process at high overpotentials

    ($O_2 + H_2O + 4\ e^- \rightarrow 4\ OH^-$)
  - 2 e^- ORR process at low overpotentials

    1. ($O_2 + H_2O + 2\ e^- \rightarrow HOO^- + OH^-$)
    2. ($HOO^- + H_2O + 2\ e^- \rightarrow 3\ OH^-$)
- Manganese containing alloys show nearly identical Tafel slopes and cathodic transfer coefficients
  - Mixed ORR process

Cyclic Voltammetry



Sweep Rate: 500 mV / min, swept from -200 mV to 900 mV

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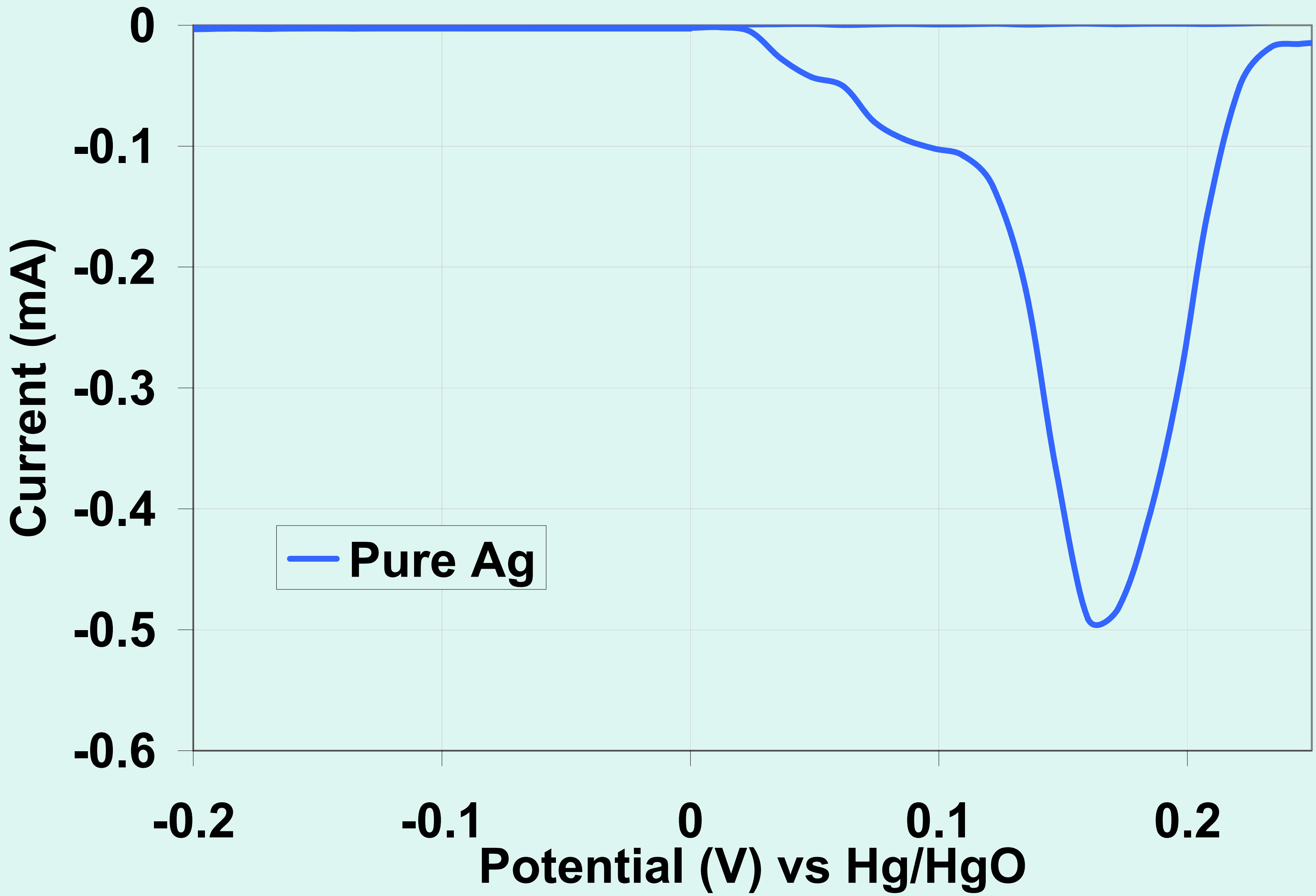
Cyclic Voltammetry – Ag_2O Reduction Peak



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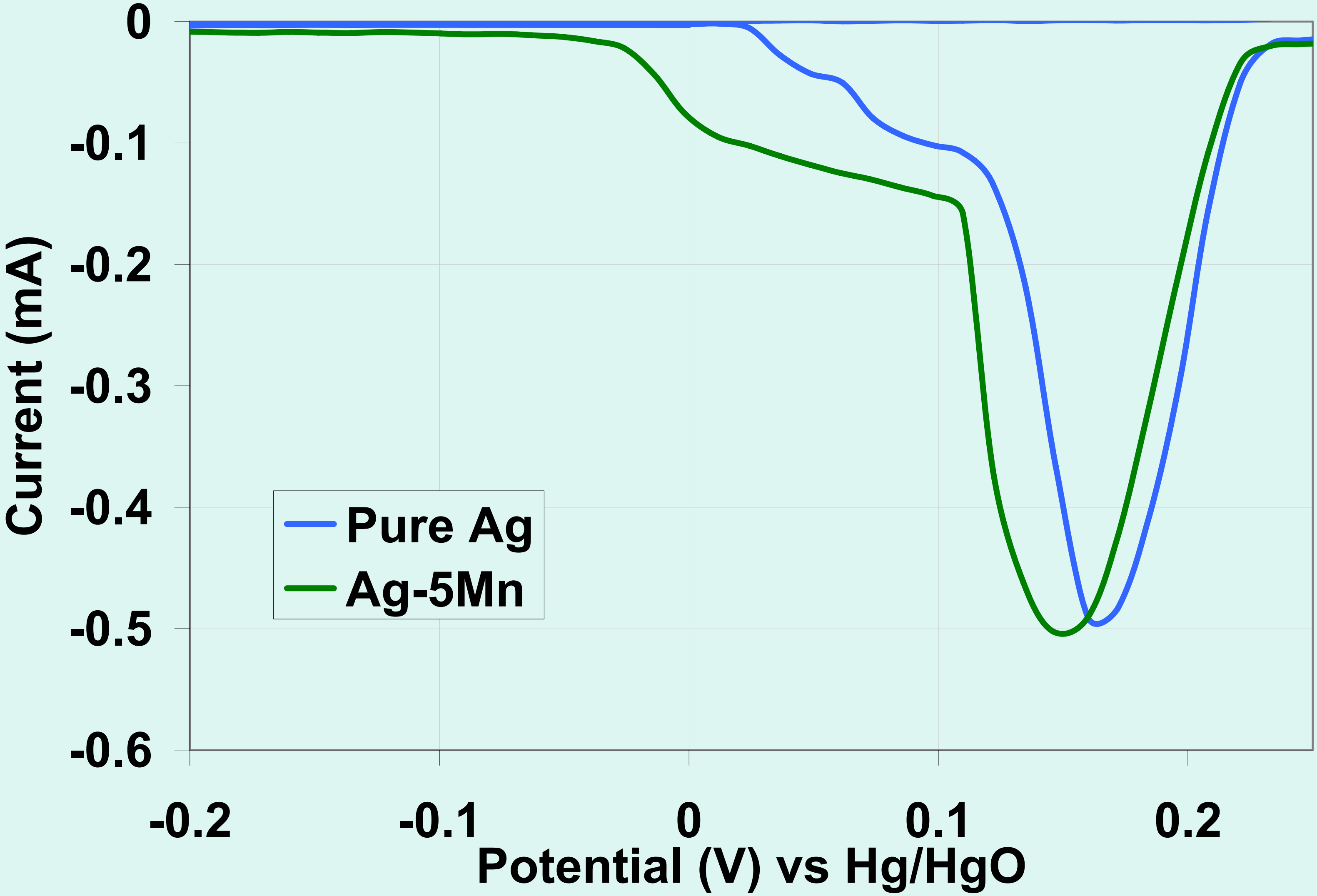

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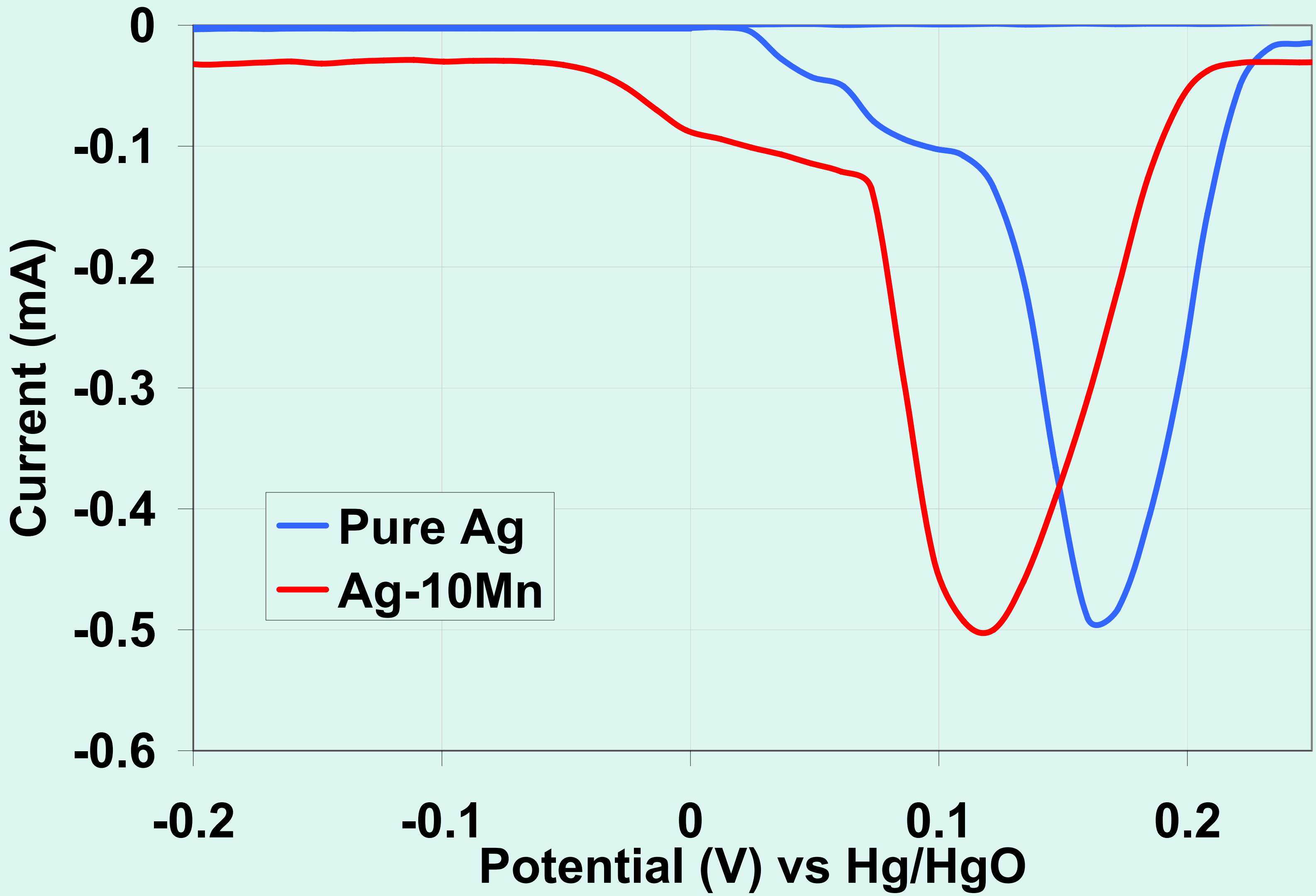
Cyclic Voltammetry – Ag_2O Reduction Peak



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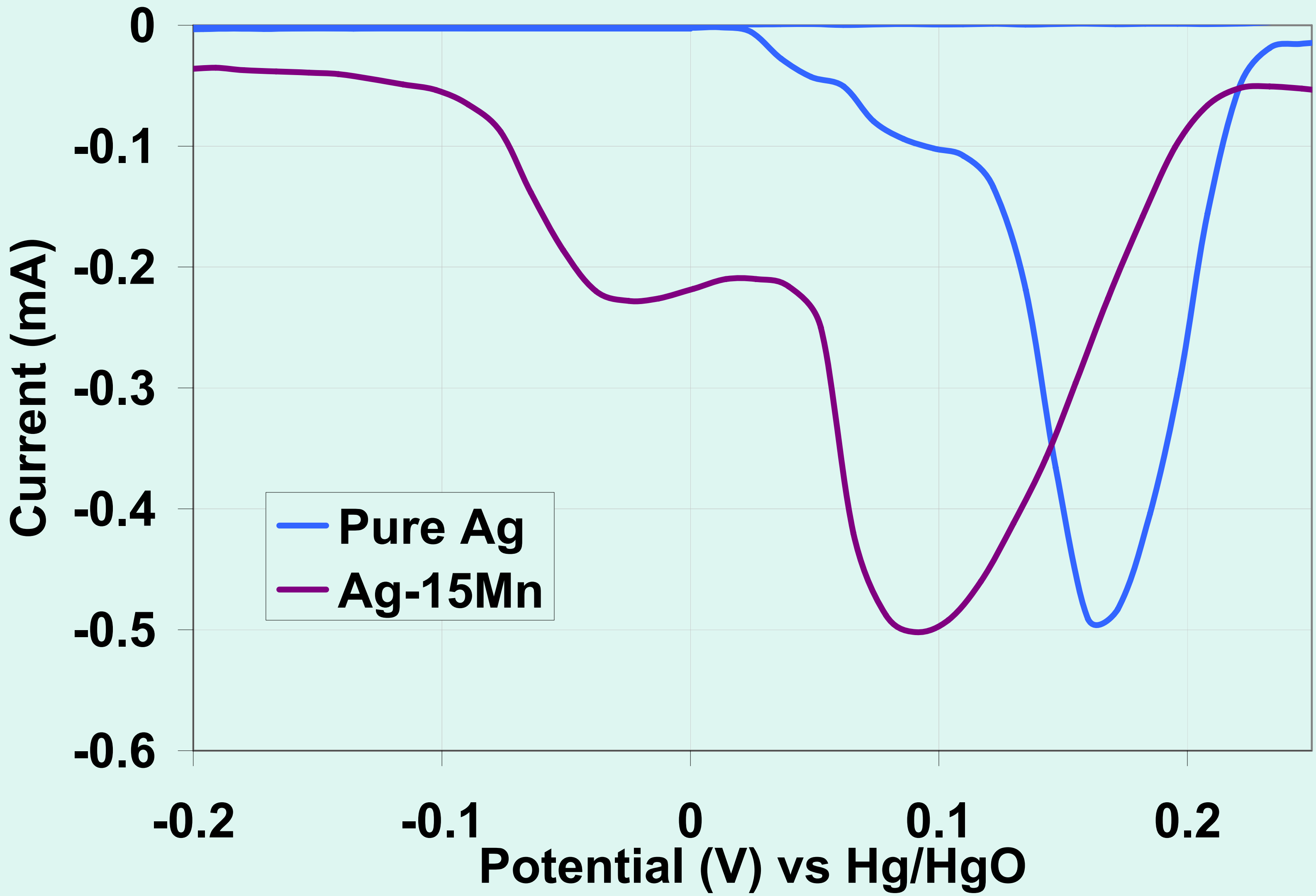
Cyclic Voltammetry – Ag_2O Reduction Peak



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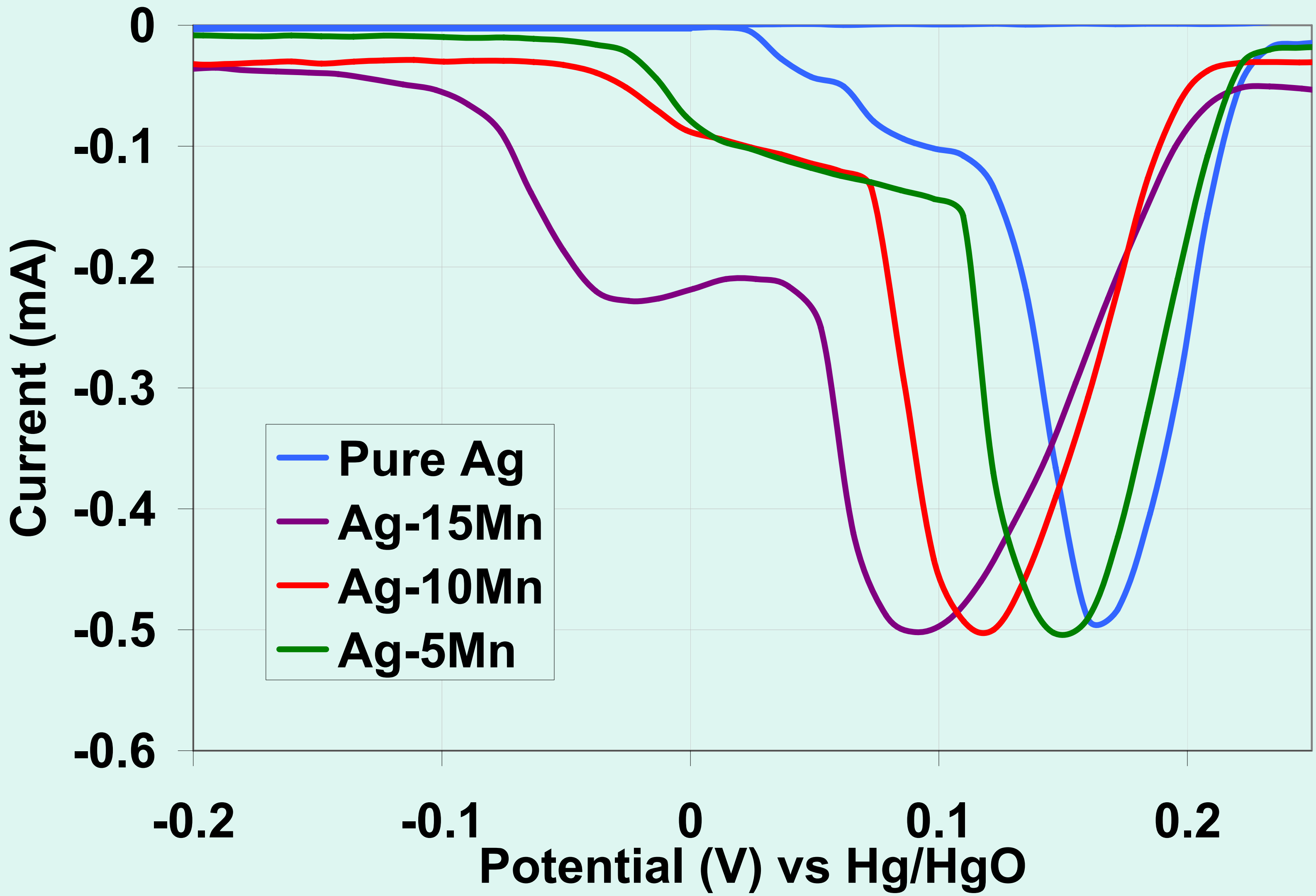
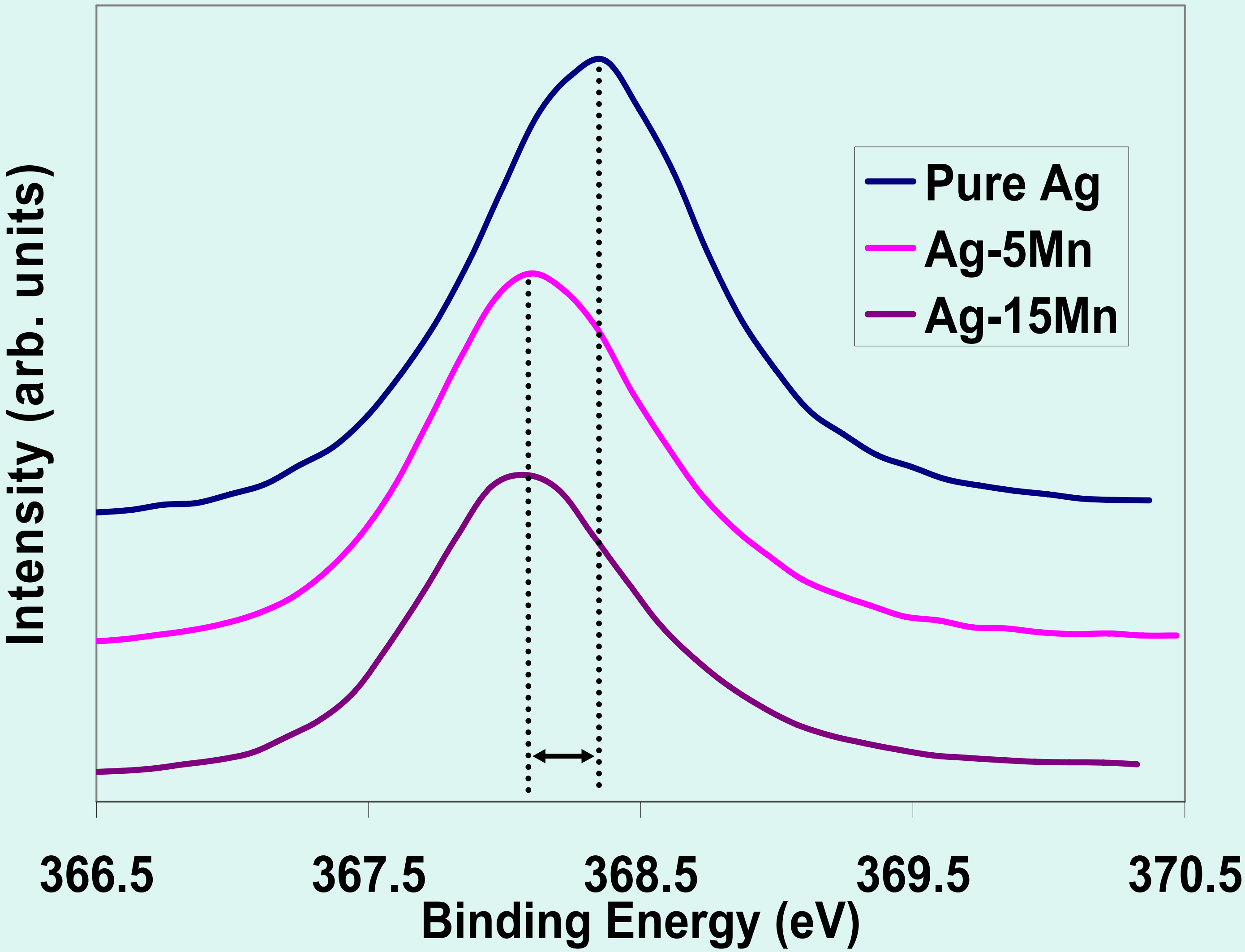
Cyclic Voltammetry – Ag_2O Reduction Peak



- **Higher affinity towards surface oxygen bonding with manganese alloying**

Silver – XPS Spectra



Silver $3d_{5/2}$ binding energy

Decrease of 0.2 eV for manganese containing alloys

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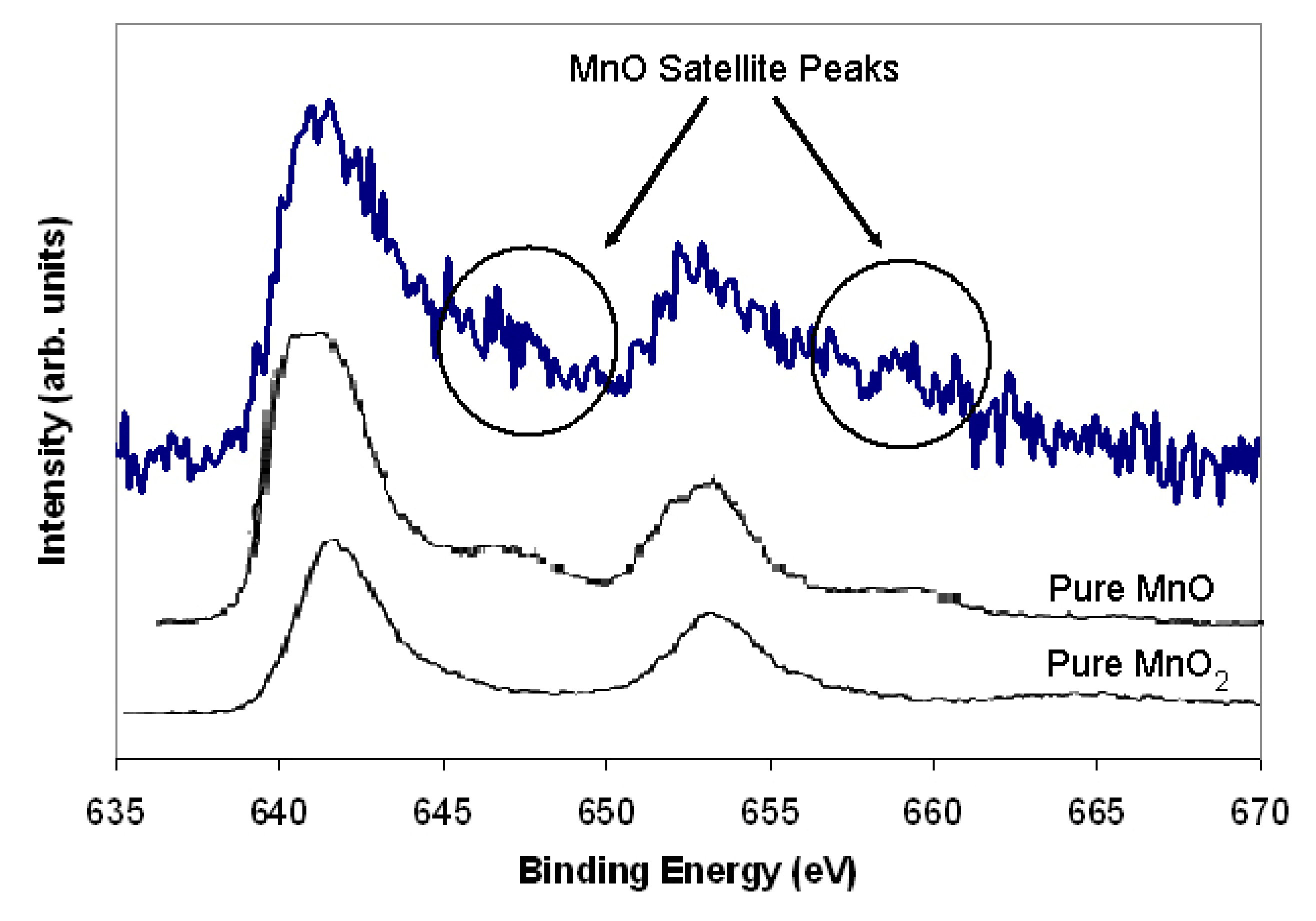
Manganese XPS Spectra



Mn 2p peaks show matching binding energies and satellite peaks corresponding to MnO (non-active).

- **Manganese surface concentration depleted on surface:**
  - **15 wt% → 10.7 wt%**
  - **5 wt% → 0.45 wt%**

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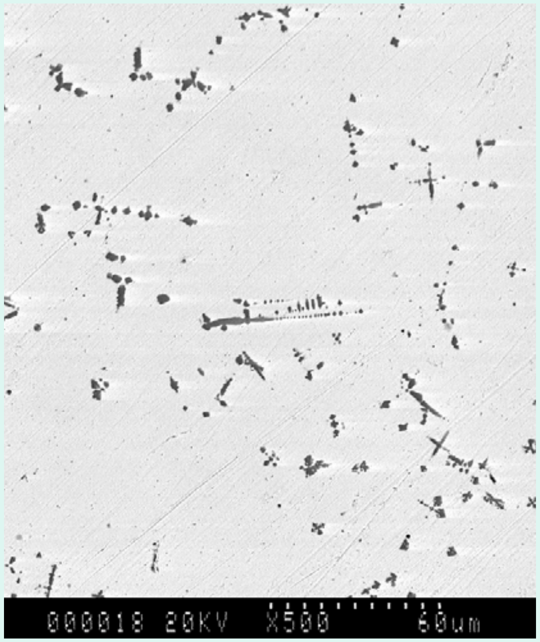
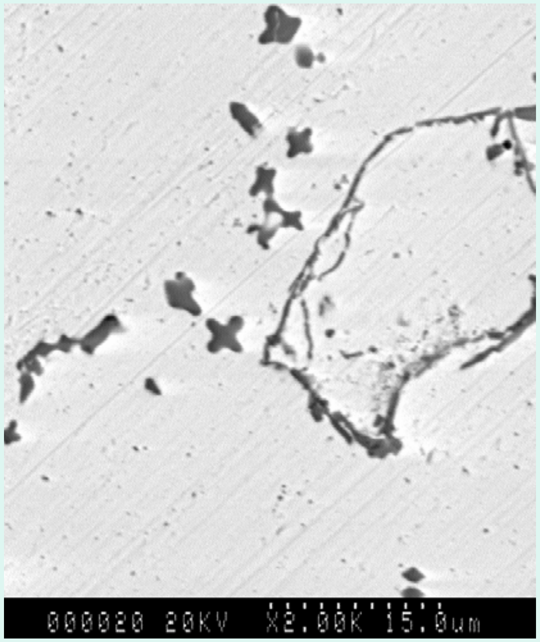
SEM Analysis



Images of Ag-15Mn



- High Mn (10 and 15wt%) alloys have non-active MnO sites on surface
  - Decreases maximum current density
- Low Mn (5 wt%) alloy has limited (~0.5 wt% Mn) on surface
  - Does not deplete active sites
  - Highest current density

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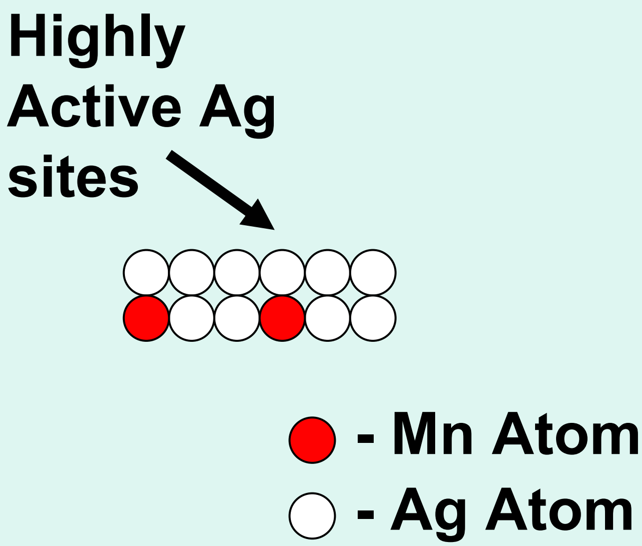
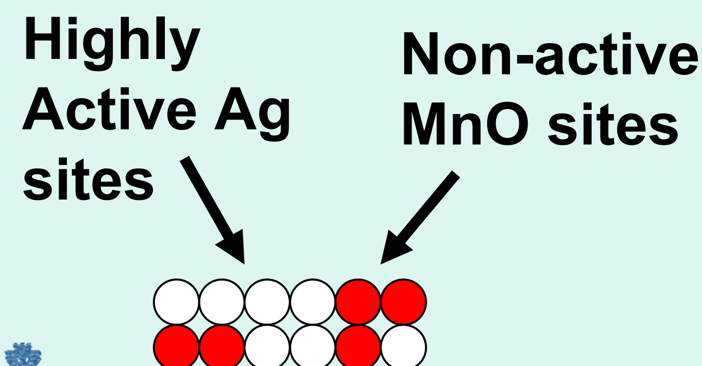
Ag-Mn Alloy Conclusions

Ag- 5 wt%Mn



Ag- 10 and 15 wt%Mn



- Manganese alloying decreases silver's d orbital binding energy
- Cathodic overpotential for Ag_2O reduction increases with increasing manganese concentration
- Manganese modifies silver's d orbital electronic structure
  - Increases the bond strength of Ag-O
  - Increasing efficiency of O-O bond cleavage

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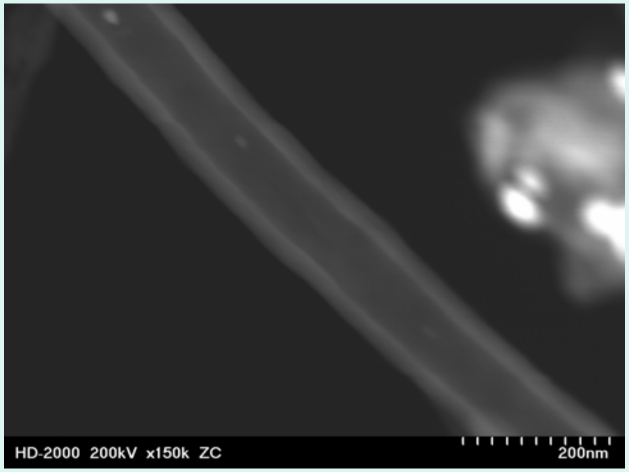
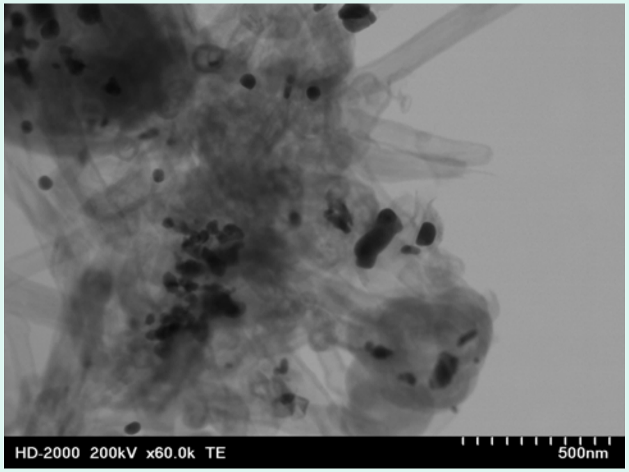
Introduction to Nano System





- **Silver and manganese dioxide catalysts were electrolessly deposited on carbon nanofibers**
- **Nanofibers range in diameter from ~50-150 nm**
- **Extremely high surface area**
- **Direct application to fuel cell electrode**

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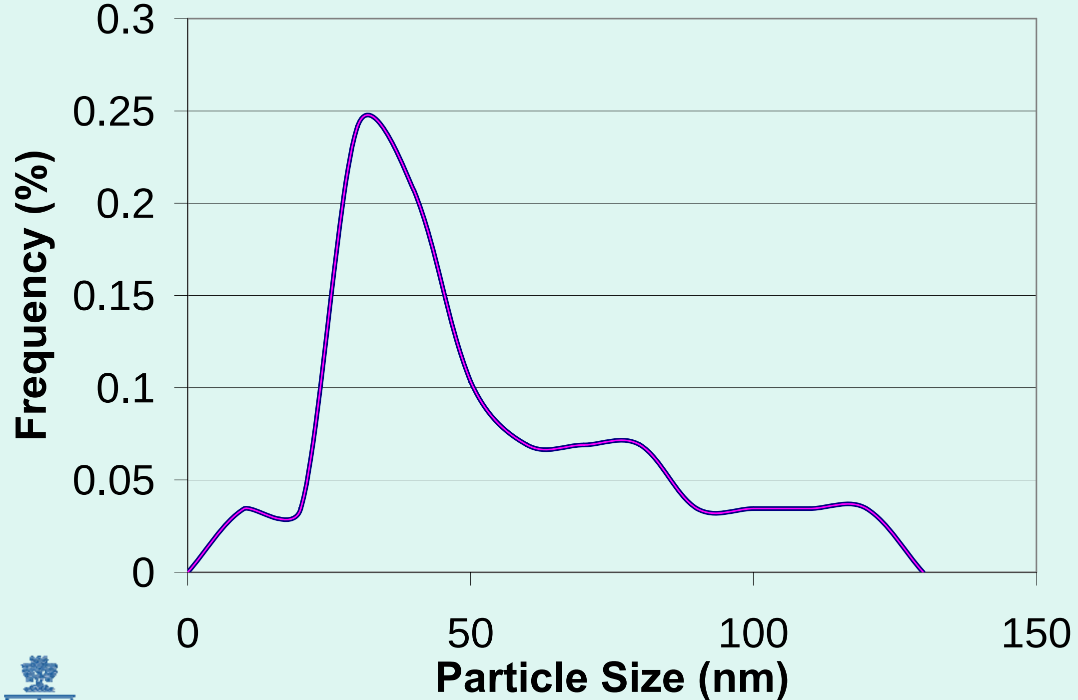
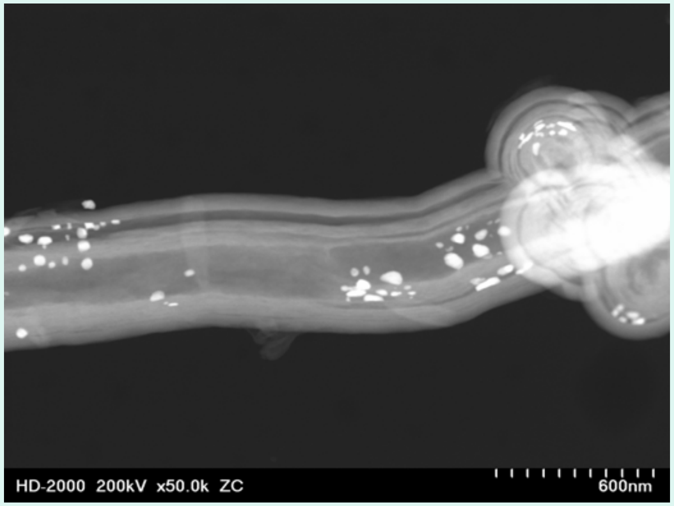
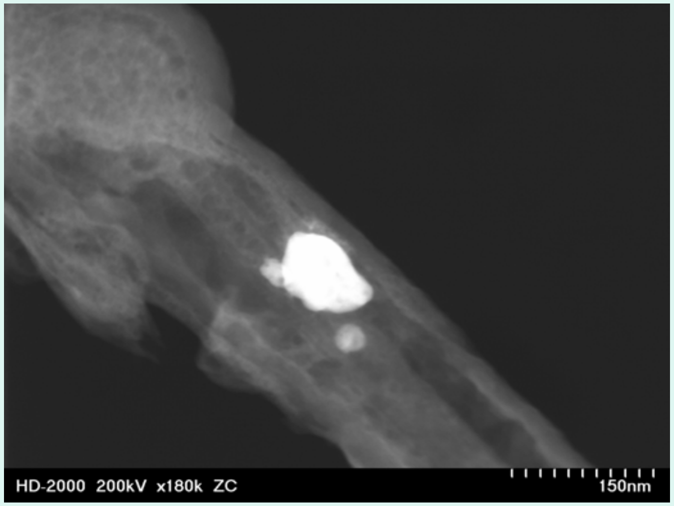
Ag Deposition

- Silver deposited using silver nitrate as precursor
- Average deposited silver particle size ~ 35-45 nm
- Primarily spherical particles - Volmer-Weber type growth







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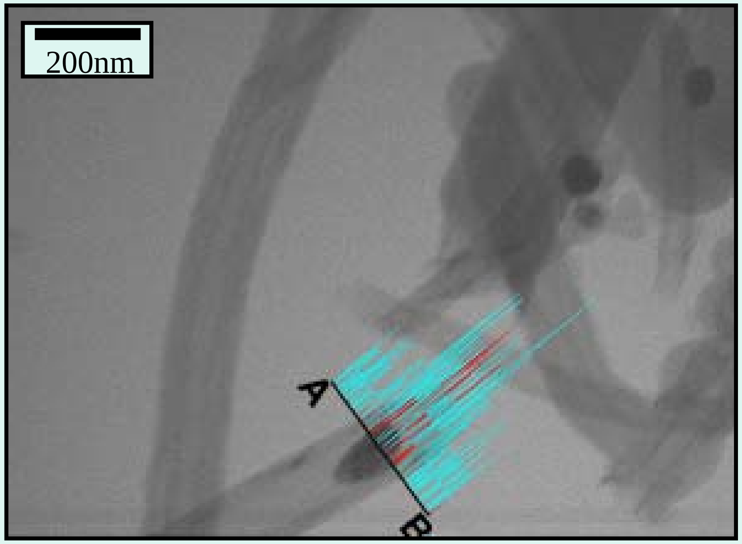
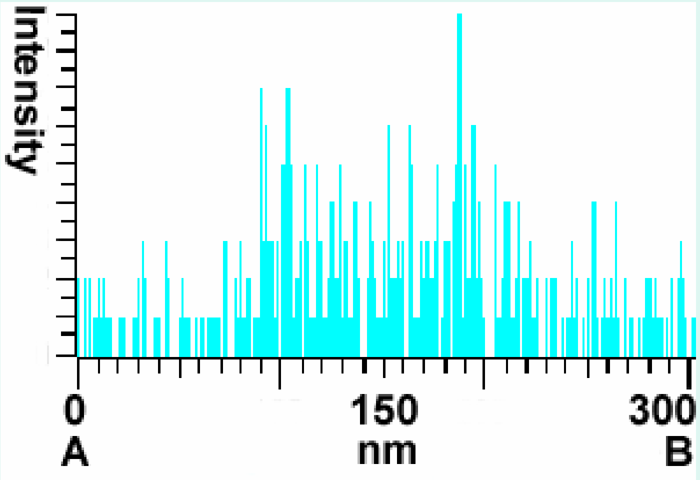
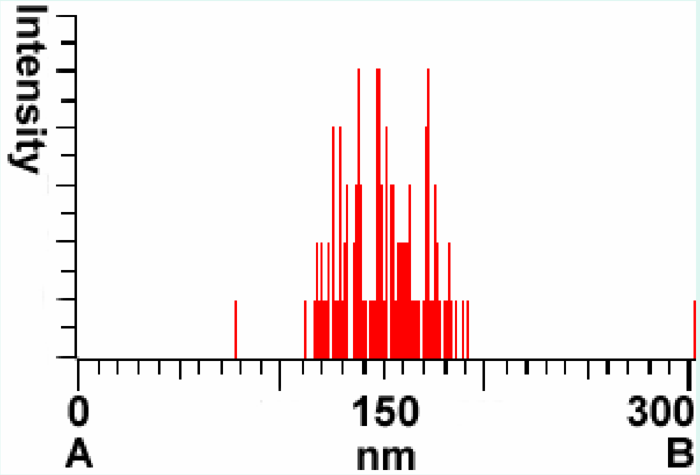
Ag Deposition – EDX Line Scan

- **EDX line scan confirming silver deposited on CNF**





Carbon signal



Silver signal

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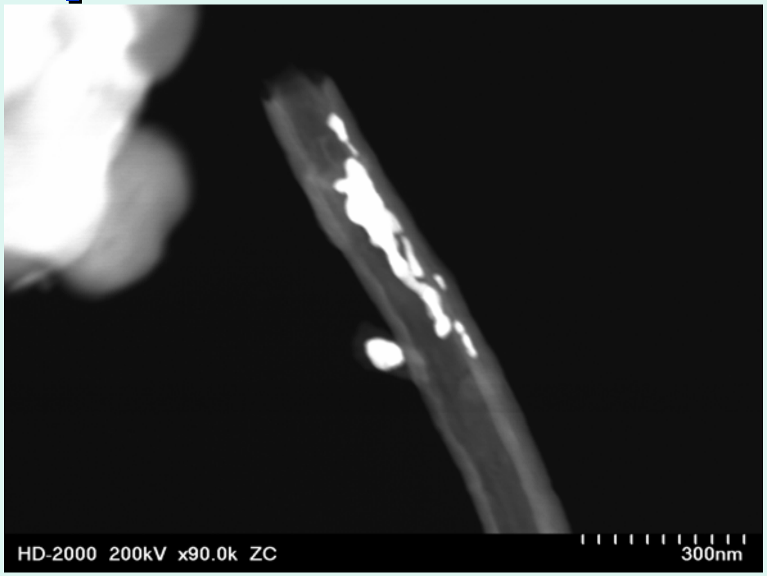
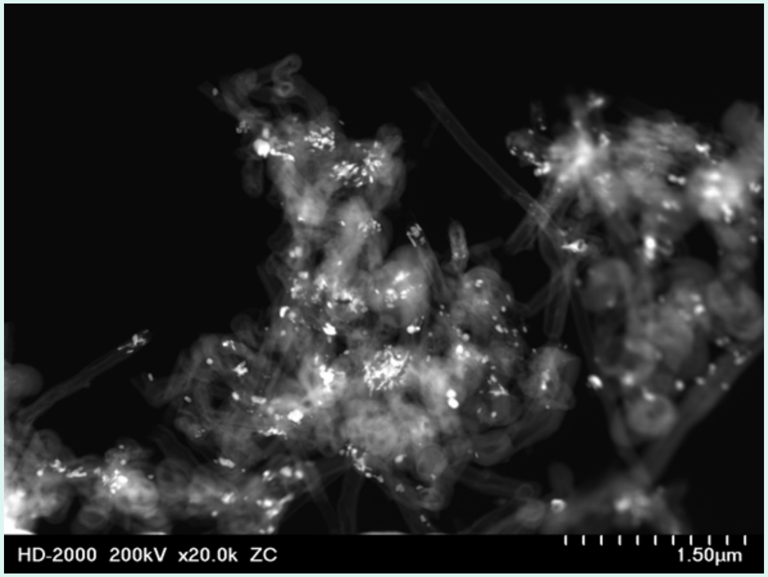
Ag + MnO_2 Deposition

- Silver and manganese dioxide deposited with silver permanganate as precursor – reduced with hydrazine
- Silver exhibited spherical and dendritic type growth
- Manganese dioxide appeared to deposit as a thin layer across the entire nanofiber (confirmed by EDX mapping)





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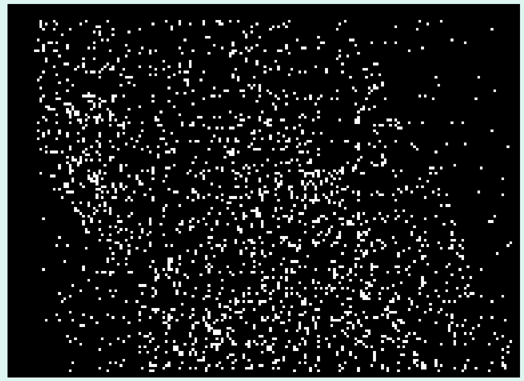
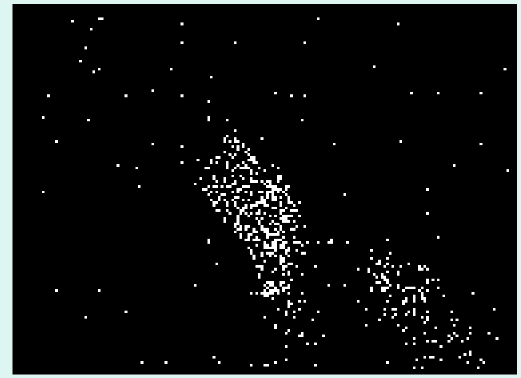
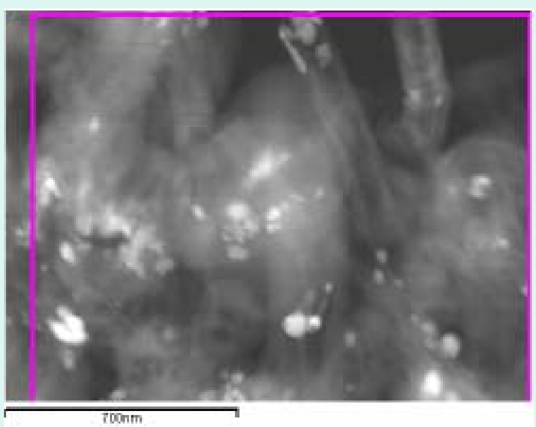
Ag + MnO_2 Deposition – EDX Mapping

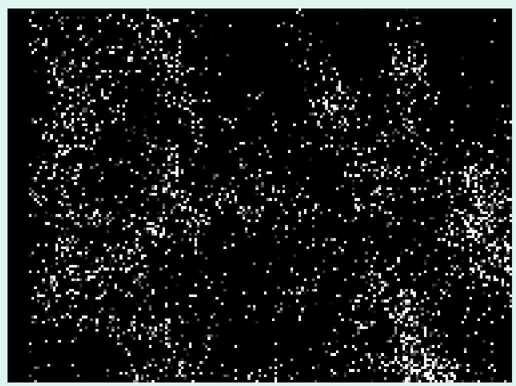


Manganese

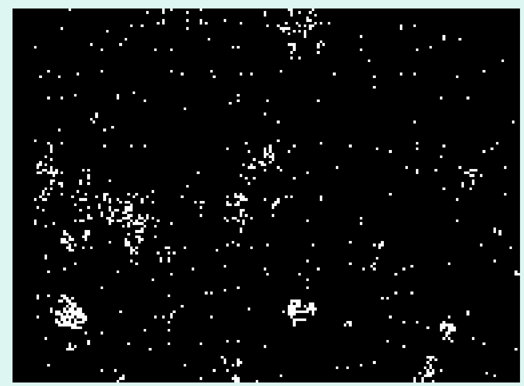


Silver





Manganese



Silver

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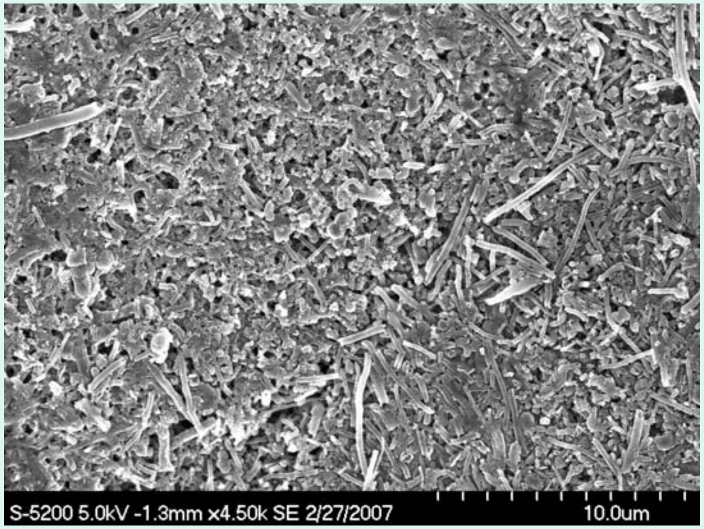
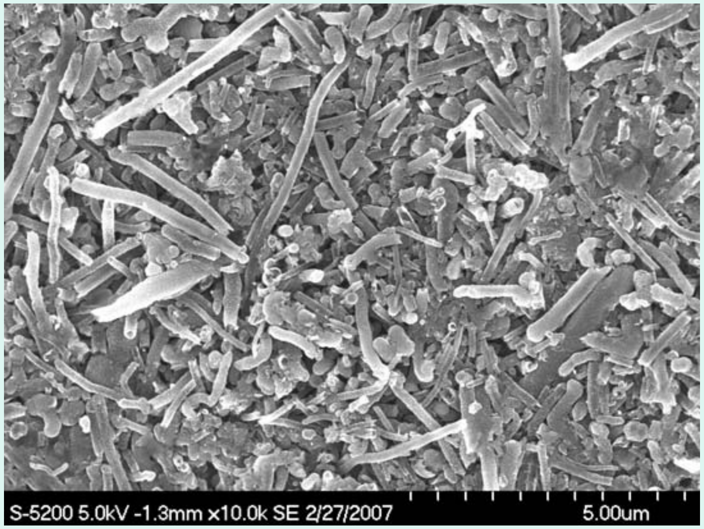
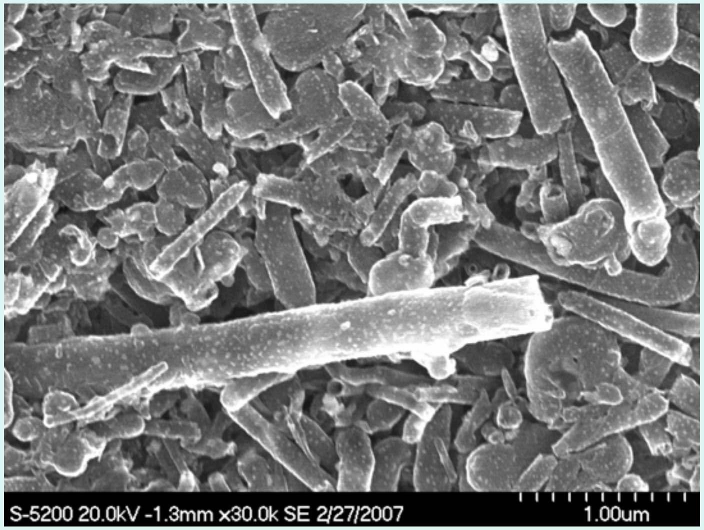
Electrode Preparation







Electrode composition:
- 30 wt% solid PTFE
- 60 wt% CNF
- 10 wt% metal catalyst

Electrode synthesis:
- rolling, pressing and heating

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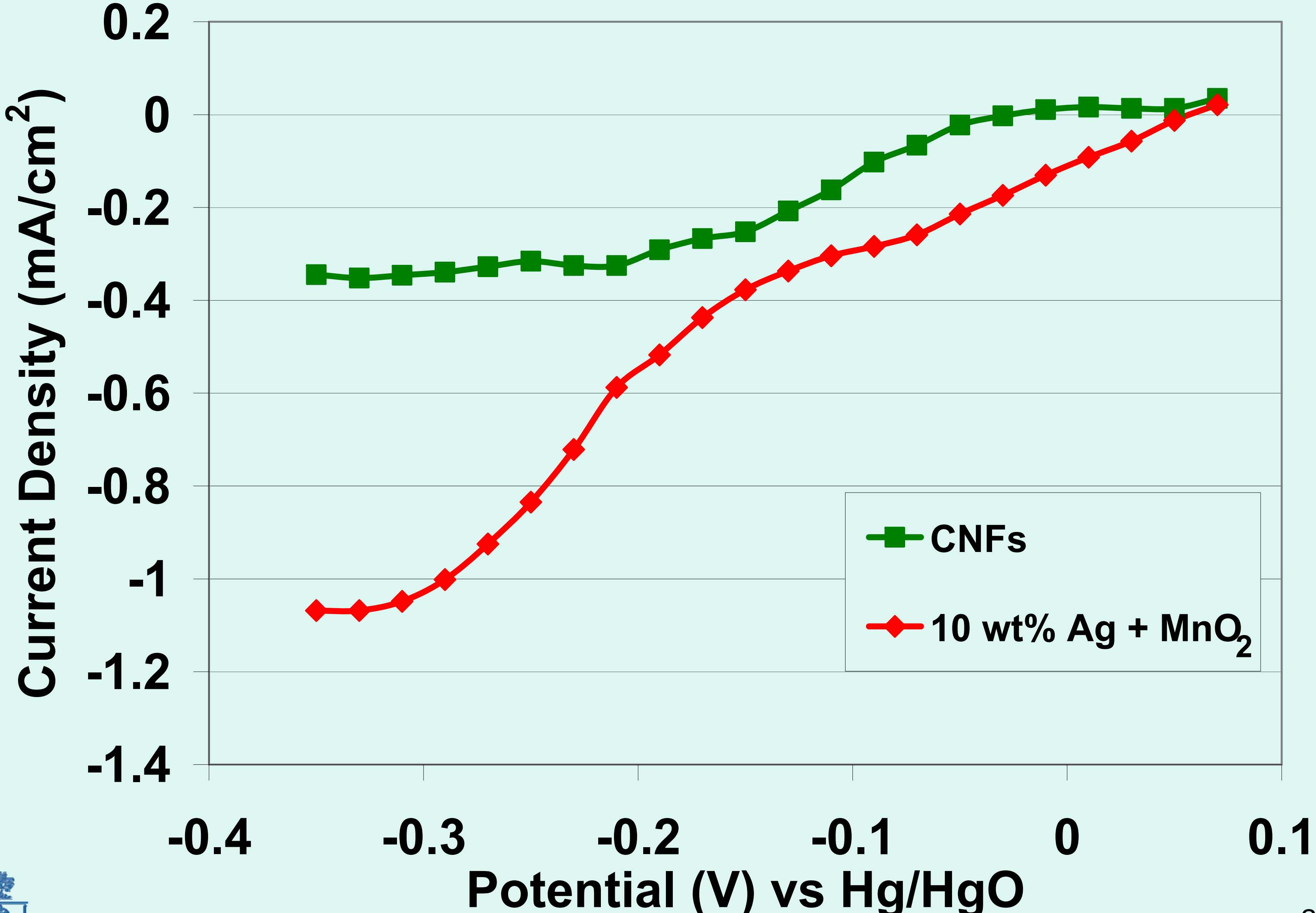
CNF – 10wt% Ag + MnO_2 in 0.1 M KOH at 80˚C



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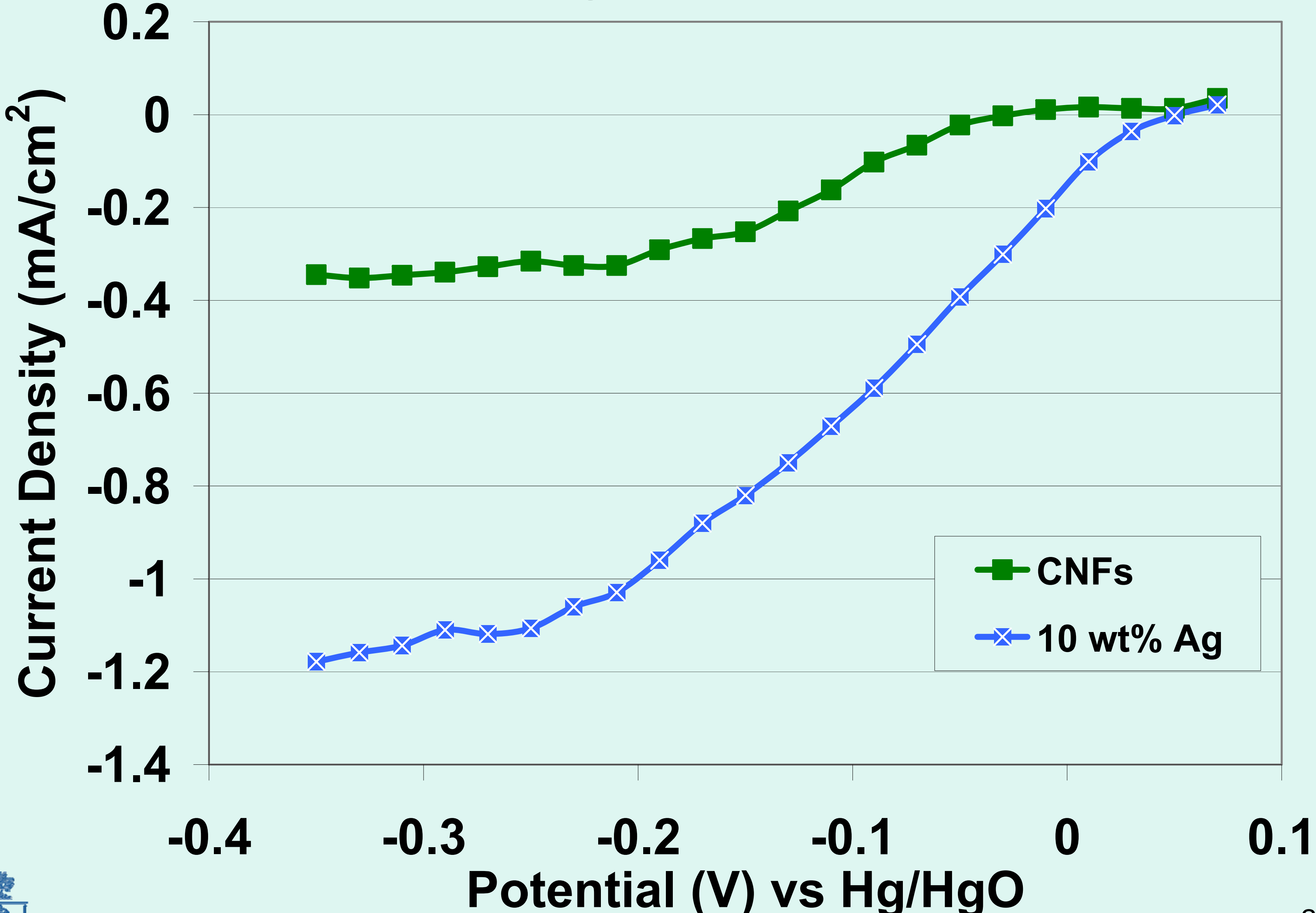
CNF – 10wt%Ag in 0.1 M KOH at 80˚C



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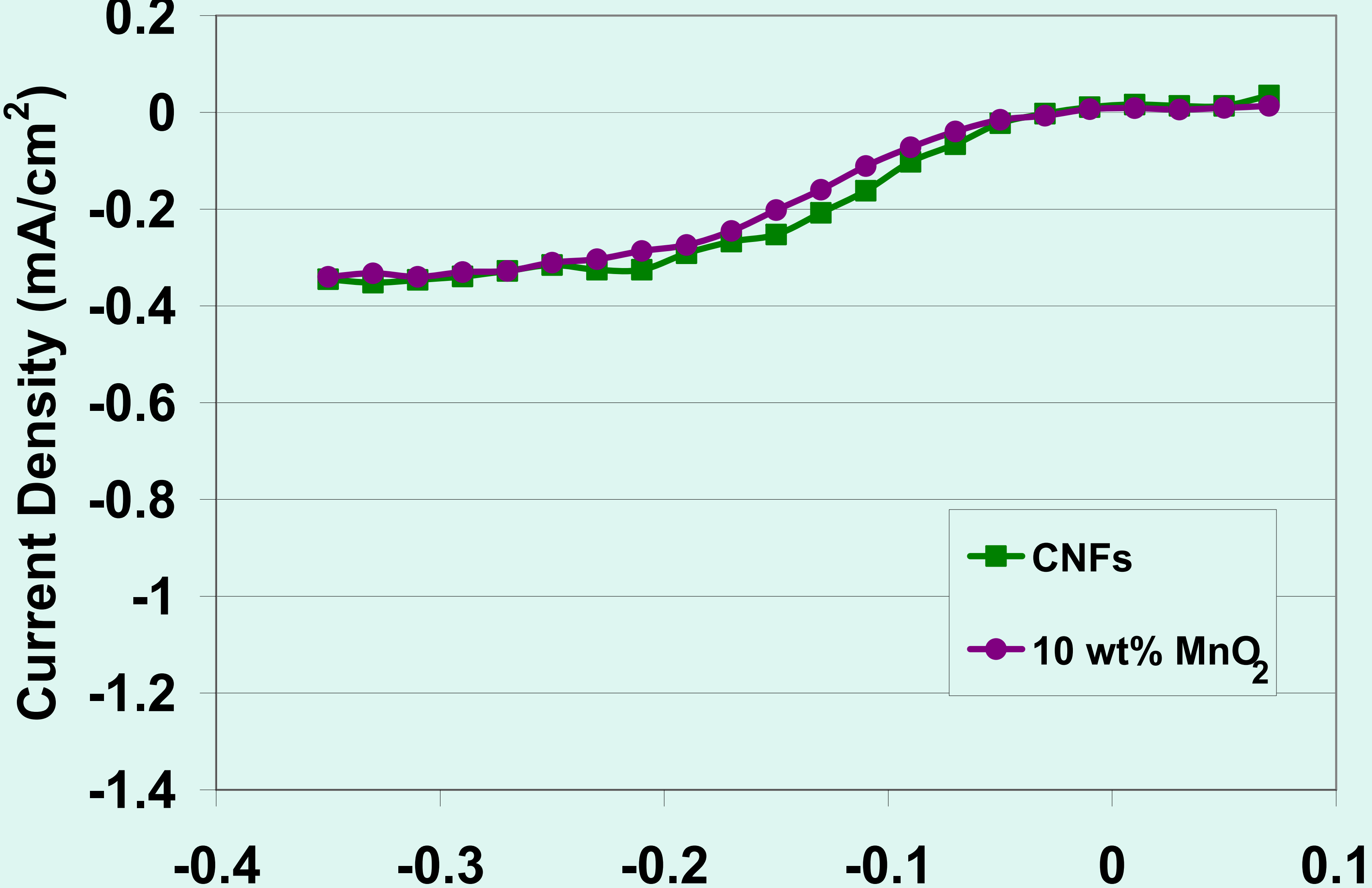
CNF - 10wt% MnO_2 in 0.1 M KOH at 80˚C



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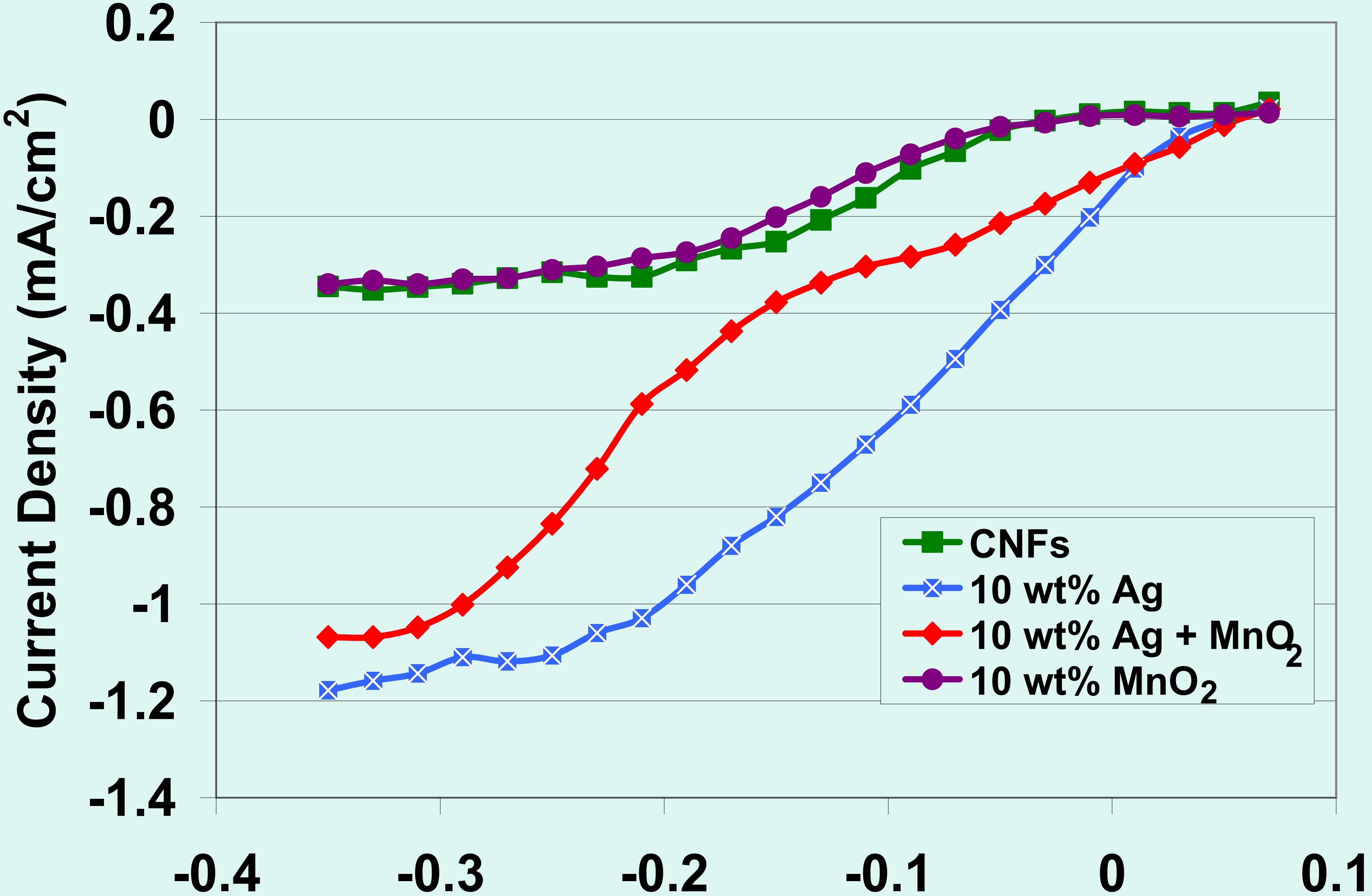
ORR Results - Comparison



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ORR Results

- 10wt% Ag - CNFs showed highest activity
- Same magnitude of maximum current density as solid polycrystalline electrodes, but at 1000X less loading
- Manganese dioxide coated CNFs have the same activity as non-loaded CNFs

Conclusions

Alloy System

- Ag-5wt%Mn alloy showed the highest catalytic activity towards ORR (15-20% better than Pure Ag)
  - Activity increase due to electronic structure effects of manganese alloying with silver

Nano System

- 10 wt% Ag + CNFs showed highest activity towards ORR
  - Manganese oxide coated samples showed identical activity to CNFs; non-active manganese oxide electrolessly deposited
  - Higher current density than pure Ag with 1000X less mass

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Potential Applications

- **Nano ball-mill Ag-5%Mn alloy**
  - **Incorporate as catalyst in CNF+PTFE alkaline fuel cell cathode electrode**
- **Use silver electroless deposition on CNFs/CNTs for AFC cathode electrode**
- **Develop a deposition process for Ag + 1 to 5 wt% Mn onto CNFs/CNTs**

Acknowledgments

- Thanks to
  - Supervisors: Prof. Thorpe and Prof. Kirk
  - ESEG Group
    - Ryan Gilliam, Paulo Borges, Holly Wonch, Mike Kostowskyj, Ella Pakravan
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