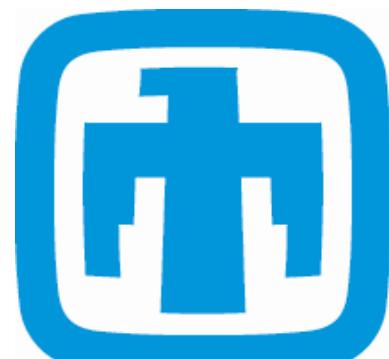# Spinel $M_xCo_{3-x}O_4$ Nanoparticles: Facile Low Temperature Solution Synthesis and Characterization

Danae J. Davis*, Timothy N. Lambert, and Marlene Bencomo

Sandia National Laboratories, PO Box 5800, MS 0734, Albuquerque, New Mexico, 87185.
Department of Materials, Devices, and Energy Technology
* Email: ddavis@sandia.gov

## Abstract

The synthesis and characterization of spinel $M_xCo_{3-x}O_4$ (M = Mn and Fe) nanoparticles was undertaken. Cobalt oxide-based nanoparticles doped with transition metals have a wide variety of potential applications, ranging from performing as cathode catalysts in fuel cells and metal-air batteries to new material coatings for concentrating solar power applications. We have recently demonstrated that $M_xCo_{3-x}O_4$ nanoparticles can be prepared using simple, low temperature solution precipitation methods, and that the final size and morphology of the nanoparticle depends on the extent of doping. These materials have been characterized by powder x-ray diffraction (PXRD), high-resolution transmission electron microscopy (HR-TEM), $N_2$ adsorption-desorption, and thermal gravimetric analysis/differential thermal analysis (TGA/DTA). The synthesis, characterization, as well as some preliminary investigations into potential applications of these materials, is presented.

## Introduction

Transition metal oxide systems, especially of the spinel structure, have generated interest for potential applications in electrocatalysis.[1-3] Many of the existing studies were motivated by the fact that these materials are economically viable, environmentally compatible, thermodynamically stable, and electrochemically active.[1]

Oxide spinels can be described by the general formula $AB_2O_4$, where A and B represent the tetrahedral and octahedral cation sites in a cubic packing of oxygen atoms.[4]
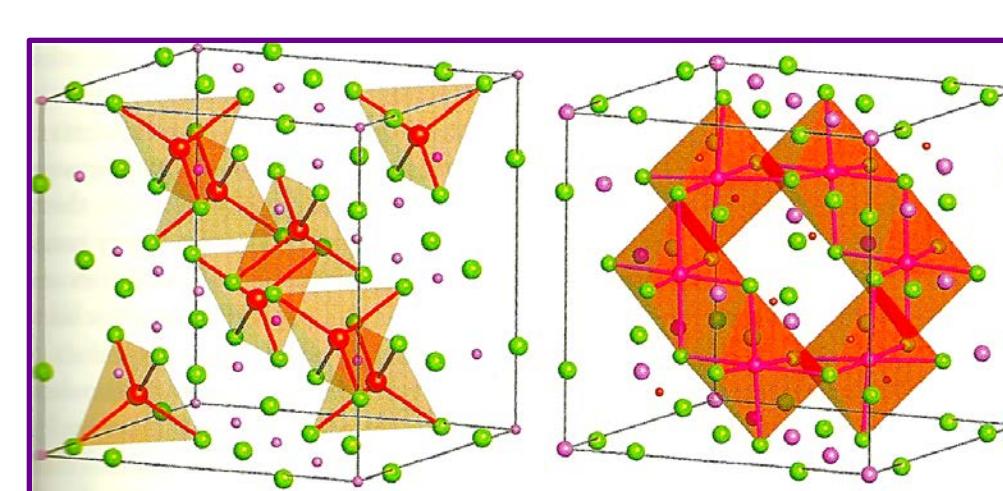
Mixed spinel transition metal oxides, the focus of this study, are spinels in which different cations exist, distributed in different ways among the A and B sites. These mixed spinels are of interest, as they possess a variety of physical and chemical properties.

The majority of previously published syntheses of mixed transition metal oxides utilize high temperature (e.g. > 400 ºC) approaches.[5] Here, we present a flexible low temperature synthesis that yields nanoparticles with high surface areas and examine their ability to serve as catalysts for reduction of oxygen.

## Goals

- **Demonstrate low-temperature synthesis of mixed transition metal oxides of the theoretical formula $M_xCo_{3-x}O_4$, where M = Mn or Fe**
- **Characterize the synthesized materials**
- **Evaluate the electrochemical properties of the synthesized materials for applications in electrocatalysis**

## References
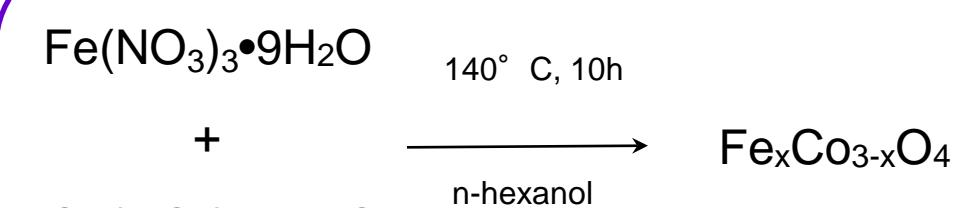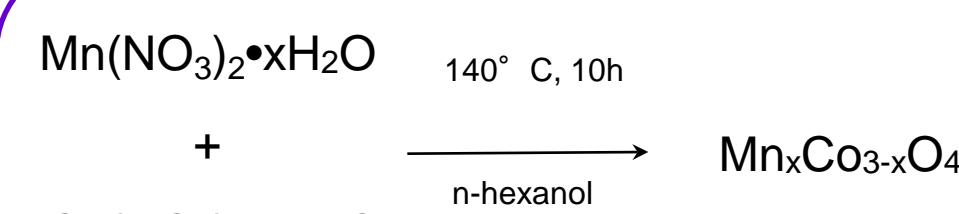
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## Acknowledgments

# Synthetic Route and Characterization Methods

## Reaction Scheme

$Mn(NO_3)_2 \cdot xH_2O$ + $Co(NO_3)_2 \cdot 6H_2O$  →(140° C, 10h, n-hexanol)  $Mn_xCo_{3-x}O_4$

$Fe(NO_3)_3 \cdot 9H_2O$ + $Co(NO_3)_2 \cdot 6H_2O$  →(140° C, 10h, n-hexanol)  $Fe_xCo_{3-x}O_4$

## Experimental Approach

The synthesis of doped cobalt oxide nanoparticles was achieved by the decomposition of metal nitrate precursors in a solution of n-hexanol at 140ºC.[6]

$Mn_xCo_{3-x}O_4$:

$Mn(NO_3)_2 \cdot xH_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ were weighted in appropriate molar ratios depending on the theoretical x-value of the desired product.
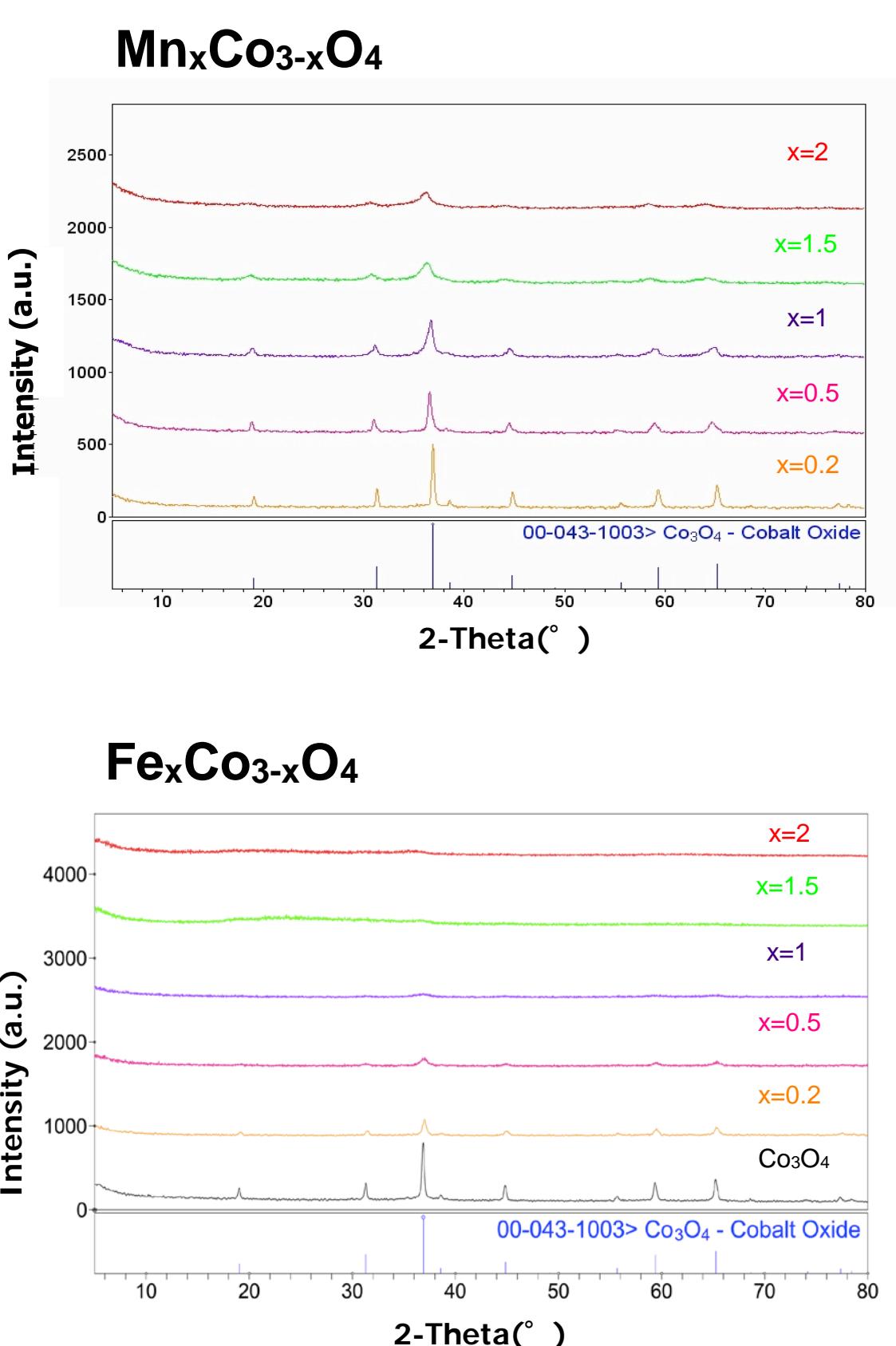
$Fe_xCo_{3-x}O_4$:

$Fe(NO_3)_3 \cdot 9H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ and were weighted in adequate molar ratios depending upon the x-value of the reaction.

Solutions were heated for approximately 10 h with stirring, under a reflux condenser.
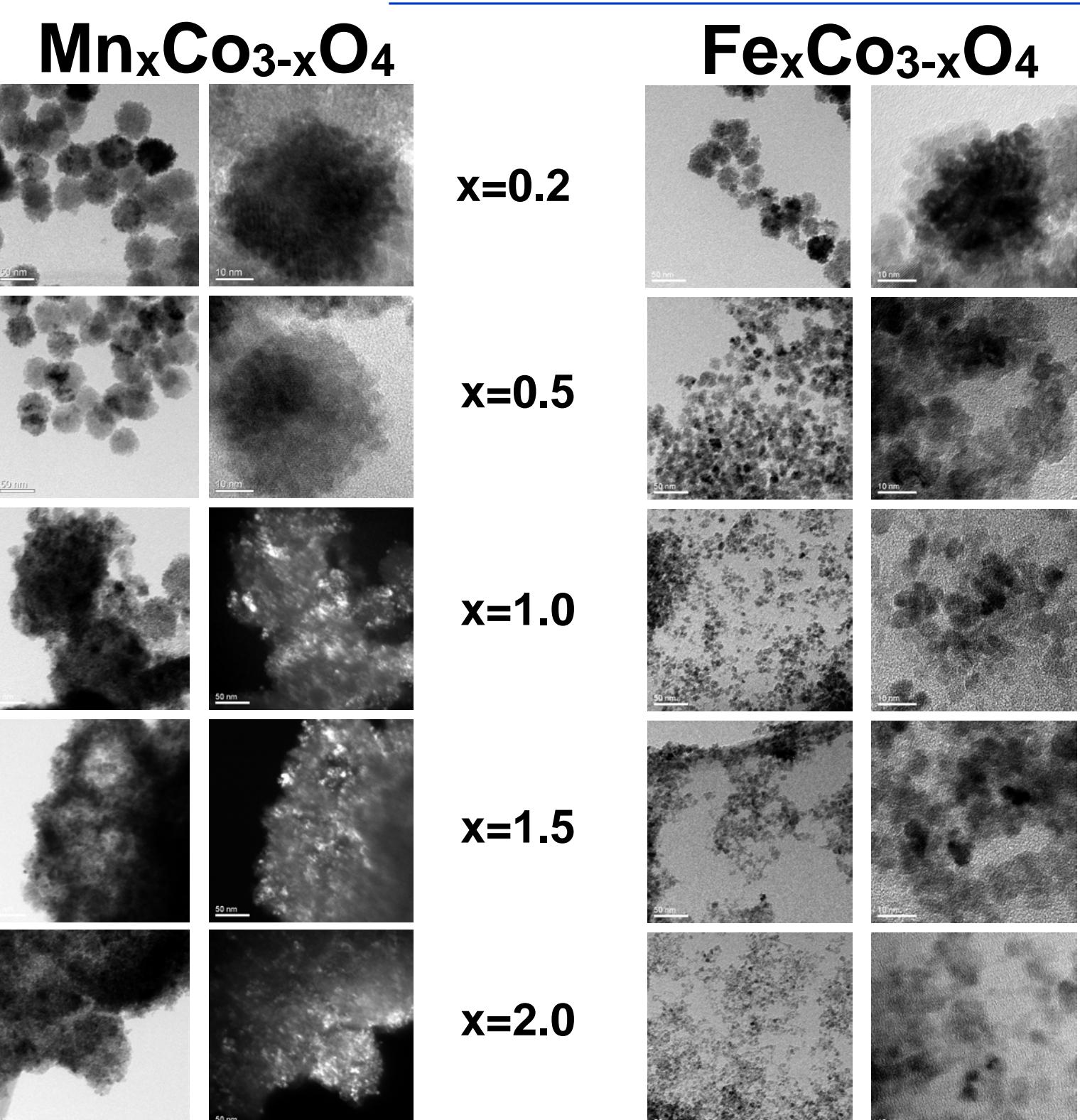
The particles were washed via repeated centrifugation, characterized with the following techniques, and tested as catalysts for oxygen reduction and as electrochemical capacitors.

## Powder X-Ray Diffraction (PXRD)



$Mn_xCo_{3-x}O_4$ — x=2, x=1.5, x=1, x=0.5, x=0.2, 00-043-1003> $Co_3O_4$ - Cobalt Oxide



$Fe_xCo_{3-x}O_4$ — x=2, x=1.5, x=1, x=0.5, x=0.2, $Co_3O_4$, 00-043-1003> $Co_3O_4$ - Cobalt Oxide

Powder x-ray diffraction of these materials reveals a slight shift of characteristic peaks to lower 2-Theta, indicative of Mn and Fe ion substitution into their respective crystallographic lattices. Initial investigations into dimensions of lattice parameters display trends which confirm an increase in doping. As the degree of doping (represented by the x-value) increases, the diffraction peaks broaden, which is indicative of decreasing particle size.

## Transmission Electron Microscopy (TEM)



$Mn_xCo_{3-x}O_4$ and $Fe_xCo_{3-x}O_4$; x=0.2, x=0.5, x=1.0, x=1.5, x=2.0

Images obtained by transmission electron spectroscopy reveal that particle morphologies change as the amount of cation insertion is varied.

At x ≤ 0.5, mesoporous clusters ~ 50 nm in size are observed. At x ≥ 1, clusters of smaller nanoparticles ranging from 2-5 nm are observed.
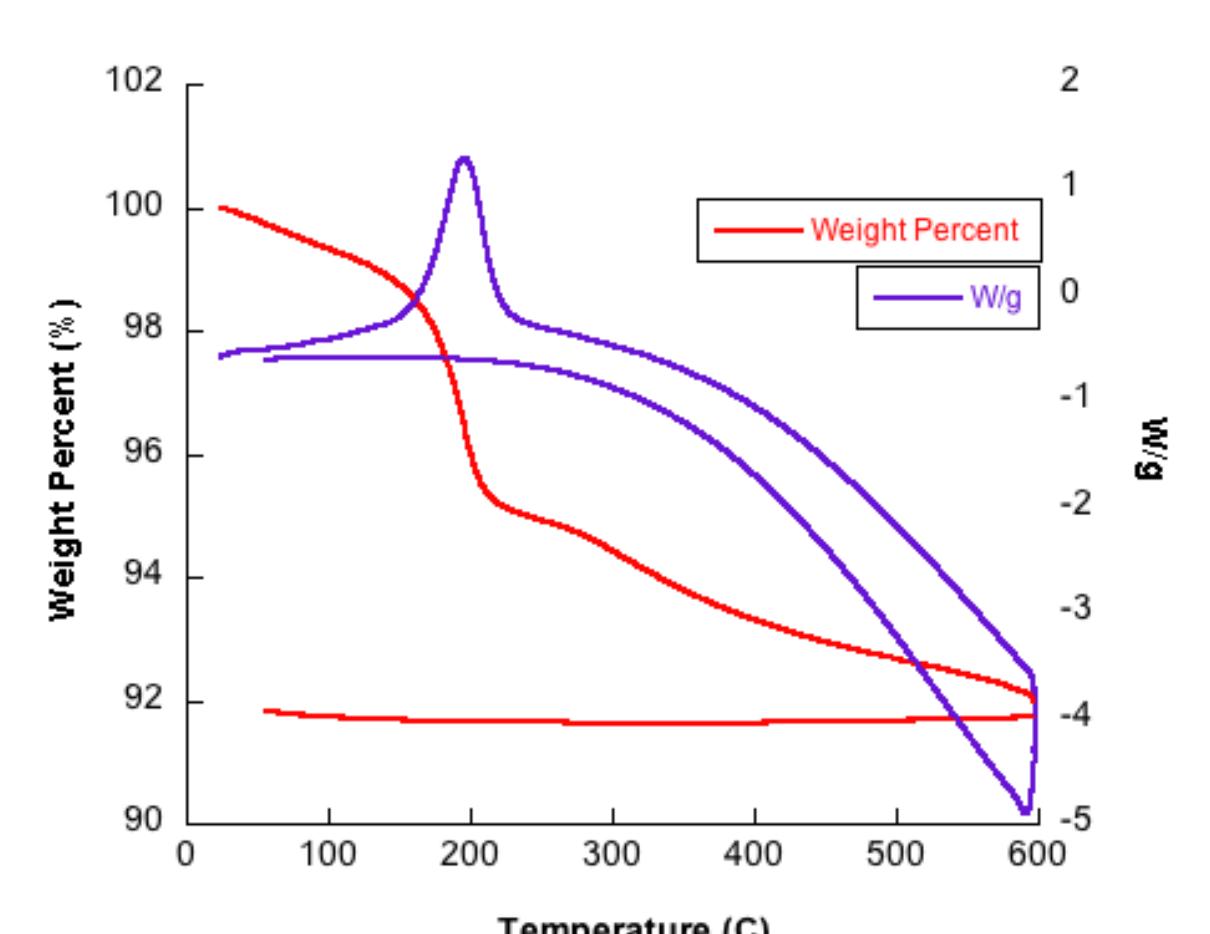
The fact that we observe smaller particle sizes as the degree of doping increases is consistent with the data from XRD – namely, the broadening of diffraction peaks indicates decreasing particle sizes.

## X-Ray Photoelectron Spectroscopy (XPS)

| x-value | Predicted Formula | Actual Formula |
|---|---|---|
| 0.2 | $Mn_{0.2}Co_{2.8}O_4$ | ~ $Co_3O_4$ |
| 0.5 | $Mn_{0.5}Co_{2.5}O_4$ | ~ $Co_3O_4$ |
| 1.0 | $MnCo_2O_4$ | $Mn_{0.6}Co_{2.4}O_4$ |
| 1.5 | $Mn_{1.5}Co_{1.5}O_4$ | $MnCo_2O_4$ |
| 2.0 | $Mn_2CoO_4$ | $Mn_{1.5}Co_{1.5}O_4$ |

XPS reveals that Mn-doping does not occur to the extent intended. Theoretical x-values of 0.2 and 0.5 result in negligible amounts of Mn in the composite. An x-value of 1 or greater does result in Mn-ion insertion, but always at a lower level (~ 60-75%) than attempted.
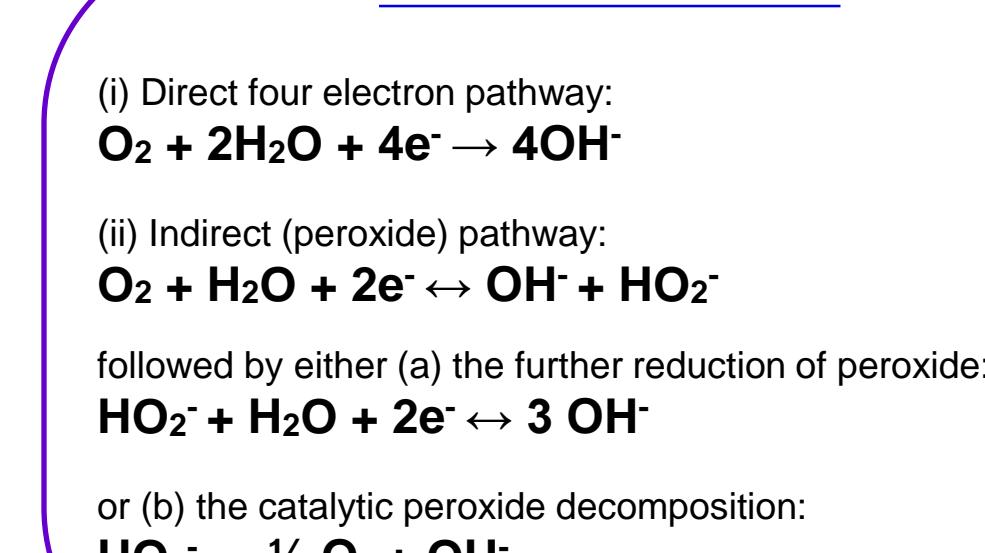
## Thermal Gravimetric Analysis (TGA)

In the TGA curve for $Mn_xCo_{3-x}O_4$ shown to the right, we observe an exothermic process occurring at ~200ºC. This is likely the ligand (related to the reaction solvent) being burned off. When the heating cycle is complete, approximately 8% of the material's mass has been lost, which we attribute to the removal of the surface ligands.



## Surface Area Analysis (BET)

| x-value | $Mn_xCo_{3-x}O_4$ | $Fe_xCo_{3-x}O_4$ |
|---|---|---|
| 0.2 | 39.6 m²/g | 92.9 m²/g |
| 0.5 | 46.8 m²/g | 143.8 m²/g |
| 1.0 | 51.3 m²/g | 65.4 m²/g |
| 1.5 | 67.8 m²/g | 182.6 m²/g |
| 2.0 | 51.2 m²/g | 260.7 m²/g |

# Electrochemical Application

## Air Cathode: Catalyst for the Oxidation Reduction Reaction

### Reaction Scheme

(i) Direct four electron pathway:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

(ii) Indirect (peroxide) pathway:
$O_2 + H_2O + 2e^- \leftrightarrow OH^- + HO_2^-$

followed by either (a) the further reduction of peroxide:
$HO_2^- + H_2O + 2e^- \leftrightarrow 3\ OH^-$

or (b) the catalytic peroxide decomposition:
$HO_2^- \rightarrow \frac{1}{2} O_2 + OH^-$

### Electrode Preparation, Testing, and Evaluation

Solutions of the activated catalyst in isopropanol with 5% Nafion were prepared and sonicated to achieve dispersion. A known volume of the material was deposited on a 5 mm diameter glassy carbon rotating disk electrode and allowed to dry, forming a thin film.
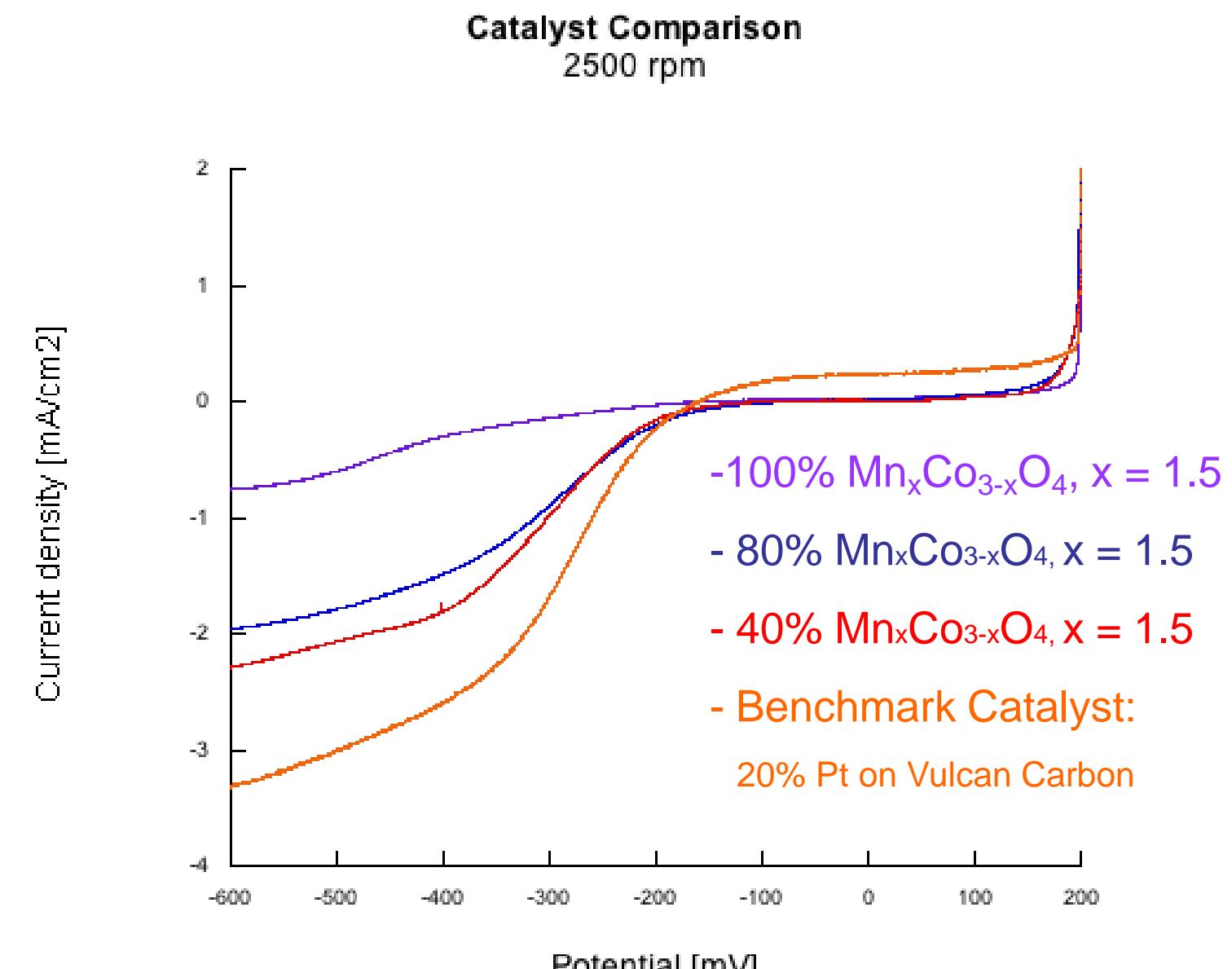
Catalyst testing was performed in 0.1M KOH solution that had been purged with oxygen or nitrogen. Current levels were monitored at various electrode rotation rates.

Once the most active catalyst had been identified, further tests were conducted with varied amounts of Vulcan Carbon, which was added to further enhance the conductivity and overall currents.



$Mn_xCo_{3-x}O_4$ 2500 rpm

X = 0.2
X = 0.5
X = 1.5
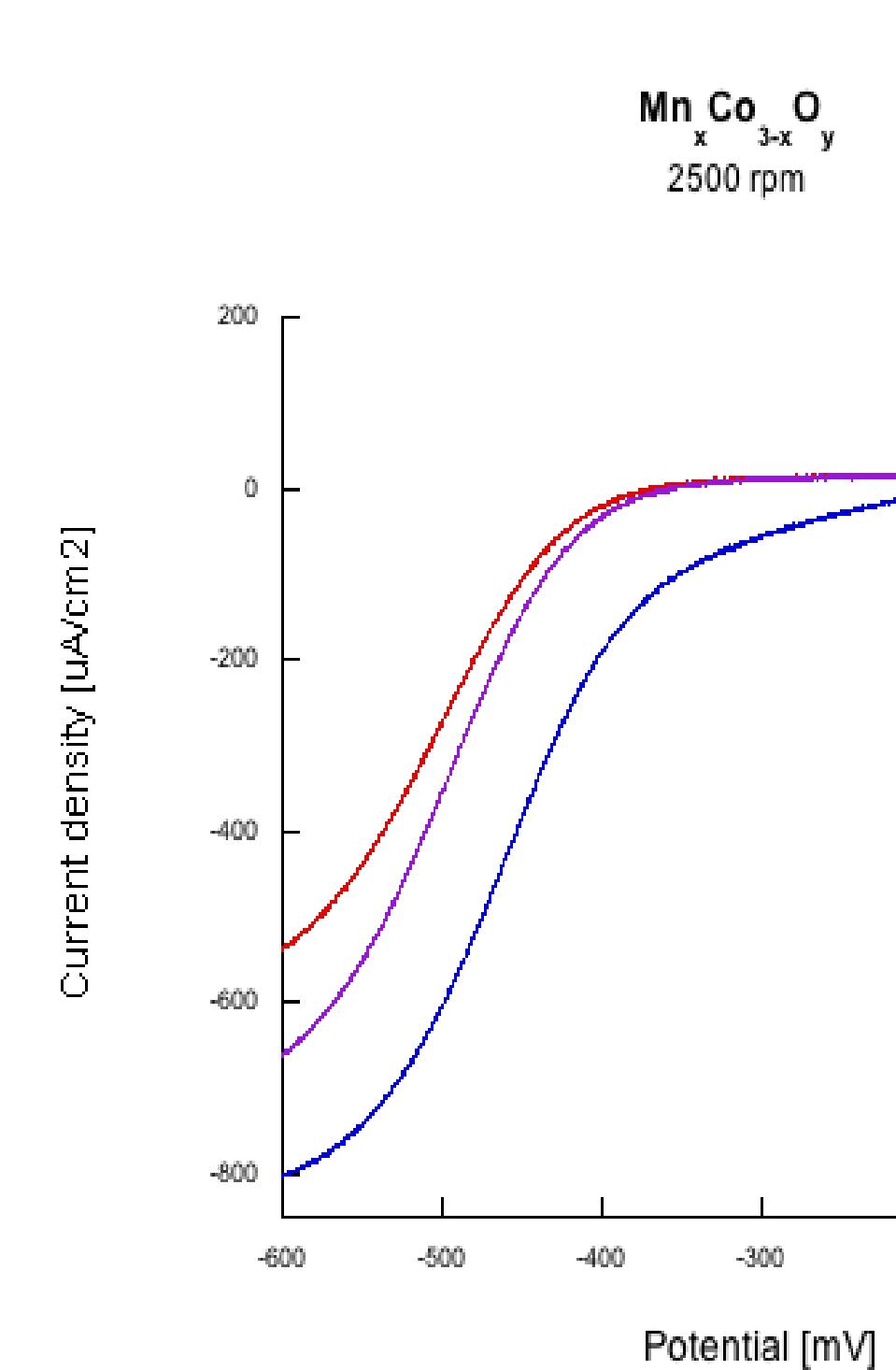
Preliminary tests for $Mn_xCo_{3-x}O_4$ nanoparticles revealed that the theoretical substitution of x=1.5 was the most catalytically active.



Catalyst Comparison 2500 rpm

- 100% $Mn_xCo_{3-x}O_4$, x = 1.5
- 80% $Mn_xCo_{3-x}O_4$, x = 1.5
- 40% $Mn_xCo_{3-x}O_4$, x = 1.5
- Benchmark Catalyst: 20% Pt on Vulcan Carbon

Once the most catalytically active material had been identified, we attempted to optimize the system by blending the ceramic material with Vulcan Carbon to further enhance the conductivity and overall currents. It appears as though a blend of 40% $Mn_xCo_{3-x}O_4$ achieves the highest current level. Also shown in this graph is the data for the benchmark catalyst, 20% Pt on Vulcan Carbon.

# Conclusions

We have demonstrated a low-temperature solution synthesis for spinel, mixed transition metal oxides $Mn_xCo_{3-x}O_4$ and $Fe_xCo_{3-x}O_4$ that possess high surface areas.

In addition, we have characterized these materials and investigated their potential as catalysts for the oxygen reduction reaction.

Preliminary catalysis results are encouraging - our materials are not only catalytically active, but might also be a more economically viable alternative to Pt on Carbon.

## Future Work

- Continue to improve blends of the ceramic material with carbon to achieve optimal current levels, onset potentials, and electron transfer.
- Determine if these materials could be utilized in the context of electrochemical capacitors via cyclic voltammetry and galvanic charge-discharge experiments.
- Expand catalysis studies to include $Fe_xCo_{3-x}O_4$, which should be ideal for the process of oxygen evolution.
- Gain a more comprehensive understanding of the ion substitution mechanism.