# Interactions of Silicon in Metallic Interconnect Materials with Perovskite Protective Coatings

*SECA Core Technology Meeting*
*Denver, Colorado*
*October 25-26, 2005*
*Presented by Christopher Johnson*

# Outline

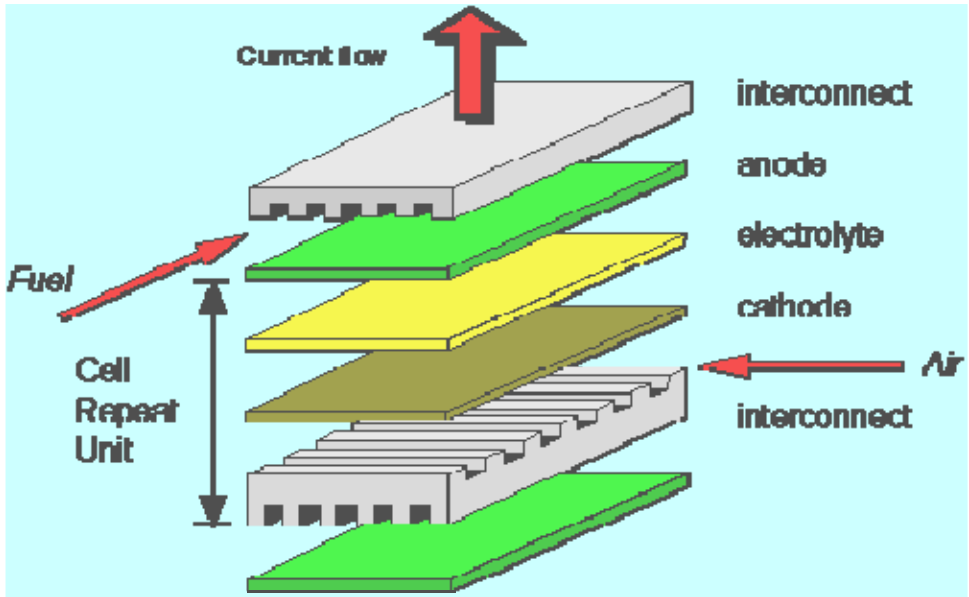
- **Effects of silicon impurities on the performance of coated metallic interconnects**
  - Background
  - What lead us to look into this issue.
  - Some initial results (ASR and SEM)
- **Electro-deposition of interconnect coatings**
  - Plans and initial results
- **Goals and plans of coal syngas work**

# Interconnects for Planar SOFCs

**Interconnect Function-** electrically connect the cells in a stack, provide separation and flow control of gases, and provides mechanical stability.

**Interconnect Requirements**:

- Gas impervious
- Electrically conducting
- Stable in both oxidizing and reducing atmospheres
- CTE
- Non-reactive
- High thermal conductivity
- Good strength
- Low cost




- **$Cr_2O_3$ layer continues to grow - increases resistance.**
- **Migration of Cr within the stack contaminates the SOFCs.**

# Technical Approach

A conductive and protective coating seemed like the best option given what we knew, from our own work and from reviewing literature reports, about the effects of chromia on cell performance.

**Coating Techniques**

1) magnetron sputtering deposition (test coating possibilities)
2) low cost technique (electrodeposition of alloys or multilayers, or electrophoretic deposition)

**Substrates**

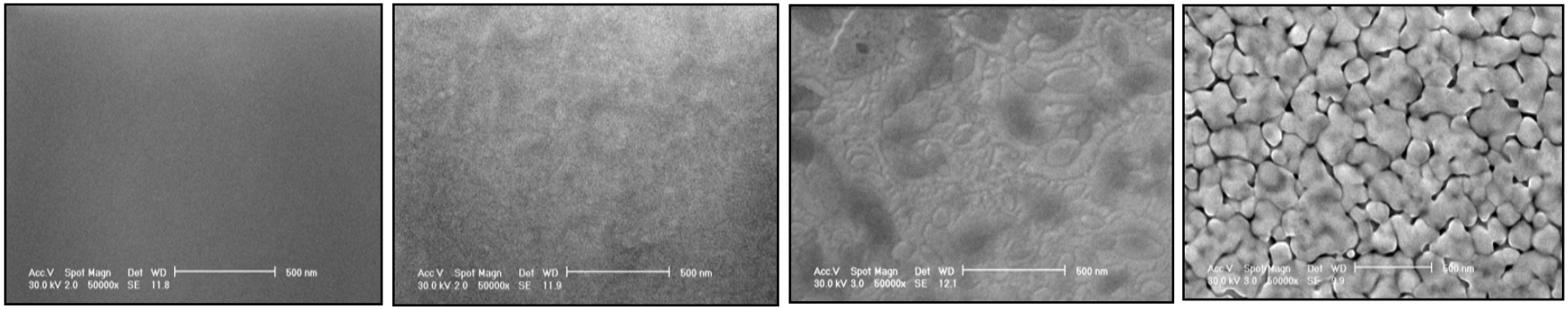
1) Stainless 446  CTE=11μm/m-°C
2) CROFER APU22 CTE=11μm/m-°C

**Conductive oxides**

**$LaCrO_3$**
**$La_{0.9}Ca_{0.1}CrO_3$**
**$La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$**
**$La_{0.7}Sr_{0.3}Cr_{0.9}O_3$**
**MnCo Spinel**

# Background

The sputtered films were amorphous as deposited and slightly substoichiometric in O, but upon heating in air transform first to $LaCrO_4$ and then subsequently to $LaCrO_3$. Doing the initial crystallization in $H_2/N_2$ avoids the $LaCrO_4$ phase.

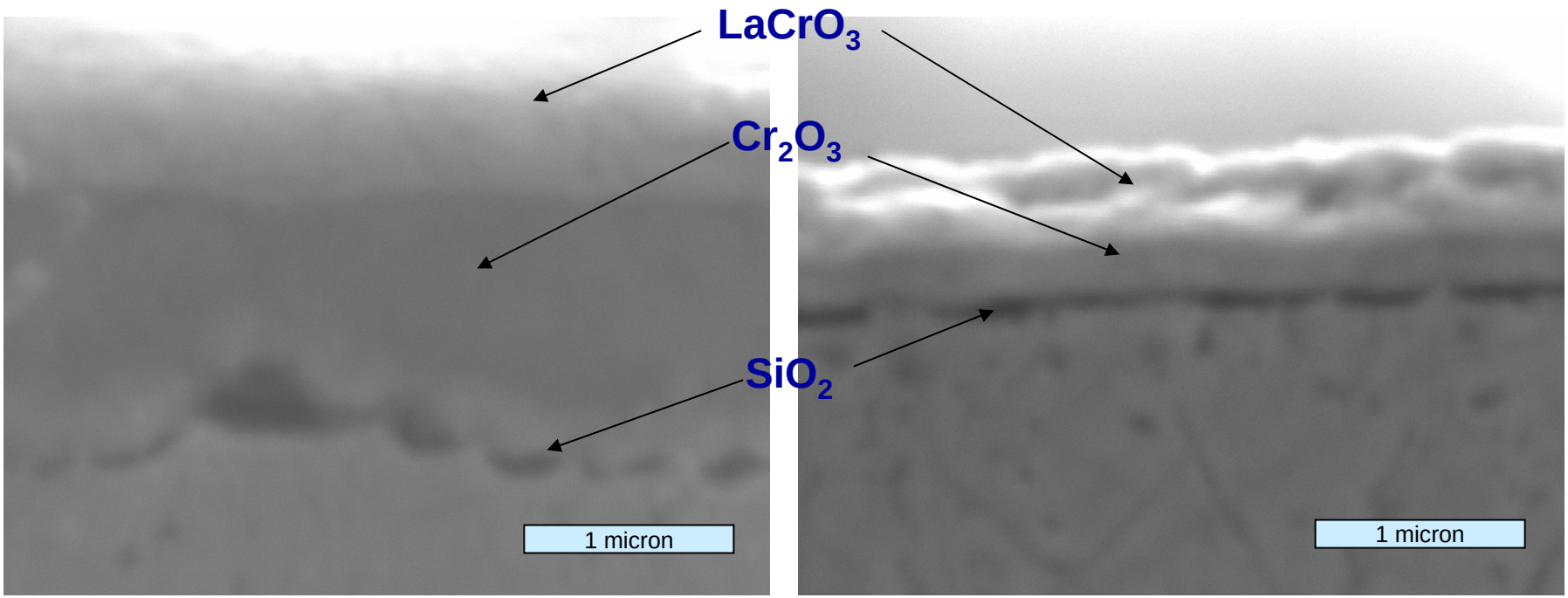


**ASR values of sputtered $LaCrO_3$ and Ca doped $LaCrO_3$ on SS446 substrates with different initial crystallization environments**

| **Initial treatment** | La0.9Ca0.1Cr03 Air 800C | La0.9Ca0.1Cr03 Forming gas 800C | LaCr03 air 800ºC | LaCrO3 Forming gas 800C |
|---|---|---|---|---|
| After formation | 0.011 Ω•cm2 | 0.014 Ω•cm2 | 0.044 Ω•cm2 | 0.013 Ω•cm2 |
| Additional 100 hours At 800ºC in Air | 0.036 Ω•cm2 | 0.44 Ω•cm2 | 0.108 Ω•cm2 | 0.21 Ω•cm2 |

# Sputtered $LaCrO_3$ coatings on SS446

Crystallization occurring in air at 800C  Crystallization occurring in $H_2/N_2$ at 800C




Each film was exposed to 100hrs in air at 800C after the initial crystallization treatment. The composition of the layers was confirmed by EDS analysis.

Note that the LaCrO3 coating annealed initially in H2/N2 showed improved resistance to oxidation. However, The SiO2 layer becomes more continuous.

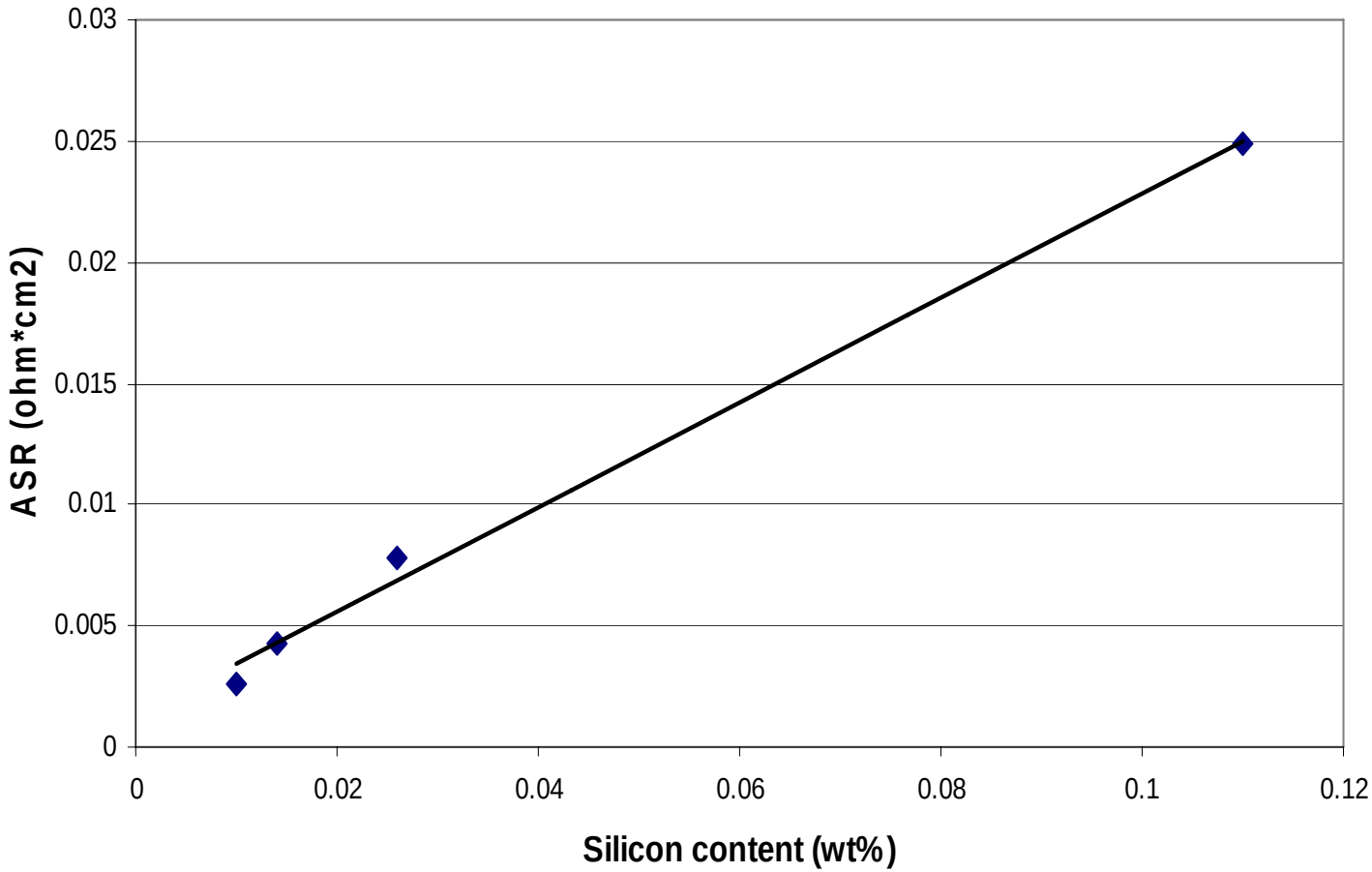
# Crofer APU22 Substrate Compositions and coating compositions

| batch | Chemical Composition (wt%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Fe | Cr | Mn | Ti | La | Si | Al | Ni | C | S | N | O |
| JGP | Bal. | 22.5 | 0.4 | 0.08 | 0.07 | 0.11 | 0.12 | 0.16 | 0.006 | 0.003 | 0.012 | 0.005 |
| JXW | Bal. | 22.6 | 0.4 | 0.048 | 0.065 | <0.01 | <0.01 | <0.002 | 0.004 | <0.001 | <0.0005 | 0.0044 |
| JZF | Bal. | 22.2 | 0.46 | 0.055 | 0.07 | 0.026 | 0.022 | 0.016 | 0.019 | <0.001 | 0.0073 | 0.0034 |
| KCB | Bal | 22.2 | 0.45 | 0.065 | 0.096 | 0.014 | 0.011 | 0.022 | 0.017 | 0.002 | 0.0023 | 0.01 |

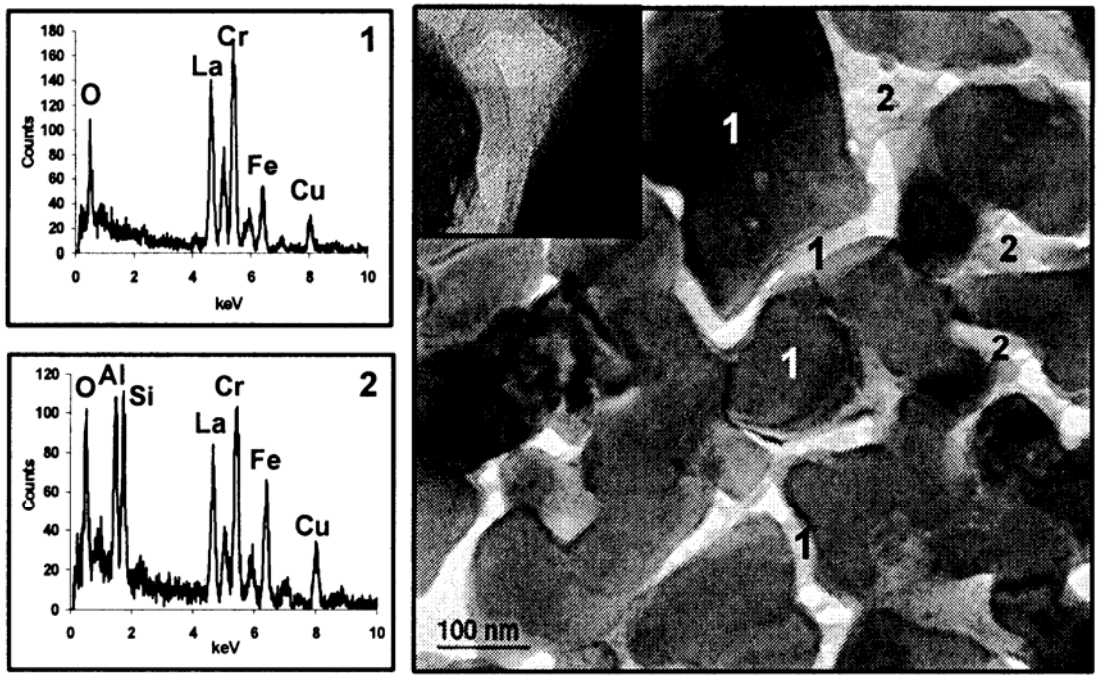
$LaCrO_3$, $La_{0.7}Sr_{0.3}Cr_{0.9}O_3$, $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$

The substrates have variable silicon and aluminum content and the coatings have different ionic and electronic conductivities

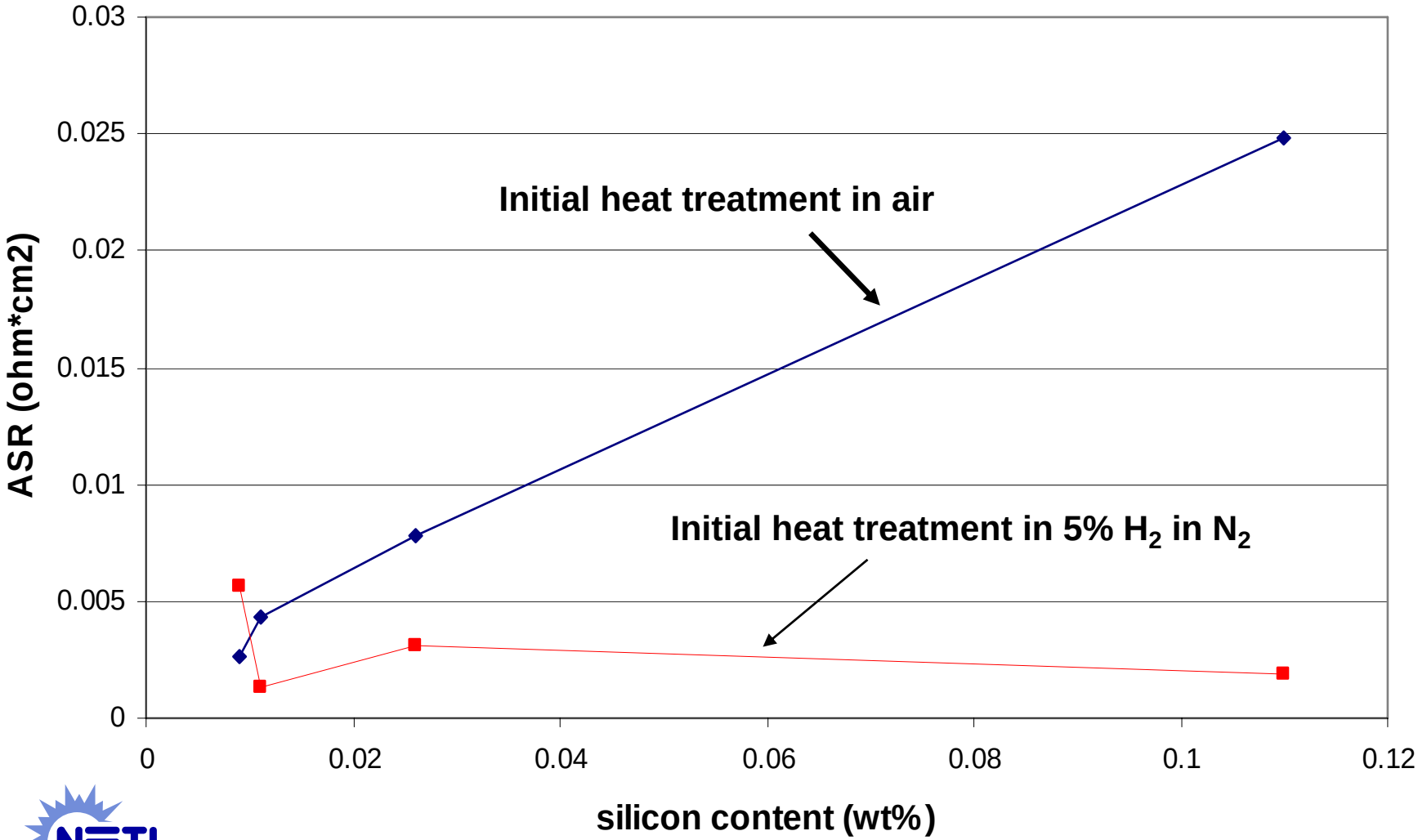
# Area Specific Resistance of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}CrO_3$ sputter coated film on Crofer substrates with varying silicon content (heated to 900C in air)



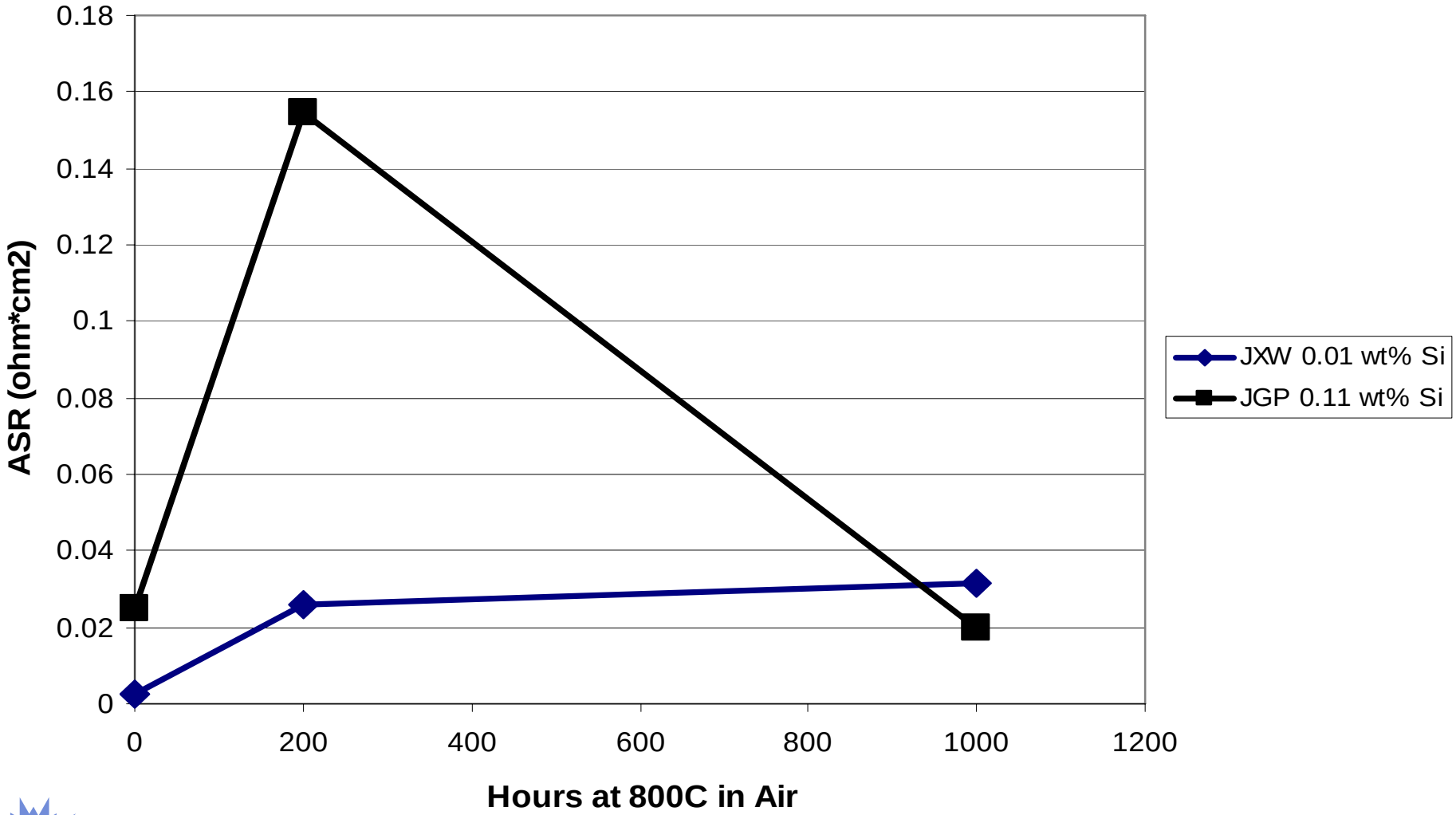
# TEM and EDS analysis of amorphous grain boundary phase



# Area Specific Resistance of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}CrO_3$ sputter coated film on Crofer substrates with varying silicon content

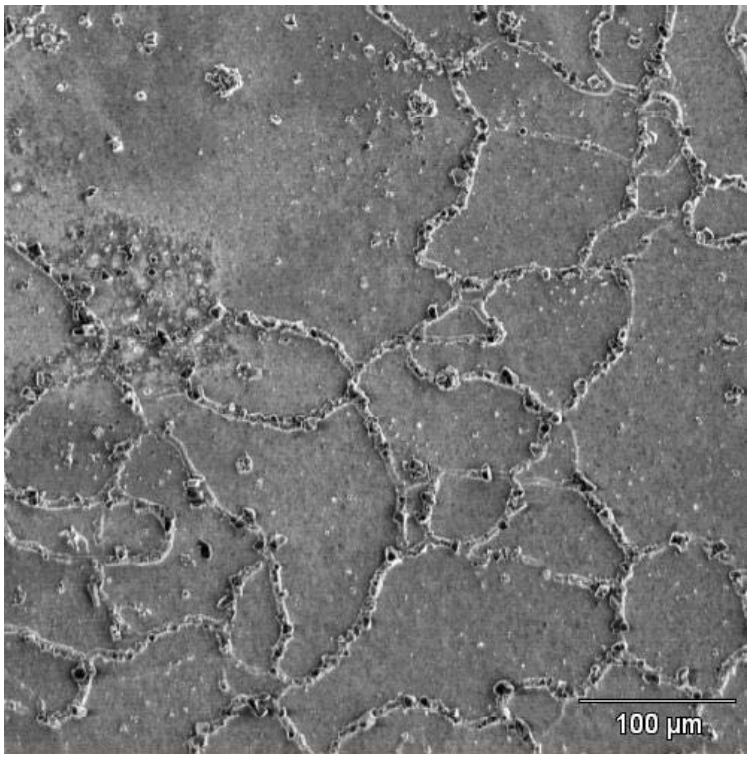


# ASR as a funtion of time at 800C in air for $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}CrO_3$ (initial heat treatment in air) sputter coated film on Crofer alloy substrates with different silicon contents

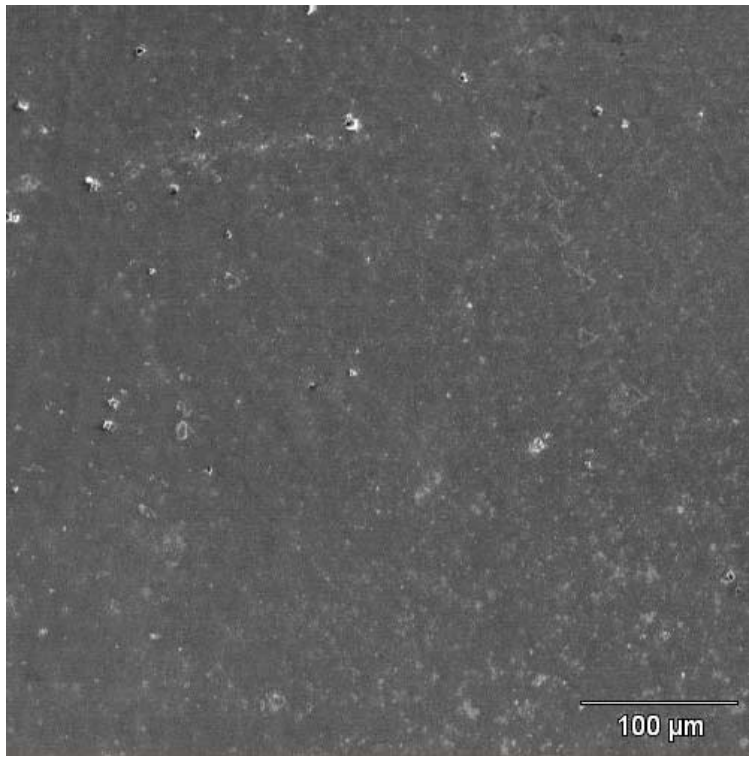


# SEM images of $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}CrO_3$ sputtered coatings after 1000 hrs at 800C

**JGP 0.11 wt% Si**




**JXW 0.01 wt% Si**



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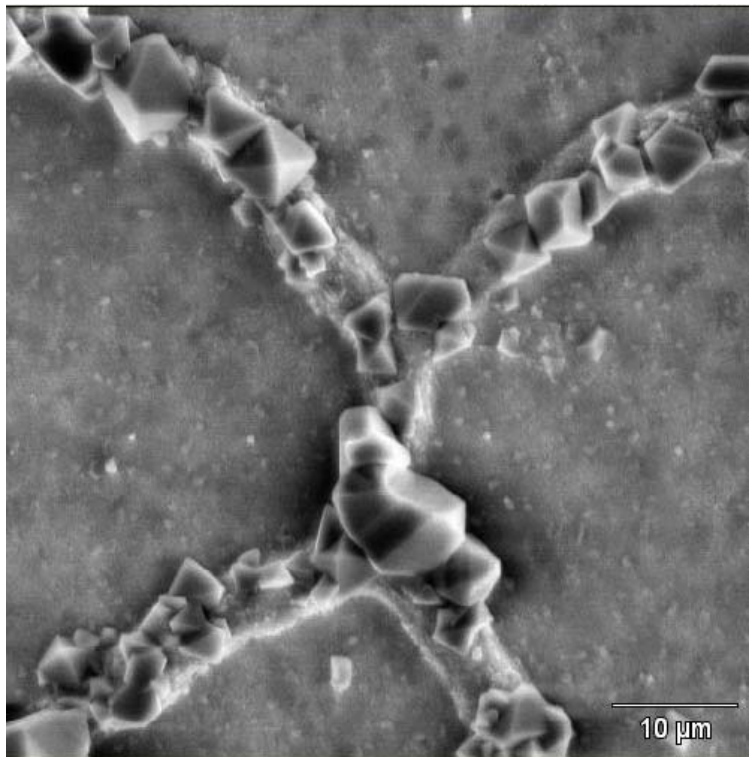


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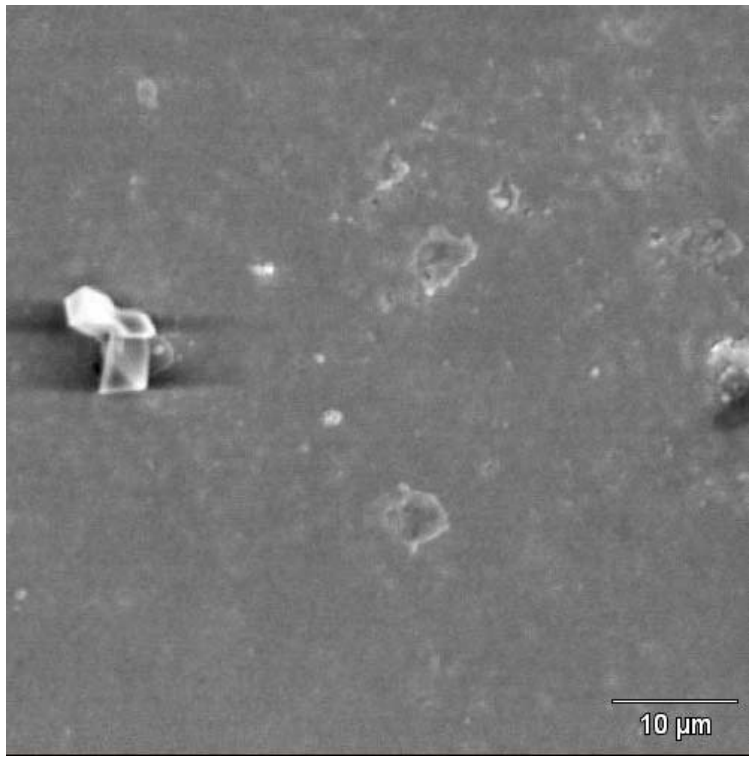



EDS analysis indicates that the surface crystallites are MnCr spinel

# Summary silicon content work

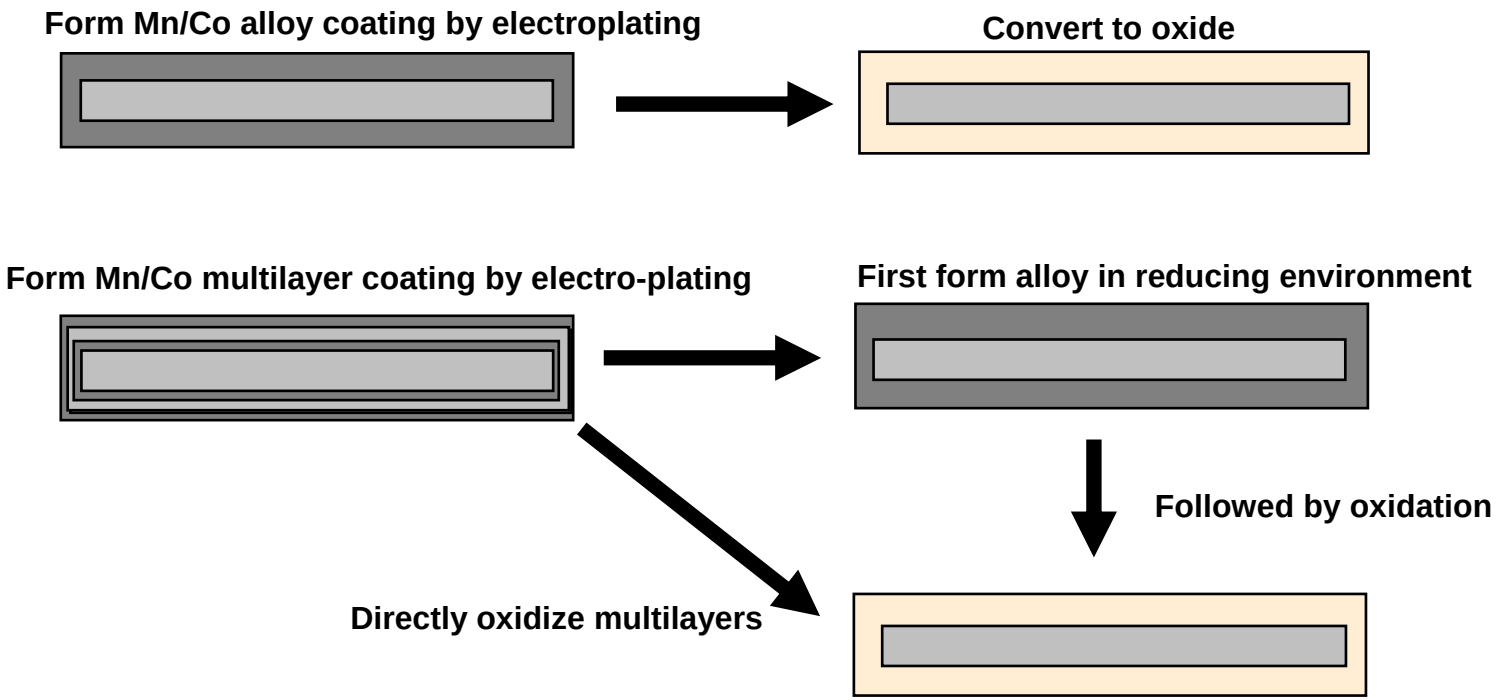
**The work needs to be completed.**

- Obtain cross sectional SEM images of the $La_{0.7}Sr_{0.3}Cr_{0.9}Co_{0.1}O_3$ samples initially treated in air and in $H_2/N_2$ after 1000 hours at 800C in air.
  - Determine if silica layers are continuous
  - Investigate the formation of substrate grain boundary phases
- Compare with $LaCrO_3$ and $La_{0.7}Sr_{0.3}Cr_{0.9}O_3$ sputtered coatings and possibly MnCo spinel

**Determine the acceptable level of silicon impurities allowable for interconnect substrates coated with dense films.**

# Electroplating of Alloys as Precursors for Oxide Protective Layers

## Targeting MnCo spinel formation




**This technique should be useful for coating complex geometries.**
**It should also be adaptable to many compositions.**

# Mn and Co Alloy deposition

- **For alloy deposition the deposition potentials for the metals must be close**
- **E° for $Mn^{2+}$ to Mn(s) is -1.18, E° for $Co^{2+}$ to Co(s) is -0.277**
  - Using the Nernst equation and assuming dilute solutions. The difference in concentration between $Mn^{2+}$ and $Co^{2+}$ would need to be 30 Orders of magnitude different.

$$E = E^\circ + \frac{RT}{\nu F} \ln a$$

E=deposition potential, E°= standard reduction potential, R = ideal gas constant, T= temperature, $\nu$= # of electrons, F= Faradays constant, a= activity

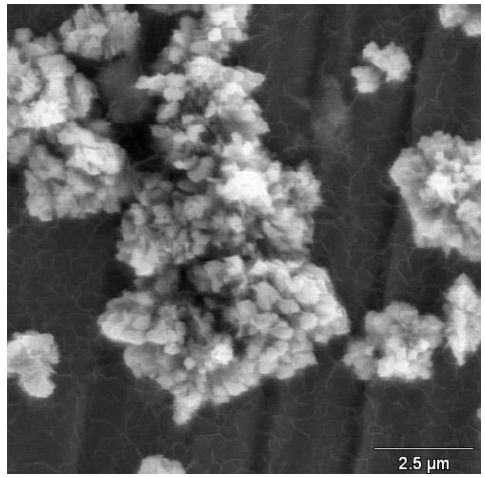
**For 0.01M $Mn^{2+}$ a concentration of $1x10^{-32}$M $Co^{2+}$ is required to have a similar deposition potential.**

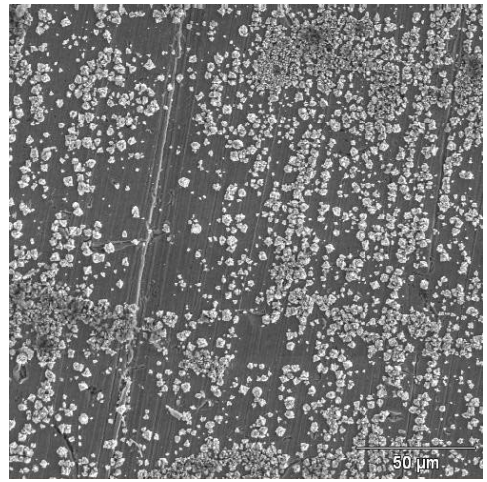
# Mn and Co Alloy deposition

- **0.008M $CoSO_4$, 0.008M EDTA, 0.075M Saccharin, 0.032M $MnSO_4$**
  - EDTA was added to the $CoSO_4$ solution and heated to achieve chelation
- **pH was varied over a range from 1-9.**
- **Current densities of 50mA/cm$^2$ and 100mA/cm$^2$ were used**
- **Platinum counter electrodes**
- **Substrates (CROFER APU22) where sanded with 600 grit sandpaper and cleaned ultrasonically in ethanol**
- **50°C**

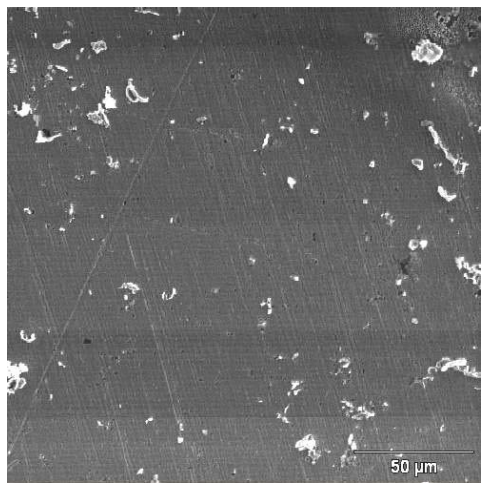
# Effect of Saccharin addition on Co morphology

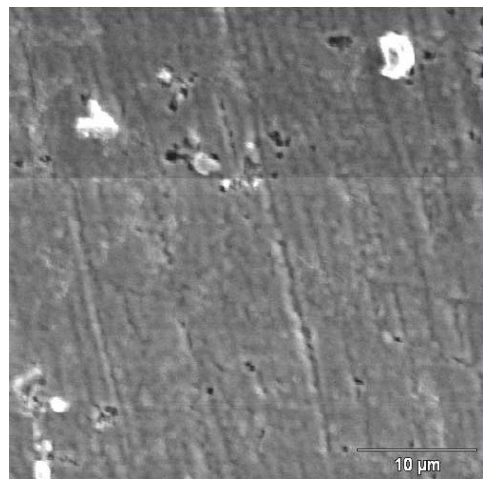
**Simple electroplating of Co**



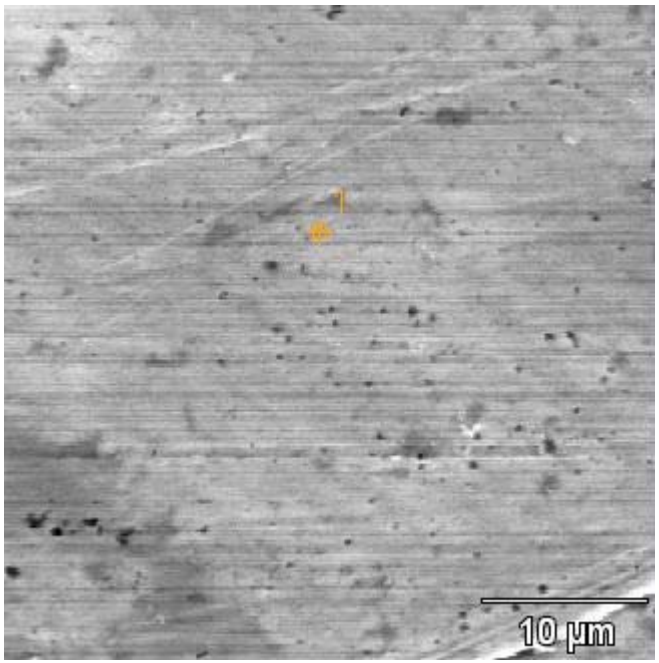

**Electro-plating of Co with Saccharin addition 0.025M**



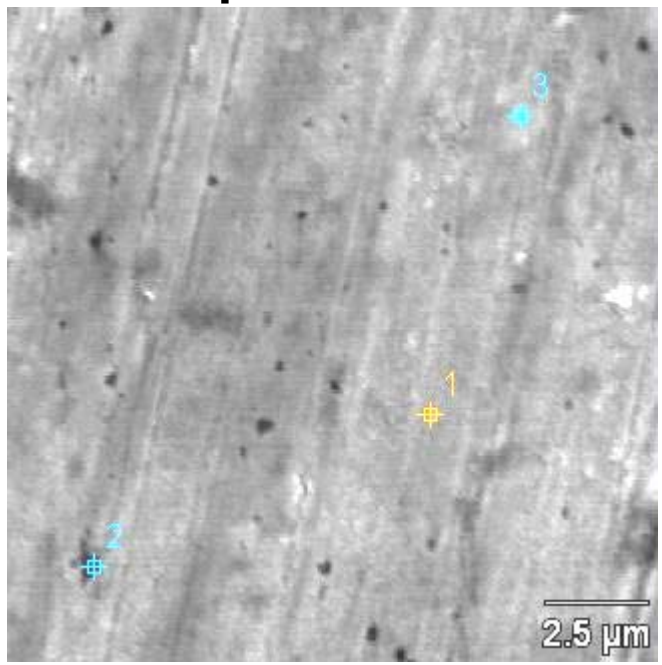
# Deposition from Co2+ and Mn2+ solutions with Saccharin and EDTA additions

**pH 1.04-6.35**




**EDS shows only Co deposition**

**pH of 8.3**




**EDS shows an approximately 47/53 Mn/Co ratio**

At pH=9.26 solid formation in solution occurred

# Possible effect of pH

- LogK for $Mn^{2+}+2H_2O \rightarrow HMnO_2^- +3H^+$ is -32.6529 **50°C**

$HMnO2^- + 3H+ + 2e^- \rightarrow Mn(s)+2H2O$ E°=-0.163

$$K = \frac{[HMnO_2^-][H^+]^3}{[Mn^{2+}]} = 1.6X10^{-32}$$

$$K = \frac{[HMnO_2^-][5X10^{-9}]^3}{[0.032]} = 1.6X10^{-32}$$

**$[HMnO2^-]=4.1E10^{-10}$**

**Using the Nernst equation to calculate the deposition potential at that concentration, then gives -0.43865V for deposition of Manganese from $HMnO_2^-$.**

# Coal Syngas with Solid Oxide Fuel Cells

The combination of coal syngas and solid oxide fuel cells represents an economical, efficient power source for future power generation.
However there are many questions regarding these systems.

**Questions**

- What problems may be associated with the use of coal syn-gas in SOFCs?
  - Coal syngas composition-high CO levels
  - Coal syngas contaminants-what clean up is necessary?
  - Particulate matter
  - BOP/Interconnects
  - To be determined

| Contaminant | Concentration (ppmv) |
|---|---|
| $Fe(CO)_5$ | 0.05-6.0 |
| $Ni(CO)_4$ | 0.01-1.0 |
| Sb | 0.03-1.0 |
| Cd | 0.01-0.2 |
| Be | 0.03-2.3 |
| Cr | 0.03-6.0 |
| K | 0-550 |
| Se | 0.15-1.0 |
| Na | 0-300 |
| Pb | 0.25-3.0 |
| Zn | 0-100 |

# Coal Syn Gas with Solid Oxide Fuel Cells

## Current Research Activities

**Baseline Operations (FY06-FY07)**

- SOFC operation on various gasified coal compositions is being completed

**Coal Contaminant Issues (FY06-FY07)**

- Major coal syn gas contaminants ($H_2S$ and Cl) are being tested.
- Thermodynamic evaluation of trace coal syn gas contaminants are being completed.

## Future Research Activities

**Trace Contaminant Testing (FY07-FY08)**

Test trace coal syn gas contaminants that may be detrimental to SOFC operation based on thermodynamic analysis.

**Anode Development (FY08-FY09)**

Develop SOFC anodes better suited for operation with coal syn gas that will reduce the clean up processing needed.

**Long Term Testing (FY10)**

Complete 8000hr SOFC stack test with coal syn gas.

# Conclusions

- **Si (or other impurities) can affect the ASR for coated ferritic interconnect materials.**
  - Substrate impurity levels, coating thickness, specific synthesis routes, or coating composition may play a role in this interaction
- **Mn/Co electrodeposited alloys can be obtained from complexed Co and Mn sulphate solutions. Solution pH plays a role in allowing the deposition of Mn.**

# Future Work

- Investigate the mechanism of MnCr spinel formation at coated metallic interconnect substrate grain boundaries
- Complete cross-sectional SEM analysis of perovskite coated samples
- Optimize the Mn/Co alloy deposition
- Oxidize the films to get the MnCo spinel
- Test coated samples on cells
- Base-line coal syngas tests

## Acknowledgments

**Dr Nina Orlovskaya and Anthony Coratollo, Drexel University**

**Dr Randy Gemmen, Chad Schaeffer, Caleb Cross, Heidi Barron, National Energy Technology Laboratory**