Surface-Modified Ferritic Interconnect Materials for Solid Oxide Fuel Cells

B. Lanning, J. Arps, and R. Wei
Southwest Research Institute

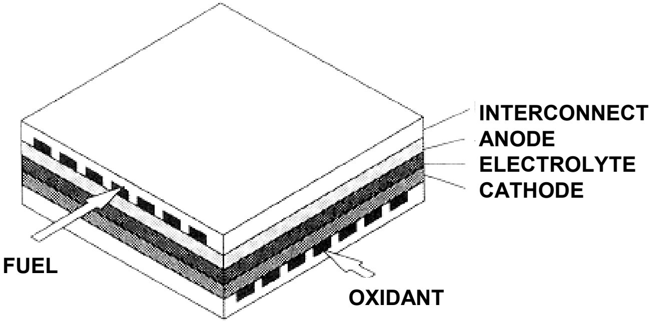
Sponsor: DOE Project # DE-FC26-02NT41579
TPOC: Dr. Lane Wilson

SECA Core Technology Workshop
February 19-20, 2003

Technical Issues Addressed

Background/Need

- As the trend in planar SOFC development is driven to lower temperatures (i.e., <800^{o} C), oxidation resistance metal alloys become feasible as candidate interconnect materials



- In comparison to ceramic materials, high-temperature metal alloys would:
  - Reduce stack costs (cheaper materials, formability)
  - Enhance mechanical integrity/fracture toughness of stack
- Ferritic stainless steels (~ 20% Cr) represent a class of metal alloys that form conductive oxide scales with thermal expansion characteristics that are well matched to their ceramic counterparts

Issues

Traditional ferritic stainless steels (i.e., 430, E-brite) form chromium oxide scales that:

1. Continue to grow at high temperatures ⇨ spallation, and
2. Do not prevent interdiffusion of cations (i.e., Cr out and Co in)

Ultimately leading to degraded fuel cell performance

R&D Objectives/Challenges

- Engineer surface oxide scale on a ferritic stainless steel that is:
  - Stable (i.e., mechanically and chemically) at 800° C in oxidizing/reducing environments, and
  - Electrically conductive (minimize stack IR losses)

- Develop/implement processes that are inherently scaleable for manufacturing

- Demonstrate stability/electrical conductivity of interconnect for extended time (> 1000 hours) at 800° C in contact with cathode materials $((La_{0.8}Sr_{0.2})FeO_3$ and $(La_{0.6}Sr_{0.4})(Fe_{0.8}Co_{0.2})O_3)$

Technical Approach

Formation of Stable Oxide

- **Basis:** Additions of Al and Y in a FeCrAlY alloy have been shown to stabilize oxide (Nuclear Industry (UK) and bond coat for TBC in turbine blades)
  - 4-5% aluminum; formation of stable scale,
  - ~1% yttrium improves resistance to spallation; (promotes thinner oxide, reduces cation diffusion along g.b.)

- **Approach:** Development of stable thermal oxide (> 850° C) on FeCrAlY alloy

- **Issue: Poor electrical conductivity**

Implantation of electronic carriers

- **Basis*:** Lead implanted polycrystalline alumina, niobium implanted α-alumina, and iron implanted MgO crystals have all shown to increase electrical conductivities

  (*See for example: Romana et al, “Phase Formation Study in α-Al_2O_3 Implanted with Niobium Ions”, Nuc. Instr. & Meth. In Phys. Res., B46 (1990), p. 94)

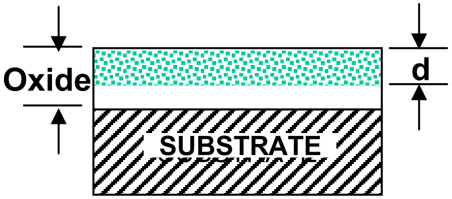
- **Approach:** Implant ions (i.e., Nb, Ti, and Y) at dosages of a few a/o at a depth of 100 – 150 nm to increase electrical conductivity

- **Issue: Matching penetration depth (concentration) to formation of stable oxide**

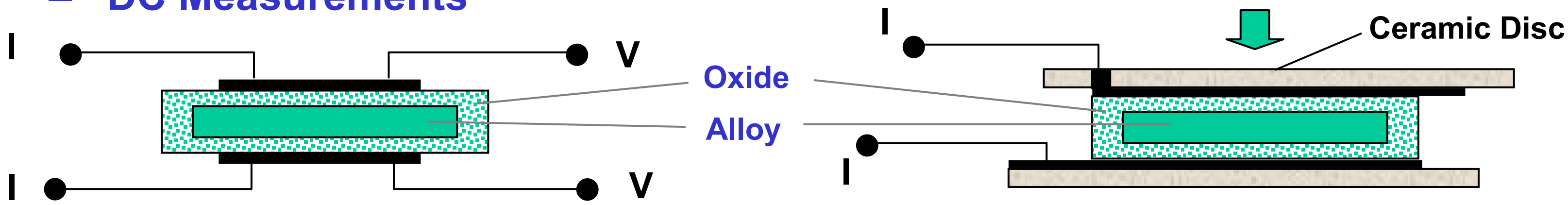
Experimental Approach

- **Ion Implantation depth, d, is held constant while varying the thickness of the thermally grown oxide (>850° C)**

	Oxide Thickness			
Ion Type	**0**	**d***	**2d***	**4d***
Nb+	x	x	x	x
Ti+	x	x	x	x
Y+	x	x	x	x

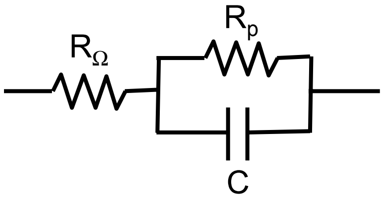


- **Area Specific Resistance (ASR) Measurement as f(temperature)**
  - **DC Measurements**



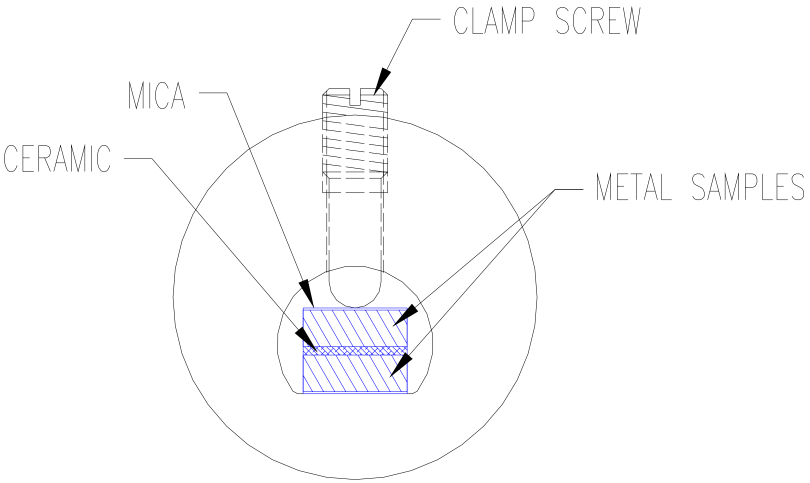
Cured Pt Paste **Mechanical Contact**

  - **AC Impedance Measurements** (equivalent circuit)



Experimental Approach

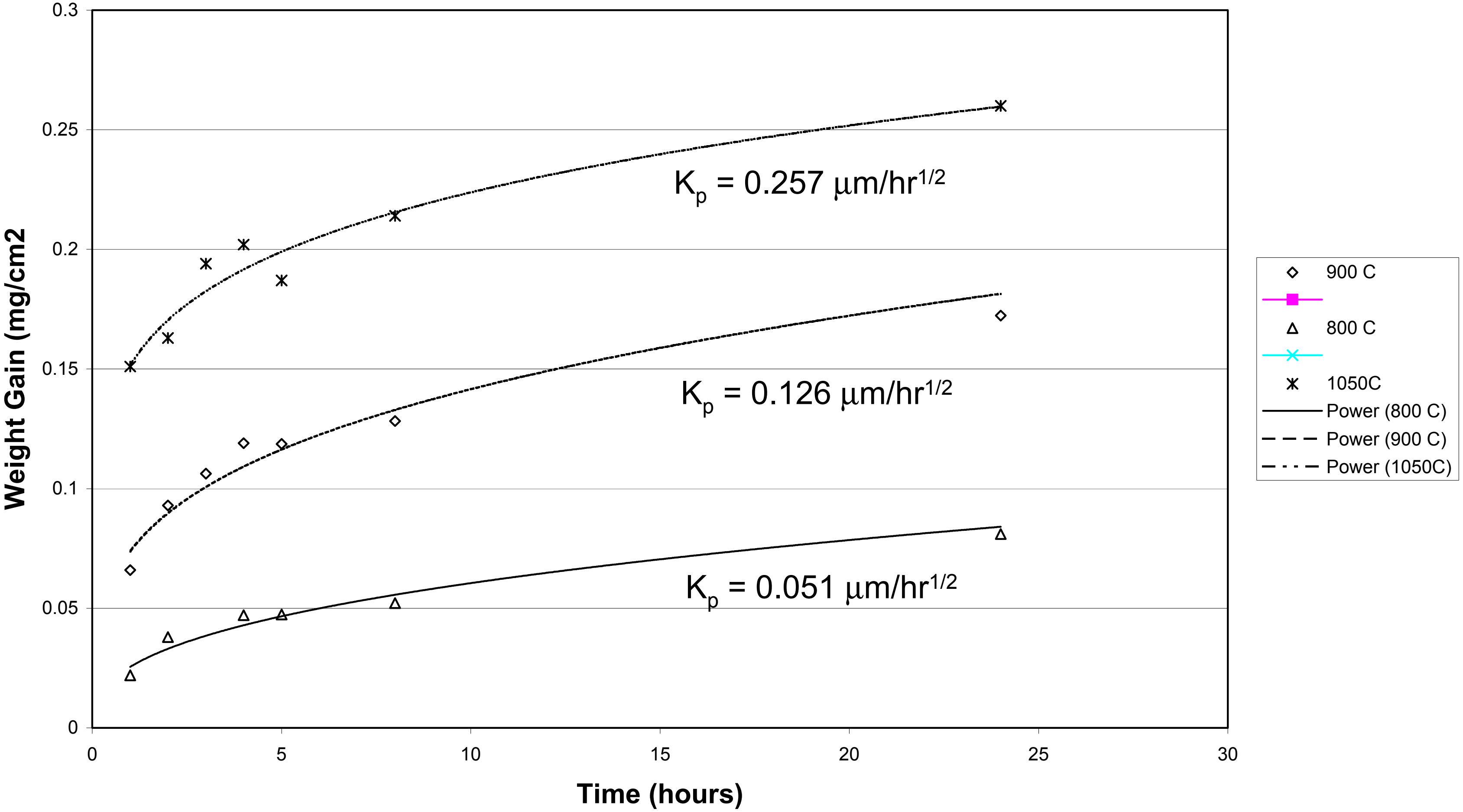
- **Interdiffusion Couple Experiment**
  - **Thick, monolithic interconnect/electrode materials under load**
  - **Pre-load compensated at temperature with thermal expansion differences**
  - **Sample size: ~1 cm x 1cm**



- **Verify stability of electrode/interconnect interface at temperature**

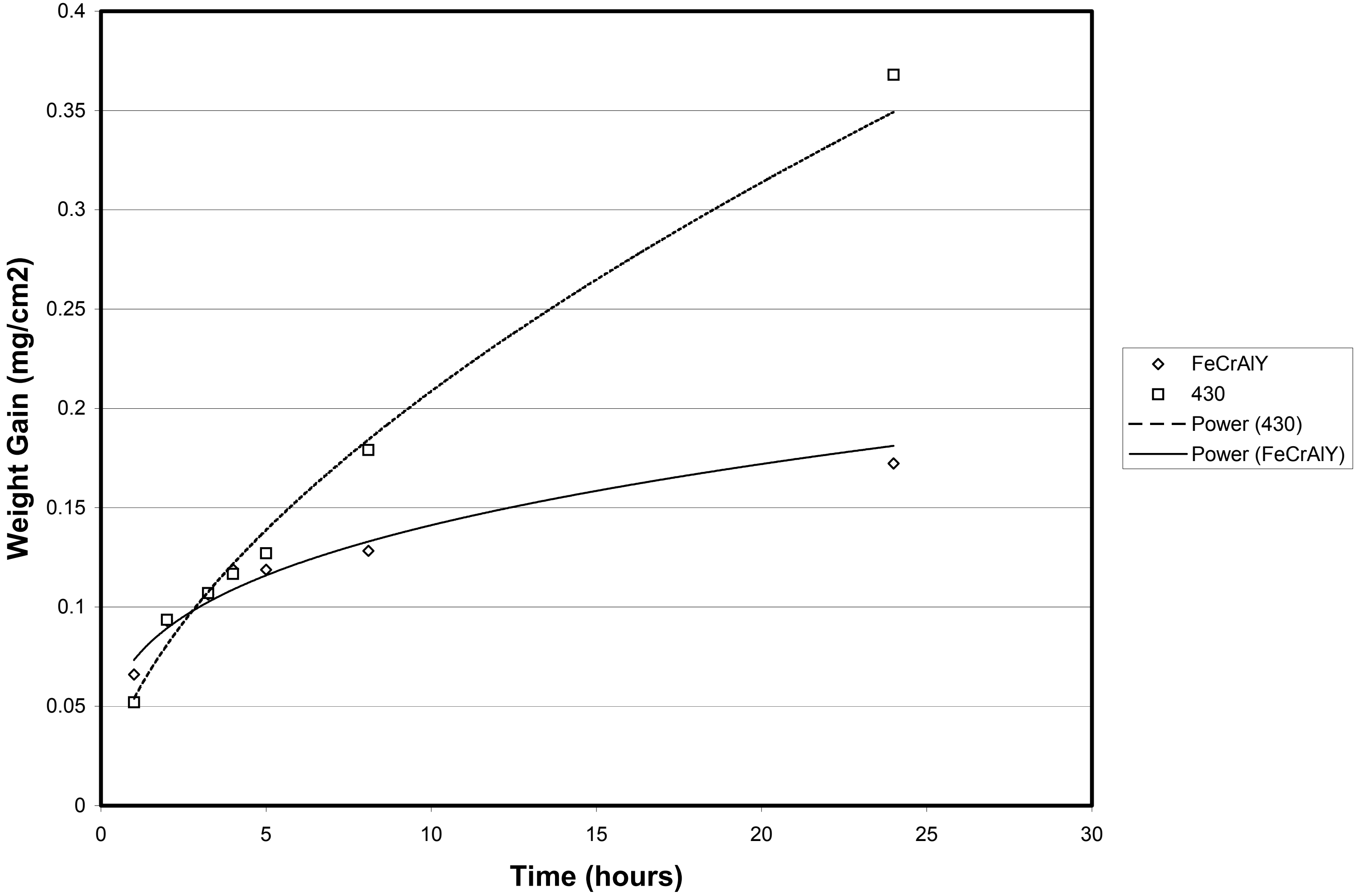
Results to Date

- Thermal Oxide Kinetics (Parabolic Growth, $T = k_p\ (t)^{1/2}$, as f(temperature))



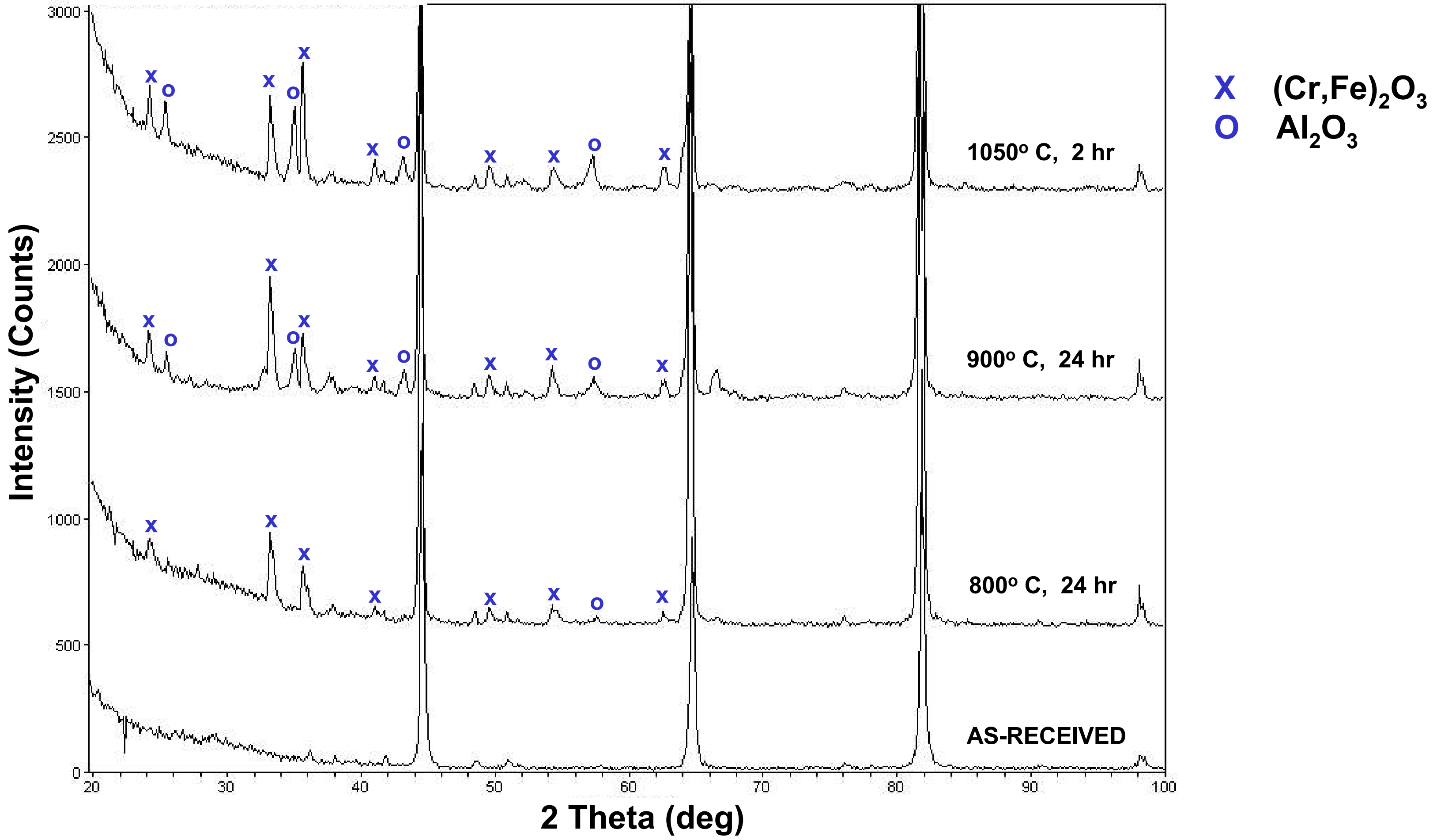
Results to Date

- Thermal Oxide Kinetics (Parabolic growth @900° C, as f(alloy type))



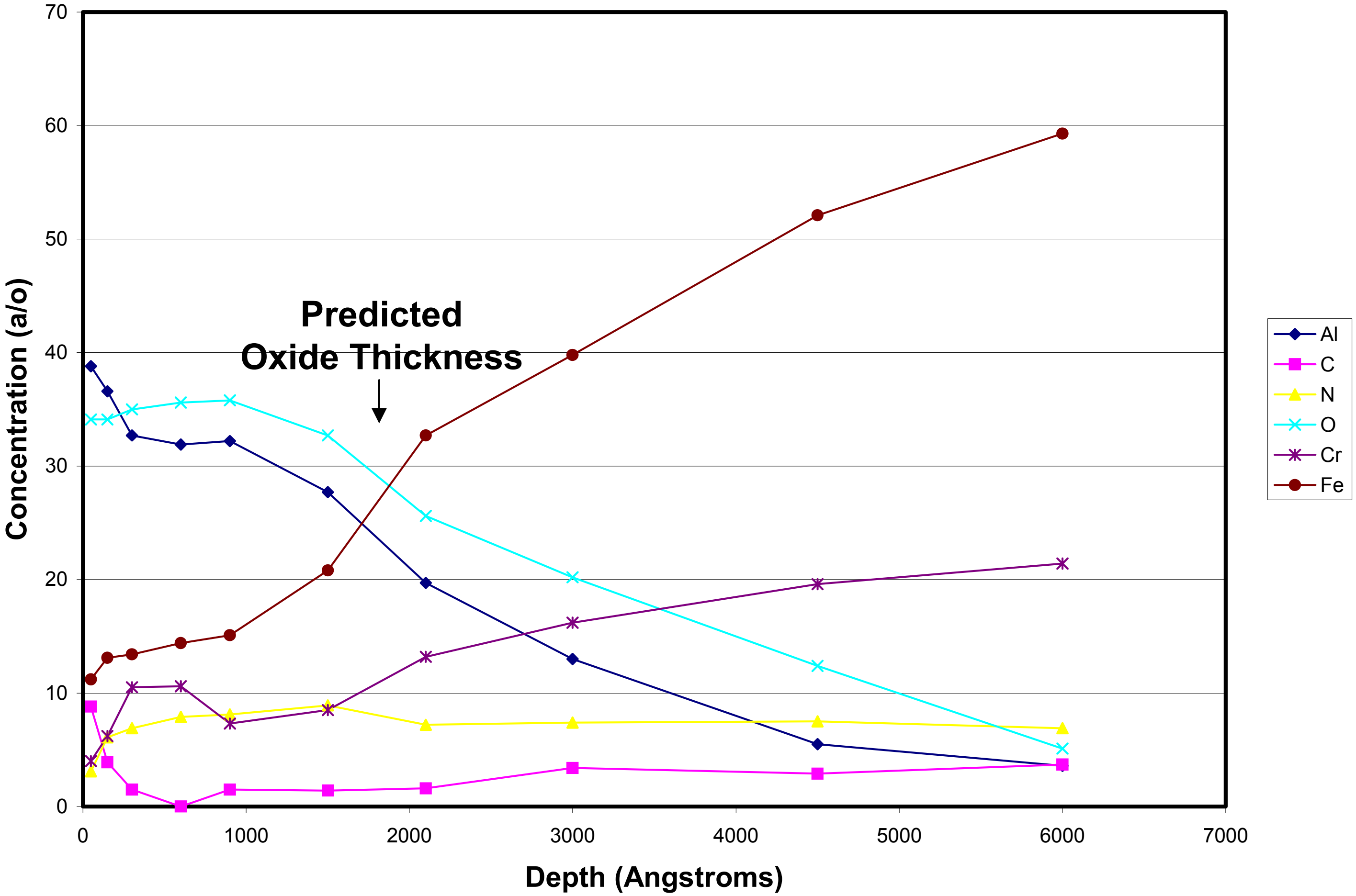
Results to Date

- X-ray Diffraction (Structure)
  - Formation of mixed oxides, $(Cr,Fe)_2O_3$ and Al_2O_3
  - Increase of Al_2O_3 at higher temperatures



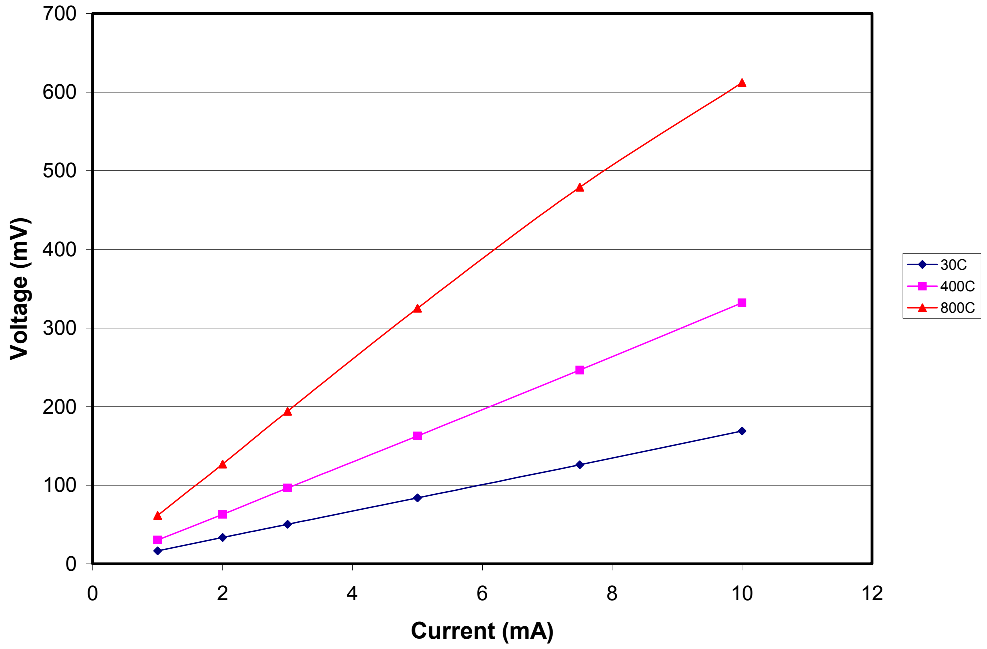
Results to Date

- AES Surface Analysis (900 °C in dry air, 2 hr.)
  - Mixed oxide with alumina segregated to surface



Results to Date

- ASR Measurements (in progress)
  - Verification of Ohms Law
  - Verification of contacting method



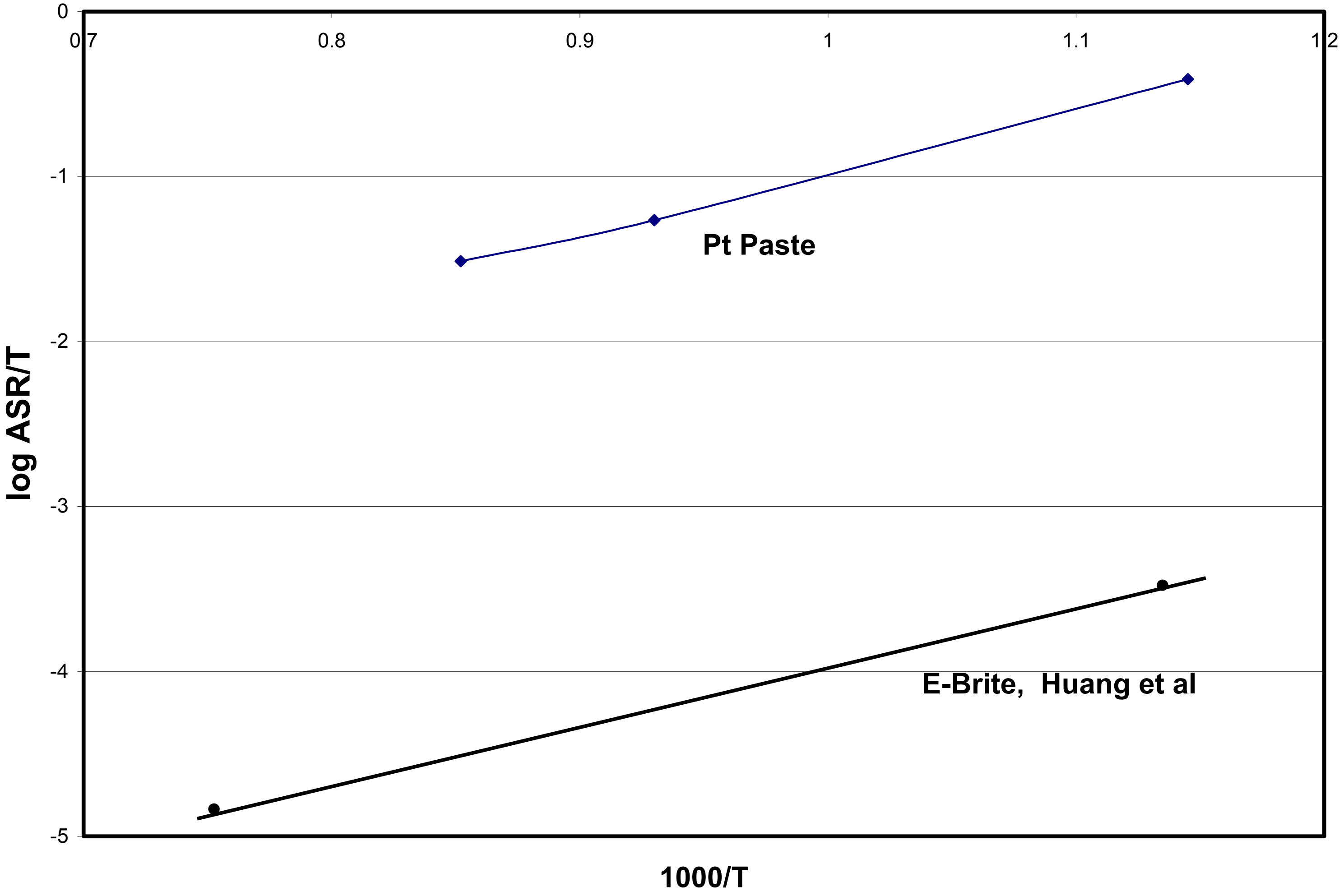
- Ion Implantation (in progress)

	Ion		
	Nb	**Ti**	**Y**
Dose, Ions/cm^2	1E16	1E16	1E16
Nominal Depth, μm	0.12	0.12	0.12
Energy, KeV	280	150	270

- Fabrication of cathode Material (UTA)
  - La0.8Sr0.2FeO3 and LSC (in progress) pellete supplied by W.J. Wan, J.B. Goodenough, Materials Science and Engineering, UTA

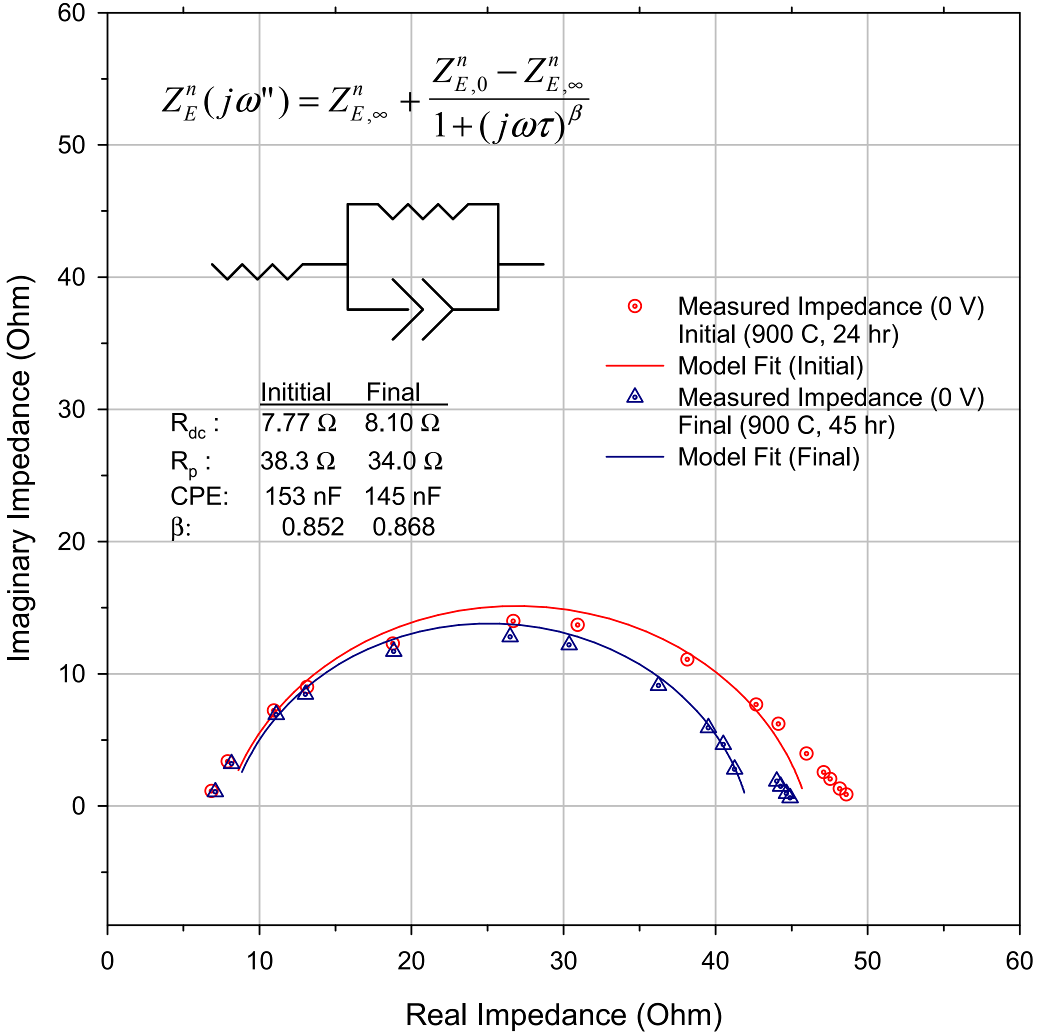
Results to Date

- **Preliminary ASR of FeCrAlY thermal oxide (950° C) with Pt paste**



Results to Date

- Preliminary AC Impedance Measurements (un-doped thermal oxide)



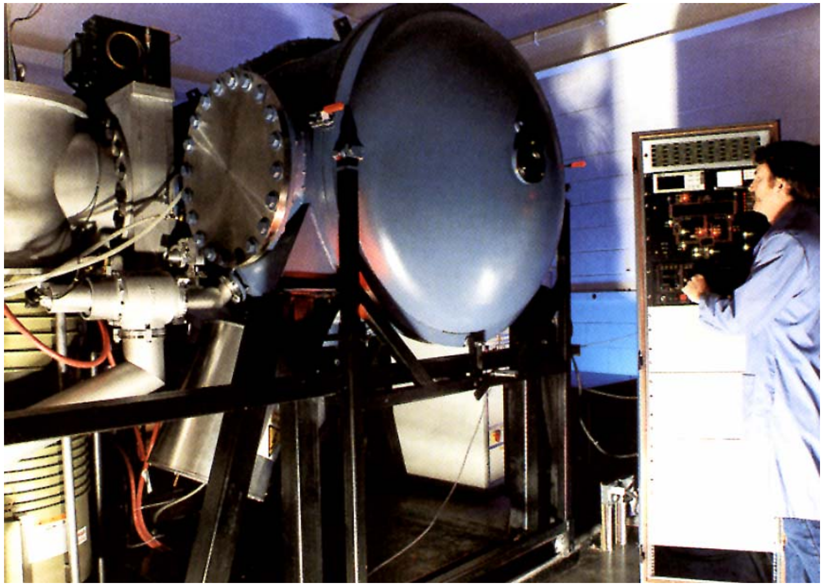
$$Z_E^n(j\omega'') = Z_{E,\infty}^n + \frac{Z_{E,0}^n - Z_{E,\infty}^n}{1+(j\omega\tau)^\beta}$$

	Inititial	Final
R_{dc} :	7.77 Ω	8.10 Ω
R_p :	38.3 Ω	34.0 Ω
CPE:	153 nF	145 nF
β:	0.852	0.868

Applicability to SOFC Commercialization

- As part of the cost share commitment, SwRI is developing a scaleable implantation process in-line with other large-scale vacuum processing

Metal Ion Source (Ar+Cr plasma)



Large-scale PIII Chamber

- Based on success of Phase I, SwRI would team with commercial partner to develop large-scale implantation capability and demonstrate applicability of process to SOFC stacks

Activities for Next 3-6 months

- Complete Ion Implantation/ Validate concentration/depth
- ASR measurements as a f(temperature) for thermally grown/ion implanted oxides
- Long term, 1,000 hour, testing in simulated fuel cell environment
- Conduct interdiffusion couple experiments with xxx cathode materials