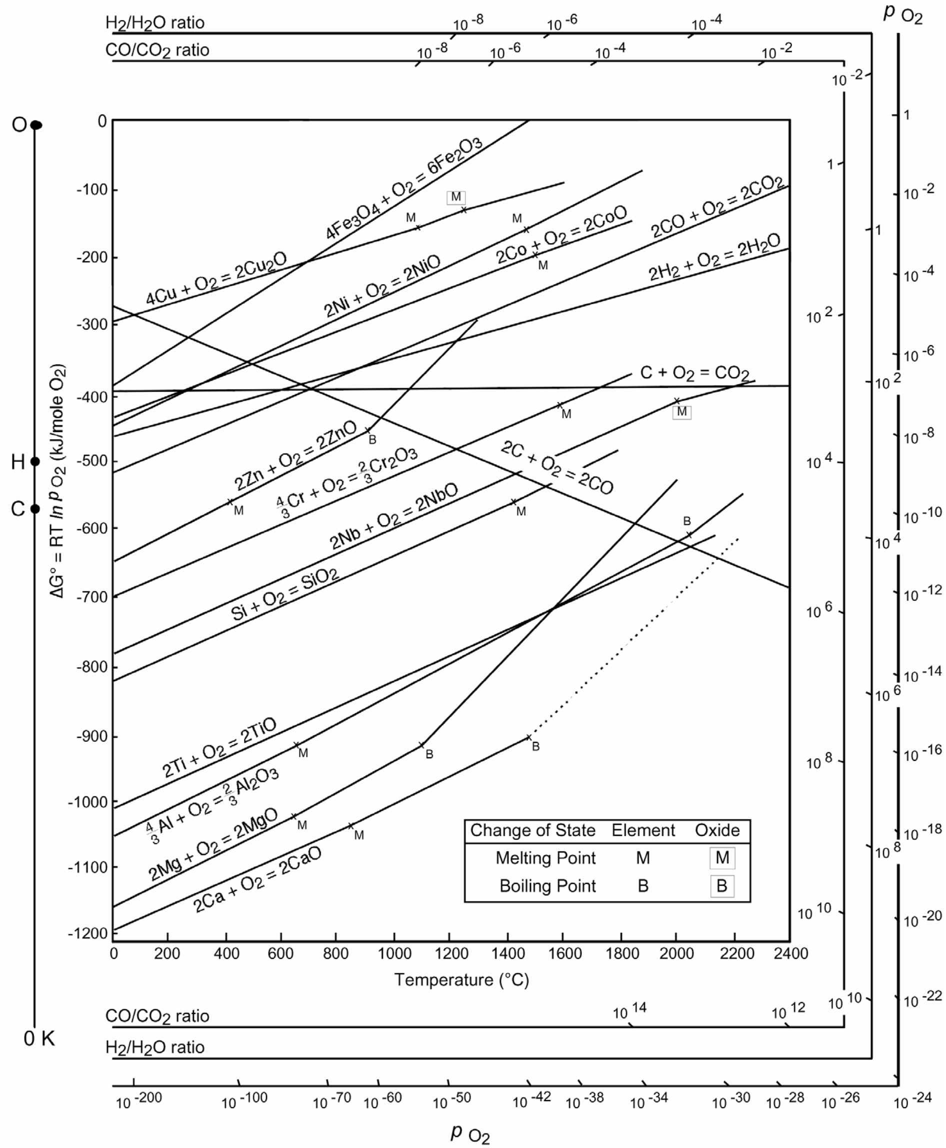
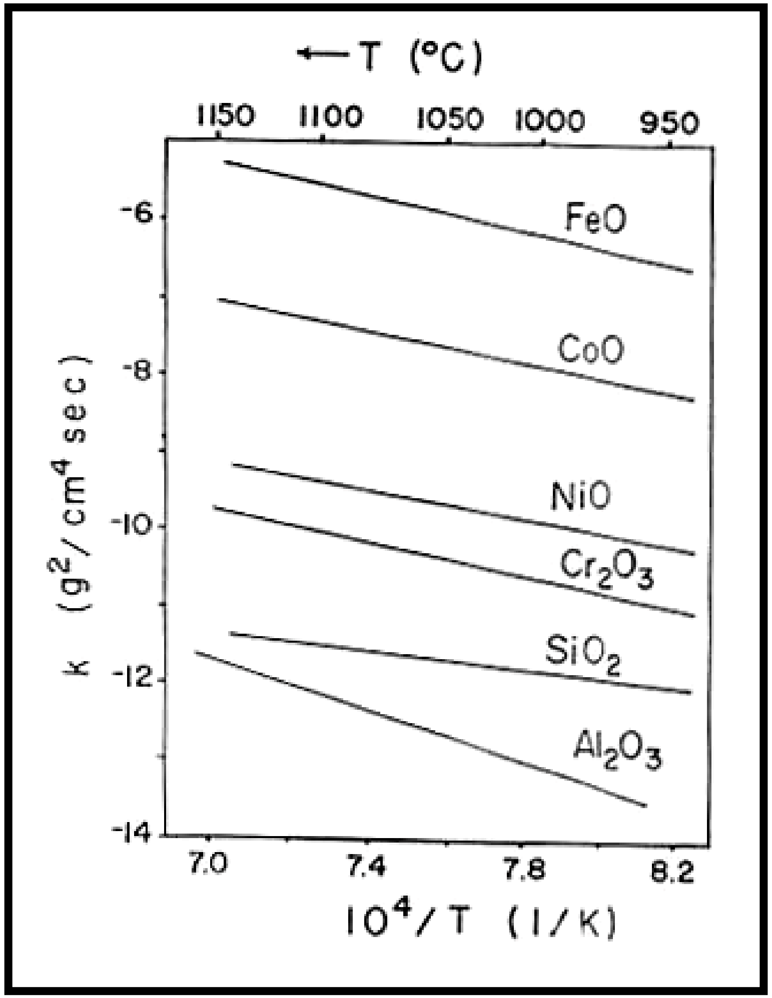
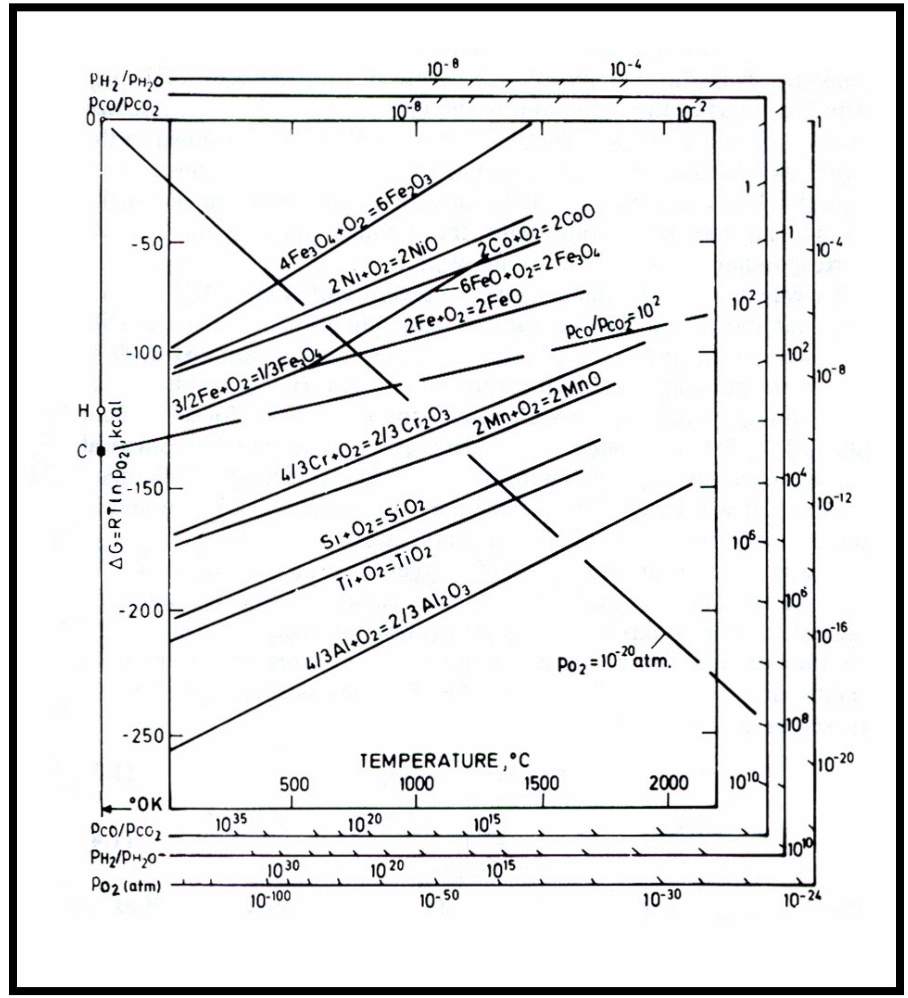
Ellingham Diagram



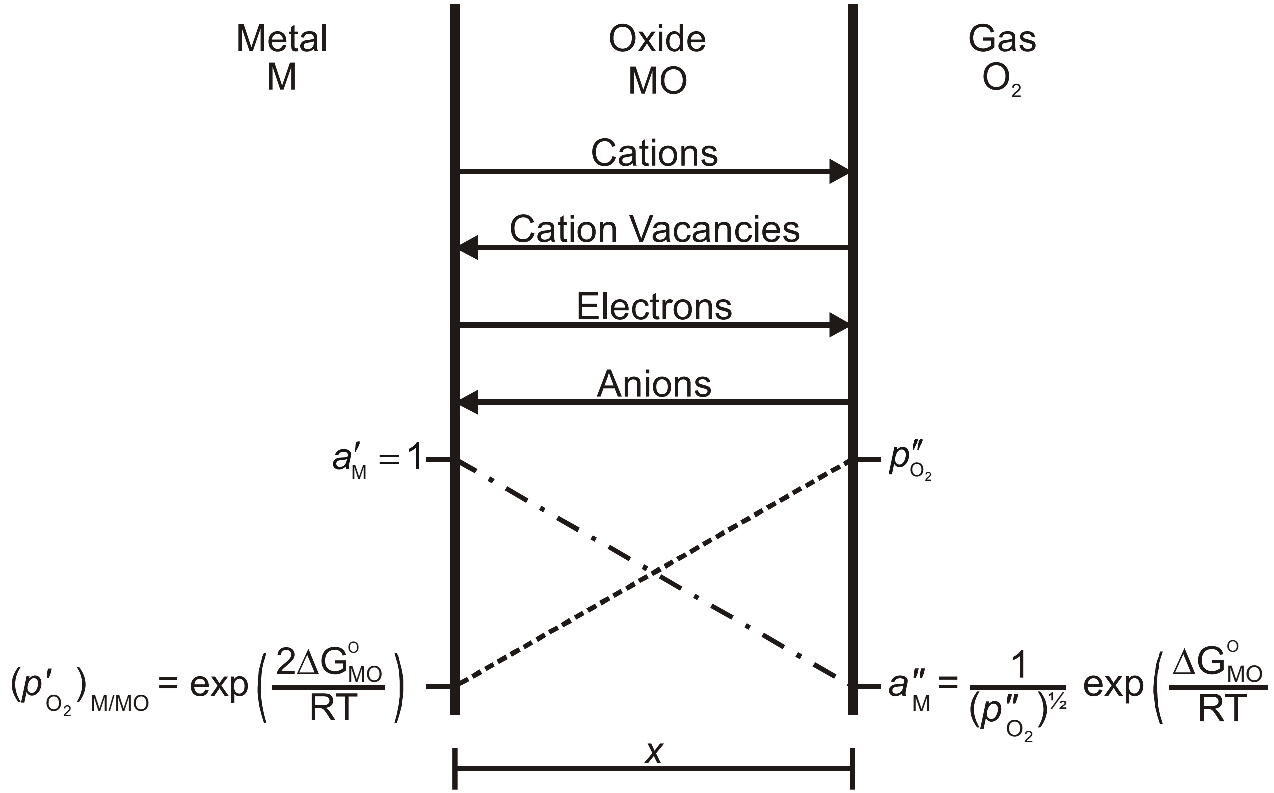


Growth rates of selected oxides
$CoO > NiO > Cr_2O_3 > Al_2O_3$



Thermodynamic stabilities of selected oxides $Al_2O_3 > Cr_2O_3 > CoO > NiO$

Effect of Electrical Current on Oxidation Rate



$$M = M^{2+} + 2e^-$$

or

$$M + O^{2-} = MO + 2e^-$$

$$M^{2+} + 2e^- + \tfrac{1}{2}O_2 = MO$$

or

$$\tfrac{1}{2}O_2 + 2e^- = O^{2-}$$

Overall reaction: $2M + O_2 = 2MO; \Delta G^\circ_{MO}$

Oxidation Under Open Circuit Conditions

$$v_i = -\frac{B_i}{N_A}\left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x}\right)$$

1

$$j_i = C_i v_i = -\frac{C_i B_i}{N_A}\left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x}\right)$$

$$kTB_i = D_i = \frac{N_A RT\kappa_i}{C_i (Z_i F)^2}$$

Replace B_i in j_i

$$j_i = -\frac{\kappa_i}{Z_i^2 F^2}\left(\frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x}\right)$$

Consider a scale growing by cations moving outward.

$$j_c = -\frac{\kappa_c}{Z_c^2 F^2}\left(\frac{\partial \mu_c}{\partial x} + Z_c F \frac{\partial \phi}{\partial x}\right) \quad \text{(A.)}$$

(B.)

$$j_e = -\frac{\kappa_e}{Z_e^2 F^2}\left(\frac{\partial \mu_e}{\partial x} + Z_e F \frac{\partial \phi}{\partial x}\right) \quad \text{(B.)}$$

Electrical Neutrality (C.)

$$Z_c j_c + Z_e j_e = 0$$

$$\frac{\partial \phi}{\partial x} = -\frac{1}{F(\kappa_c + \kappa_e)}\left[\frac{\kappa_c}{Z_c}\frac{\partial \mu_c}{\partial x} + \frac{\kappa_e}{Z_e}\frac{\partial \mu_e}{\partial x}\right]$$

The cation flux now becomes:

$$j_c = -\frac{\kappa_c \kappa_e}{Z_c^2 F^2 (\kappa_c + \kappa_e)}\left[\frac{\partial \mu_c}{\partial x} - \frac{Z_c}{Z_e}\frac{\partial \mu_e}{\partial x}\right]$$

Considering ionic equilibrium and integrating across the oxide

$$j_c = -\frac{1}{Z_c^2 F^2 x}\int_{\mu_M'}^{\mu_M''} \frac{\kappa_c \kappa_e}{\kappa_c + \kappa_e} d\mu_M$$

The relation between j_C and scale growth rate is

$$j_c = C_M \frac{dx}{dt}$$

C_M mol cm^{-3}

Comparison with the parabolic rate equation

$$\frac{dx}{dt} = \frac{k'}{x}$$

where *k'* is the parabolic rate constant in cm^{2}s^{-1}.

$$k' = \frac{1}{Z_c^2 F^2 C_M}\int_{\mu_M''}^{\mu_M'} \frac{\kappa_c \kappa_e}{\kappa_c + \kappa_e} d\mu_M$$

Oxidation in the Presence of an Impressed Current

Equations (A) and (B) are unchanged. Equation (C) is written:

$$Z_c F j_c + Z_e F j_e = i$$

$$\frac{\partial \phi}{\partial x} = -\frac{1}{F(\kappa_c + \kappa_e)}\left[\frac{\kappa_c}{Z_c}\frac{\partial \mu_c}{\partial x} + \frac{\kappa_e}{Z_e}\frac{\partial \mu_e}{\partial x} + \right] - \frac{i}{(\kappa_c + \kappa_e)}$$

$$j_c = -\frac{\kappa_c \kappa_e}{Z_c^2 F^2 \kappa}\left[\frac{\partial \mu_c}{\partial x} - \frac{Z_c}{Z_e}\frac{\partial \mu_e}{\partial x}\right] + \frac{\kappa_c i}{Z_c F \kappa}$$

$$\boxed{i_{Stop} = \frac{\kappa_e}{Z_c F}\frac{\Delta \mu_M}{x}}$$

Note: If the external oxygen pressure is 1 atm, $\Delta \mu_M = \Delta G^o_{MO}$

$$\boxed{k' = k'_{OC}\left[1 - \frac{i}{i_{Stop}}\right]}$$

For chromia at 900°C: $\kappa_e = 10^{-2}$ (ohm cm)$^{-1}$ Park & Natesan, 1990

ΔG^o = -820,000 J/mole

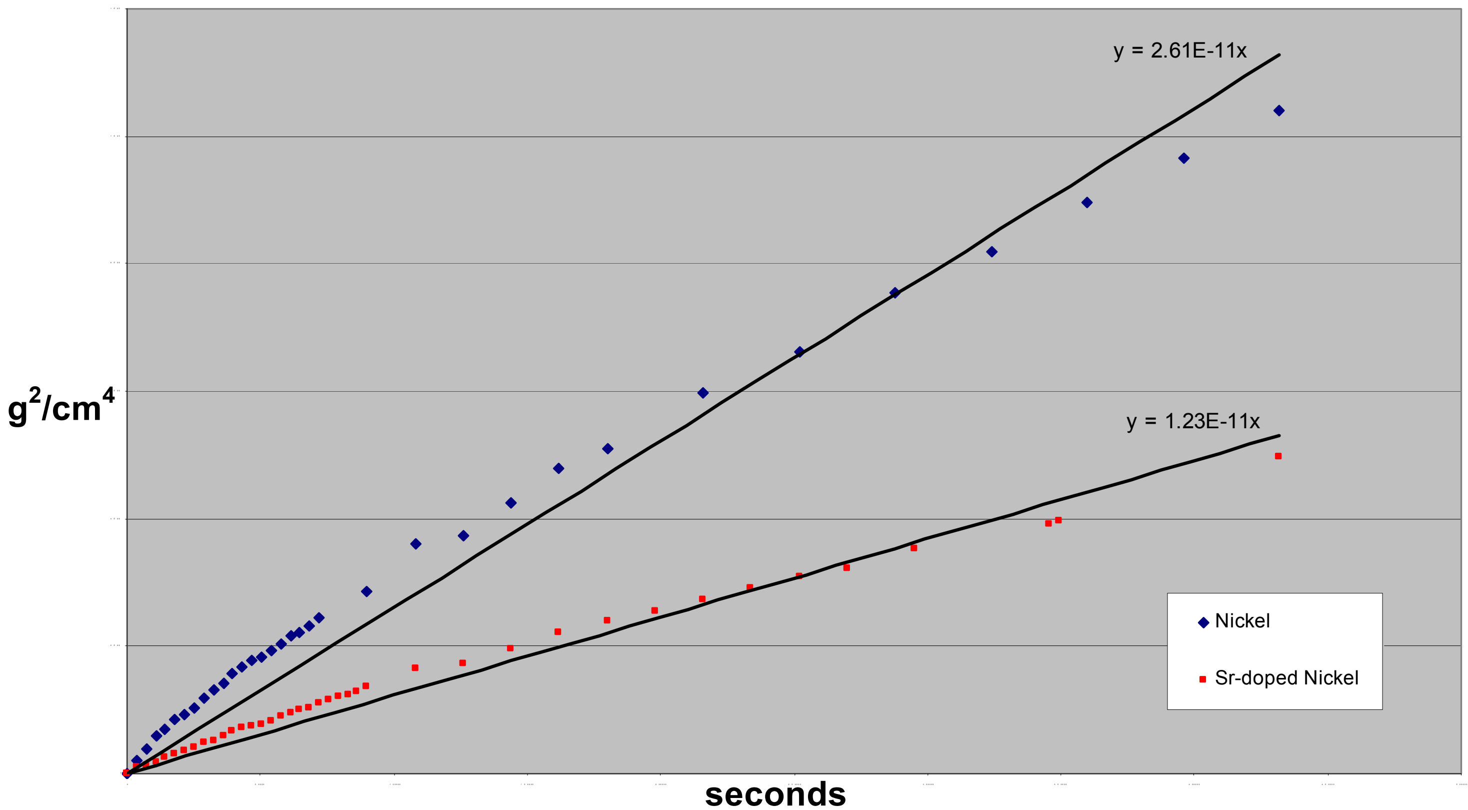
For a 1 μm thick oxide: i_{Stop} = -140 A/cm^2

For a typical Fuel Cell current density of 1 A/cm^2,

$$\boxed{k' = k'_{OC}}$$

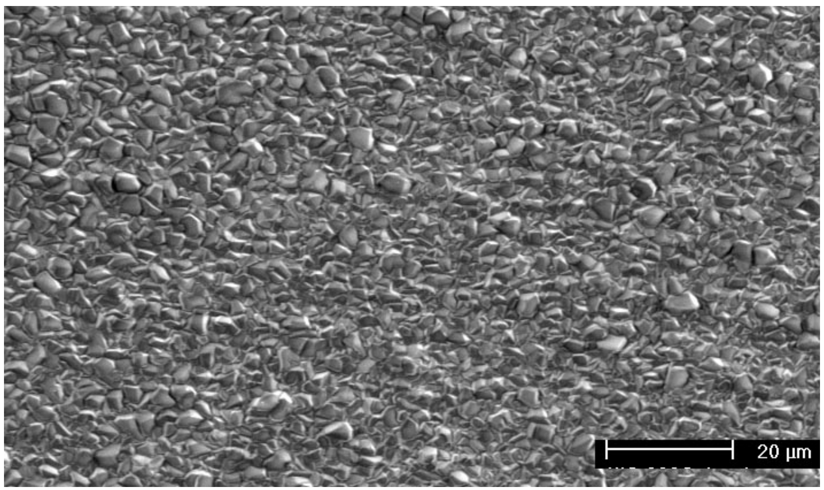
(Note: if Park & Natesan's 2-probe data are correct there could be a substantial effect of current on chromia growth.)

Parabolic Rate Constants 900C dry air

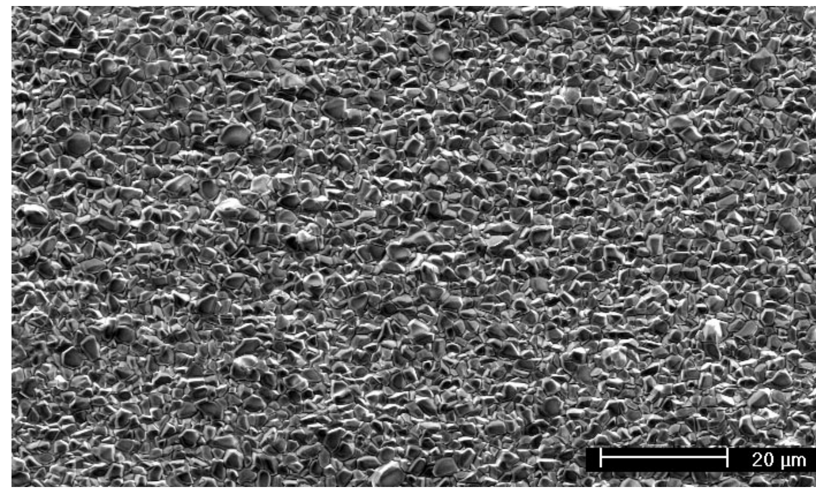


	Parabolic Rate Constant
Nickel	2.61×10^{-11} g^2/cm^4s
Sr-doped Nickel	2.23×10^{-11} g^2/cm^4s

Surface Micrographs

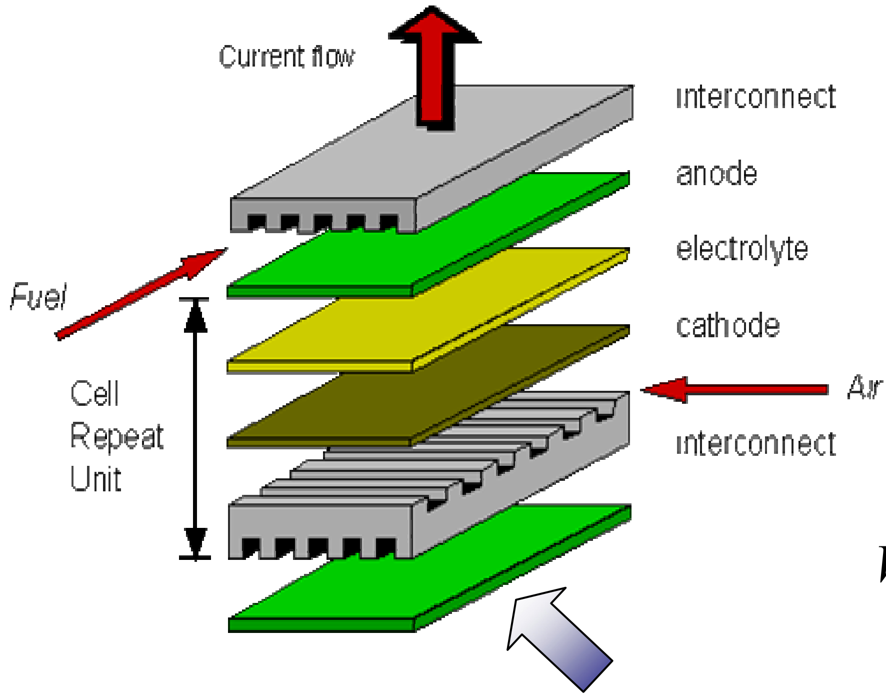


Nickel 900C



Sr-doped Nickel 900C

Planar SOFC Configuration



Repeat Components

$$V_0 = -\frac{RT}{4F}\ln\left(\frac{p_{O_2}^A}{p_{O_2}^C}\right)$$

$$V \approx 0.7 volts$$

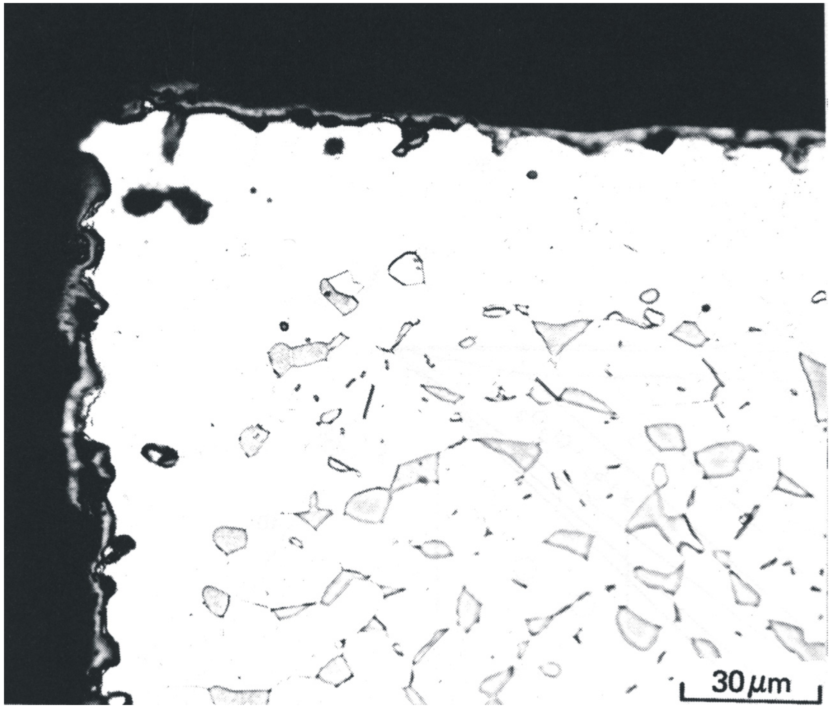
$$i \approx 1 Amp / cm^2$$

Electrolyte – YSZ
Anode – Ni/YSZ

Cathode – La/Sr-Manganite (LSM)
Interconnect – Metallic

Oxidized Ni-50 Cr Alloy

Cr-Rich Second Phase has Dissolved in the Cr-Depleted Zone

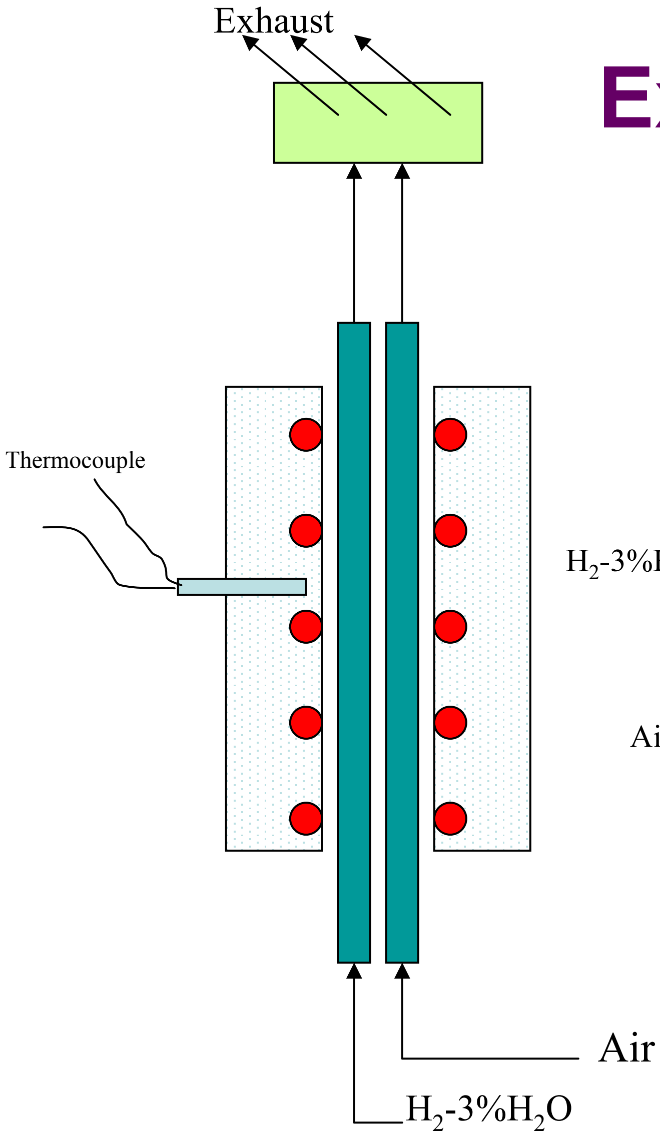


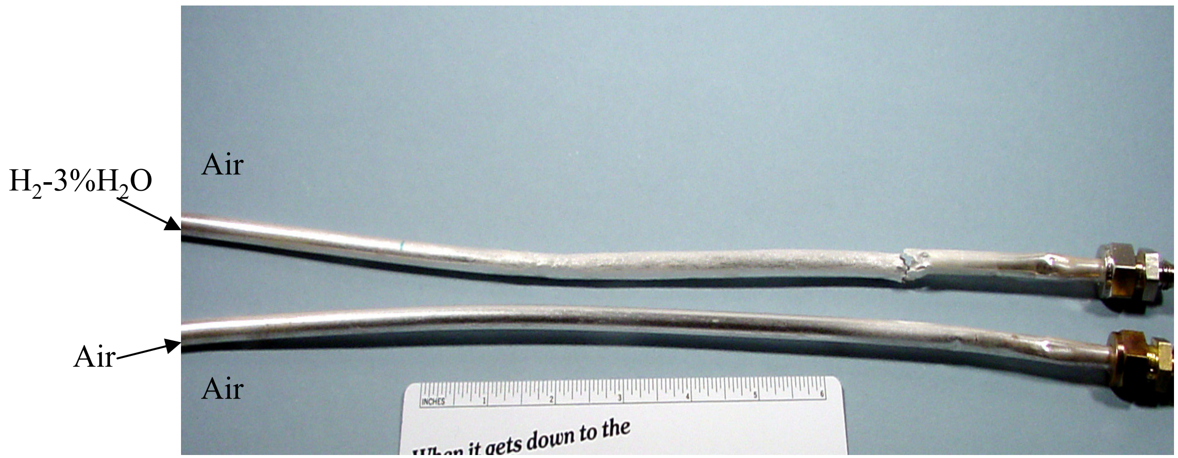
Cr_2O_3

Cr-depleted zone

Alloy

Experimental Arrangement





Materials:

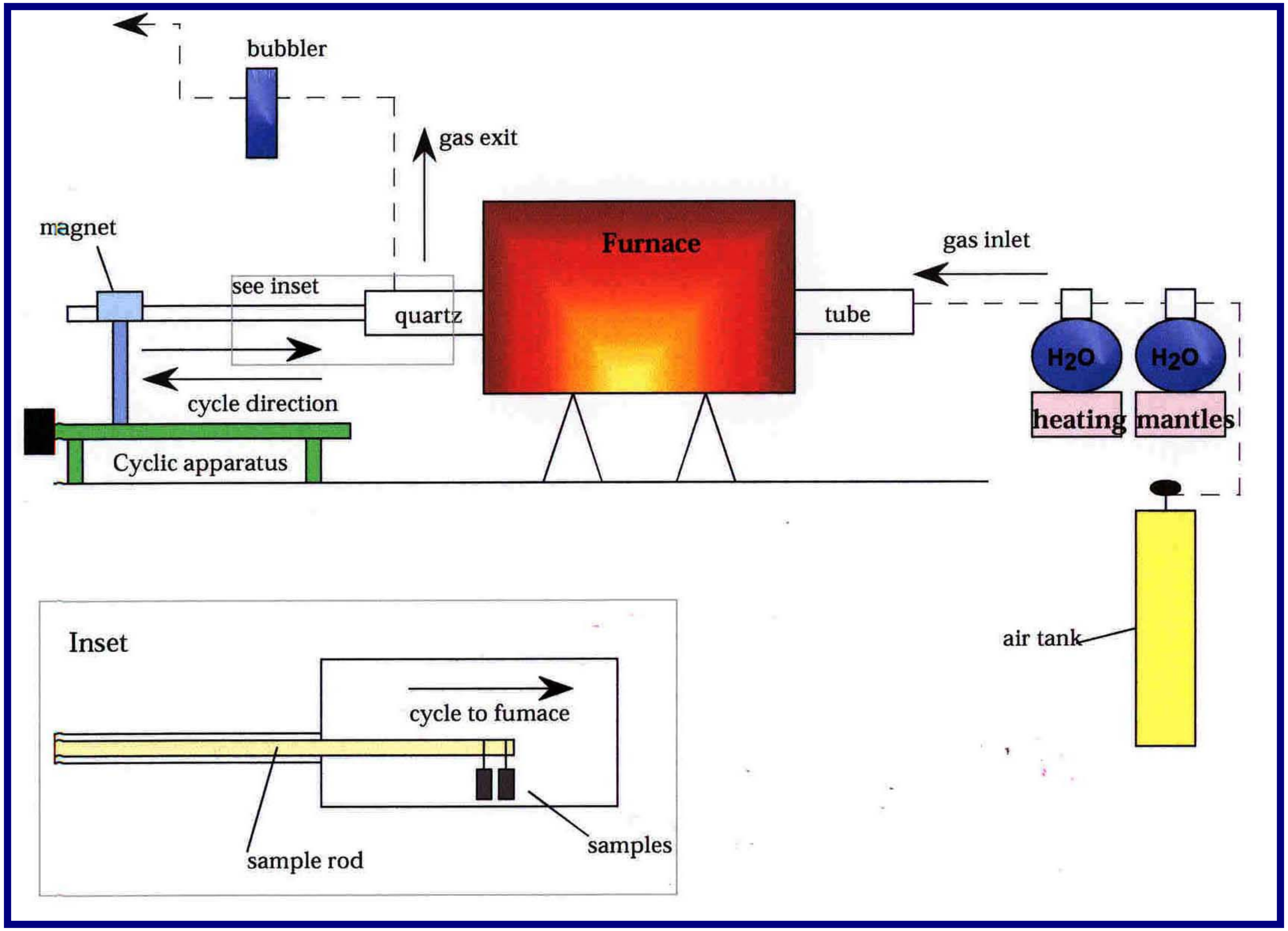
- 10 mil thick Ag tube

Variables:

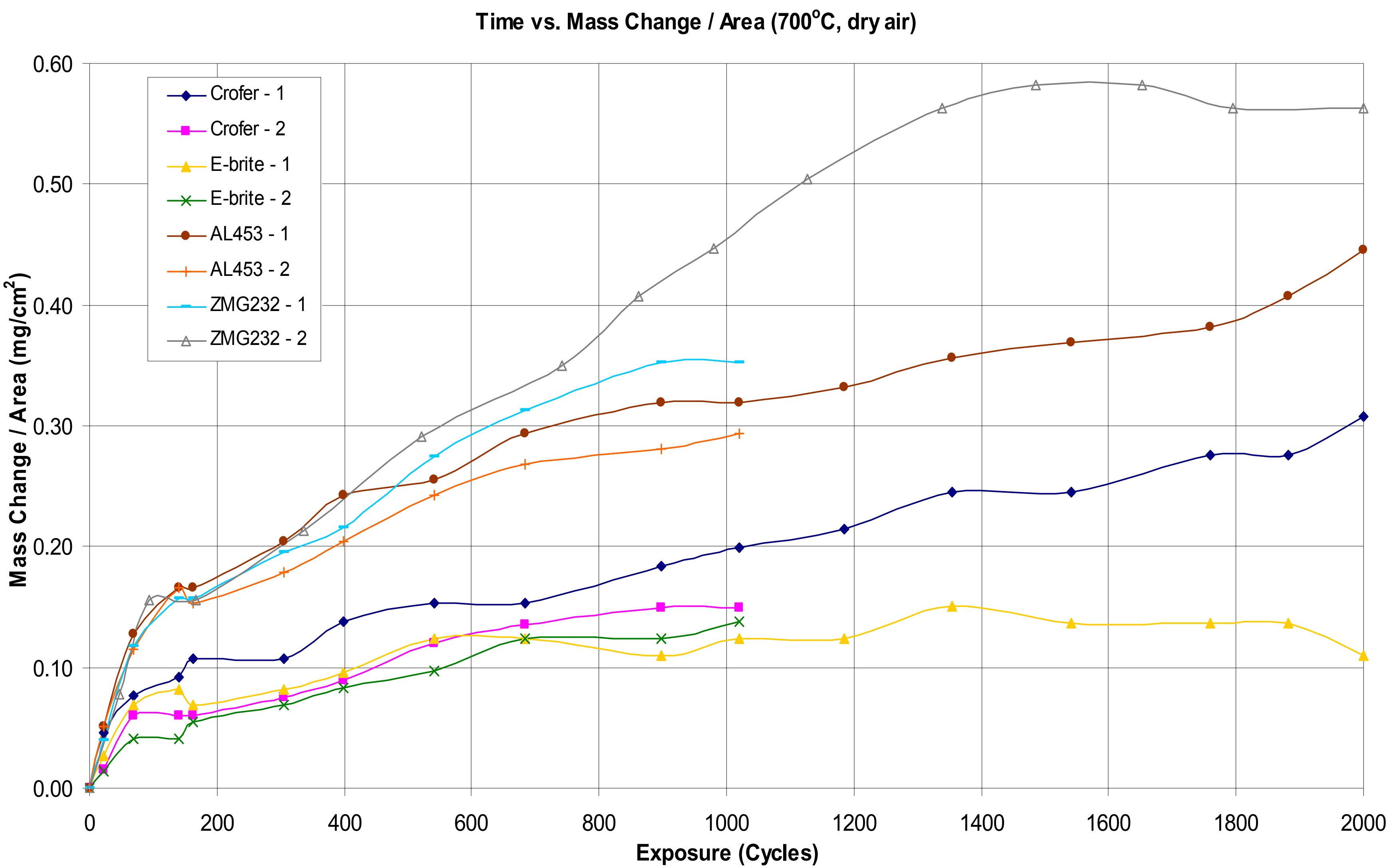
- Temperatures, 700, 600, 500°C;
- Simultaneous exposures to H_2+3%H_2O and air;

Courtesy of Dr. Prabhakar Singh, PNNL

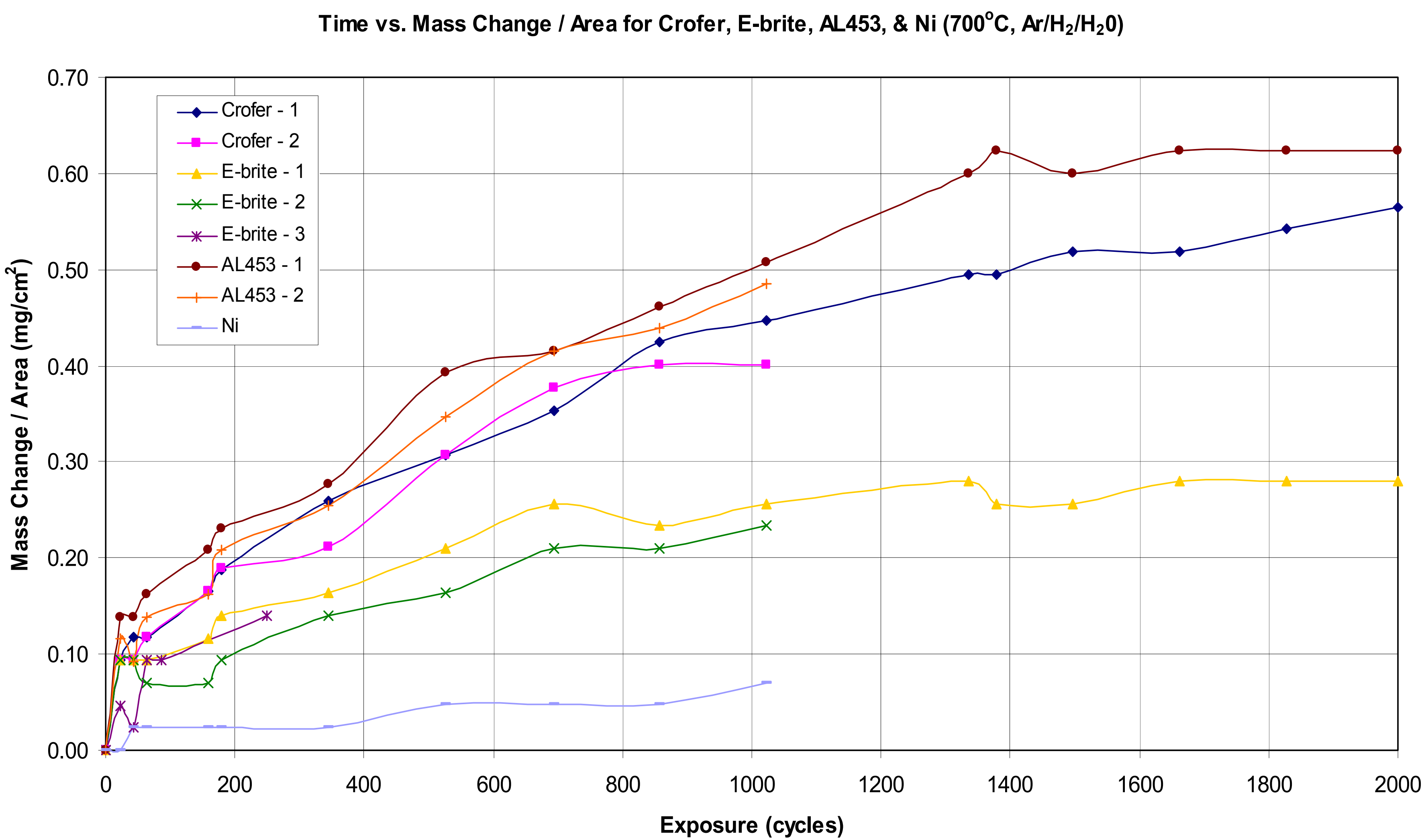
Diagram of Apparatus



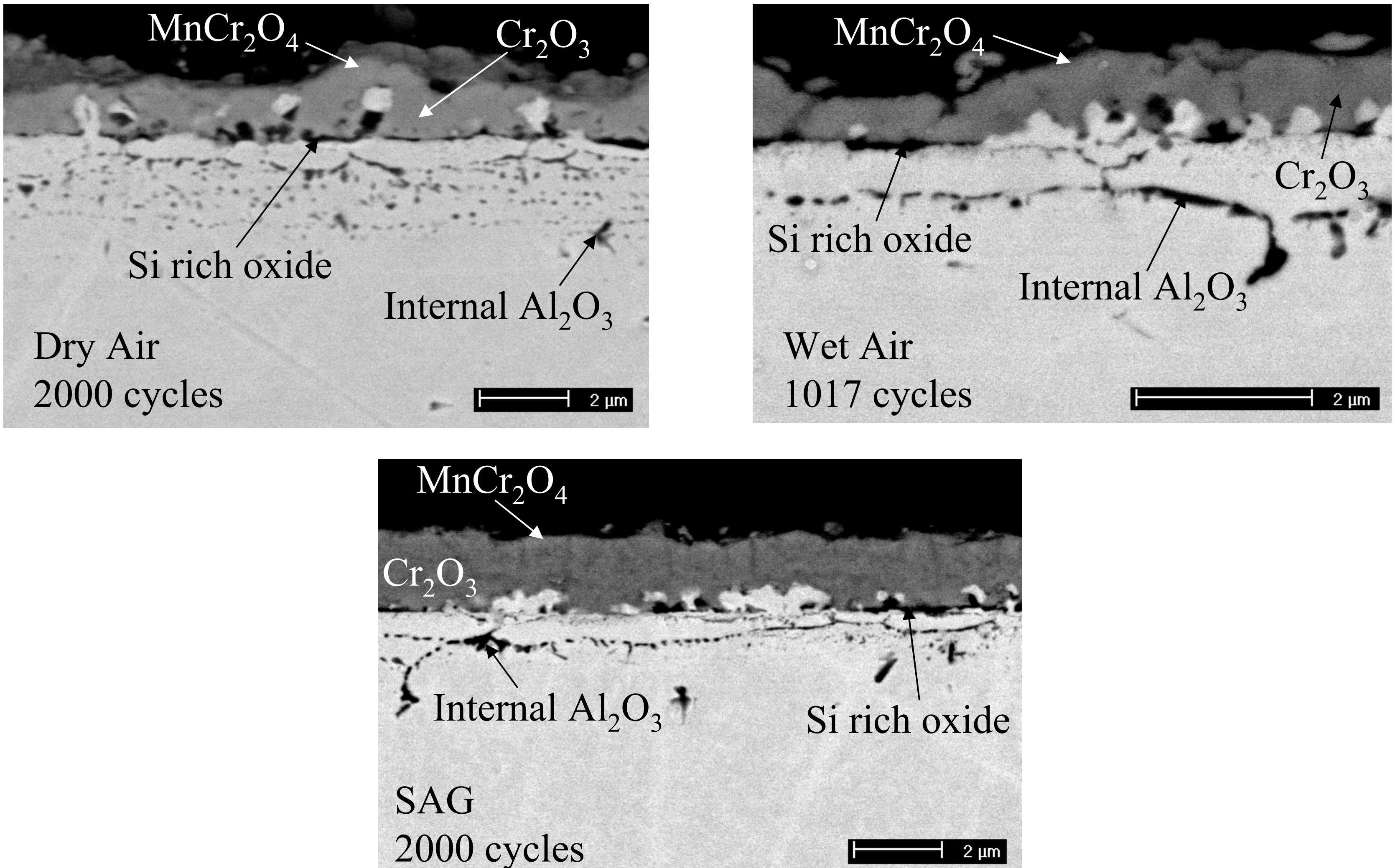
Dry Air Exposures – 700°C



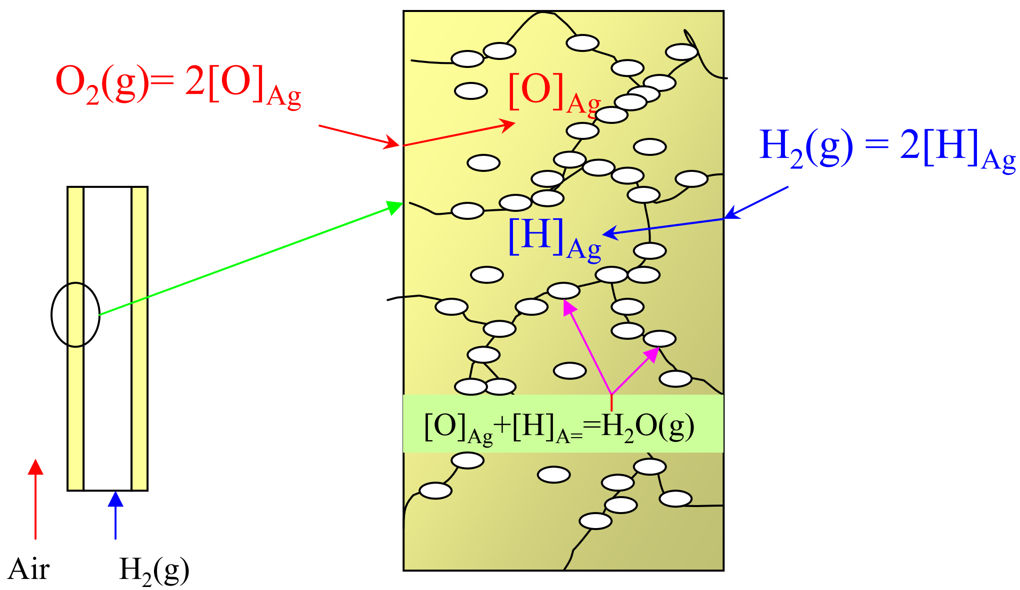
Simulated Anode Gas (Ar-4%H_2, H_2O) Exposures – 700°C



Microstructural and Phase Identification Crofer 700°C



Degradation Mechanism



Reaction Steps

1. $(H_2)_g = 2(H)_{Ag}$ Ag/Fuel interface

2. $(O_2)_g = 2(O)_{Ag}$ Ag/ Air Interface

3. $2(H)_{Ag} + (O)_{Ag} = (H_2O)_g$ Bulk Ag

Bulk Degradation Related to :

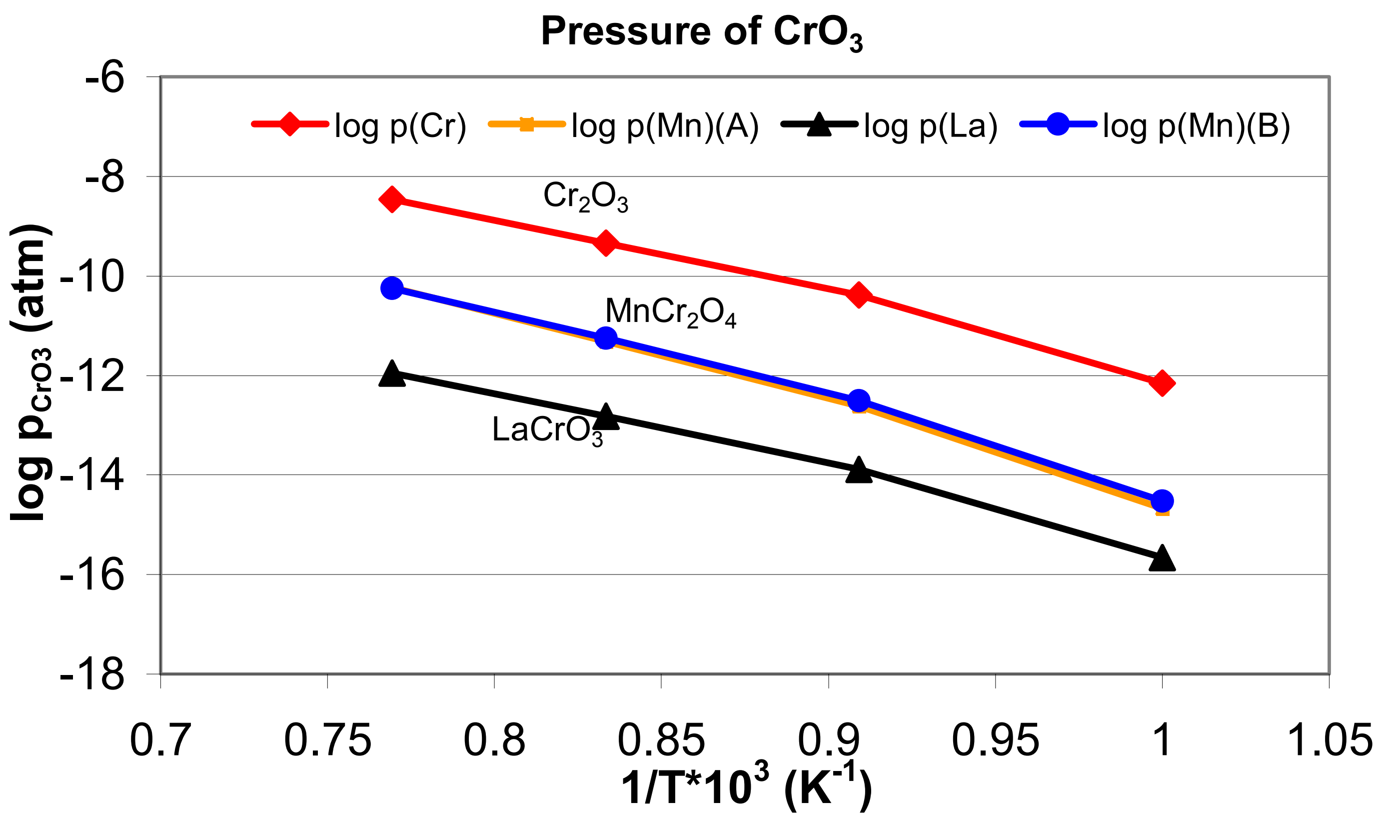
1.Dissociation and dissolution of H and O in the bulk metal

2. Interaction between dissolved H & O to form High pressure H_2O gas

3. Nucleation and growth of steam bubbles/voids at GB/defects

Courtesy of Dr. Prabhakar Singh, PNNL

Partial pressures of CrO_3 in Equilibrium with Cr_2O_3, MnO-saturated $MnCr_2O_4$, and $LaCrO_3$

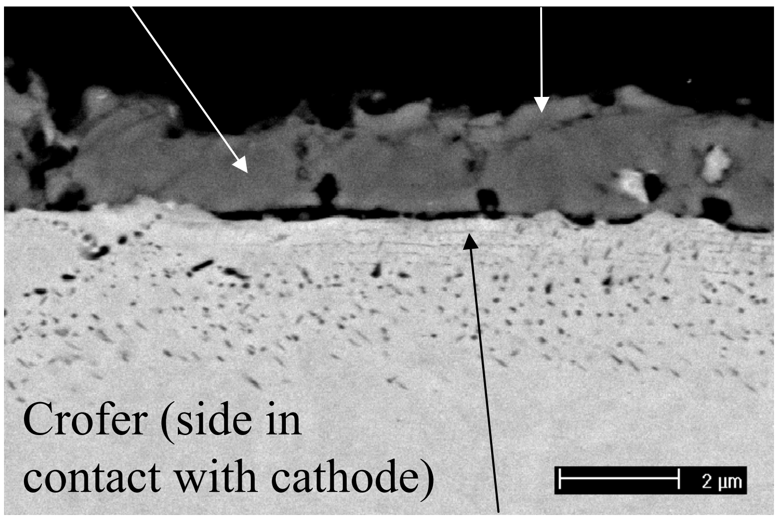


Note: **similar reductions would be achieved in the pressure of $CrO_2(OH)_2$**

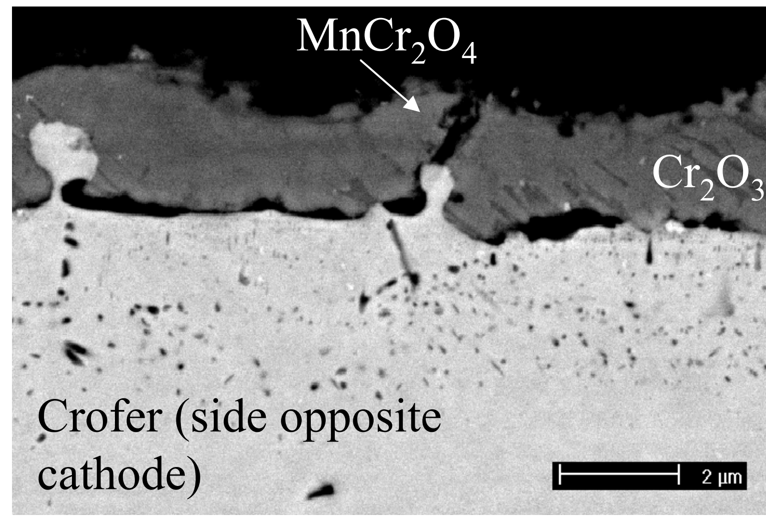
Crofer oxidized in contact with $LaSrMnO_4$ (cathode) for 88hrs at 900°C in air + 0.1atm H_2O

Cr_2O_3 with ~2% Sr, ~4% La, and ~4.7% Mn

$MnCr_2O_4$ with ~1.5% Sr and ~2.6% La



~74.9% Fe
~20% Cr
~2.2% La
~2% Mn
~0.9% Sr



After exposure, the cathode contained ~0.9% Cr and ~1.8% Al