

ELECTROCHEMICAL PATHWAYS TOWARDS CARBON-FREE METALS PRODUCTION

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The message

The road to sustainability is paved
with advanced materials.

problems with metals extraction

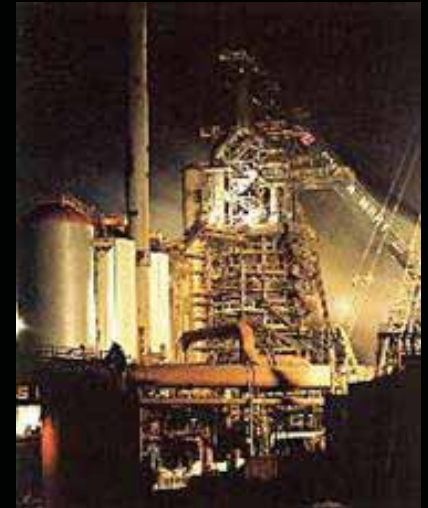
□ unfavorable by-products ☹️

⇒ **steelmaking makes CO₂** 🌍

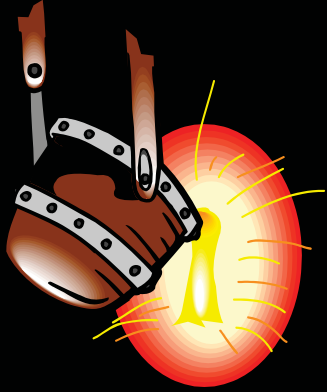


(½ kg C / kg Fe) x 1.2 billion tonnes

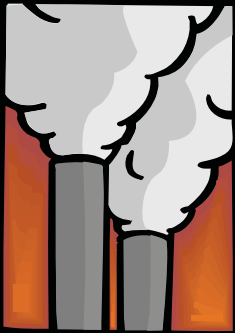
⇒ **sundry HAPs including Mn & Pb,
polycyclic organics, benzene, & CS₂**



Why is metal production so dirty?

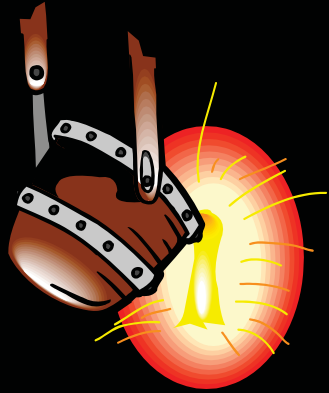


- many processes are over 100 years old



- attitude then of indifference towards the environment

Why is metal production so dirty?



© Cartoonbank.com



“Where there’s smoke, there’s money.”



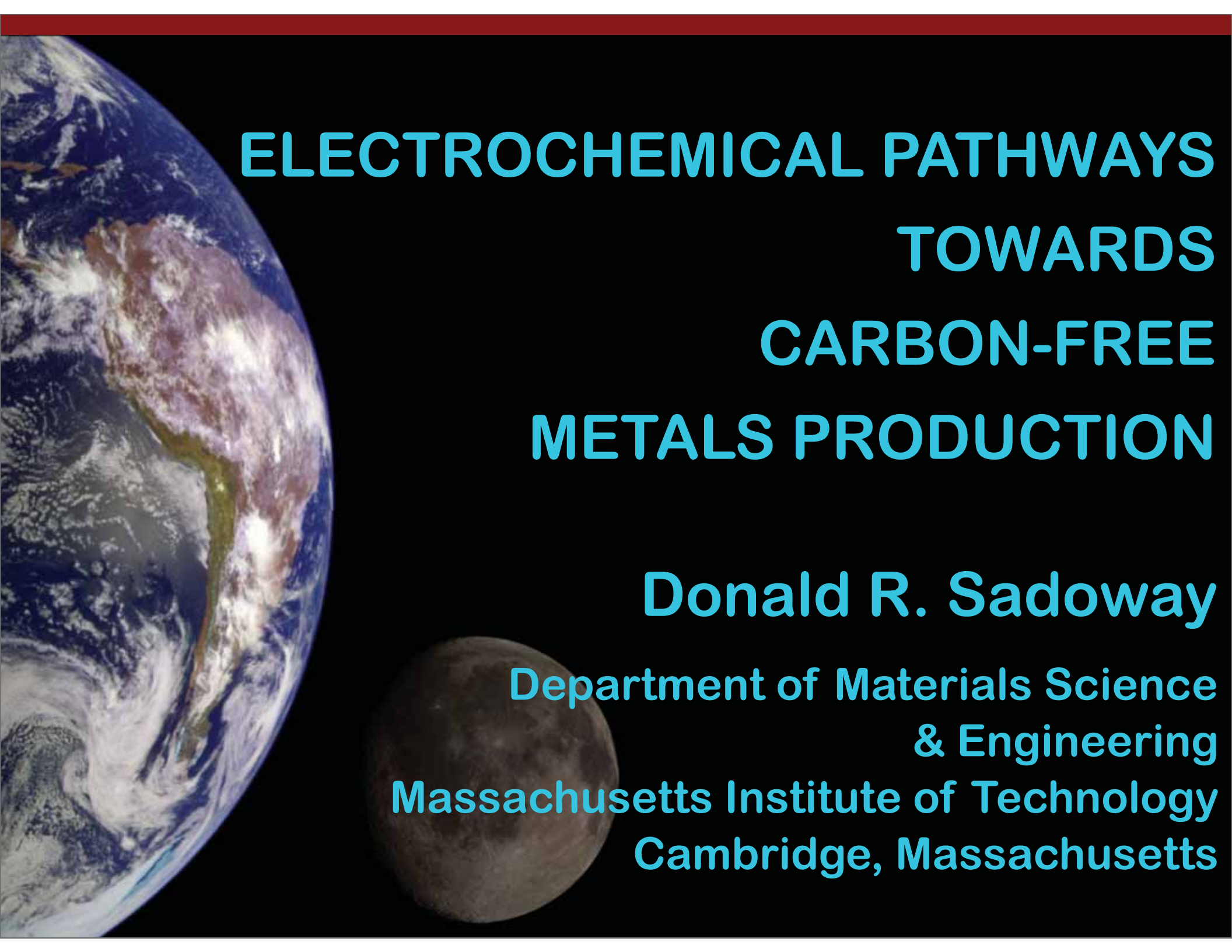
We're all just temporarily visiting this planet

Towards sustainability



Green technology






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Where do metals come from?

- ⇒ occur naturally as compounds
- ⇒ beneficiated  high-purity feed
- ⇒ reducing agents: H, C, M, e⁻
- ⇒ options for sustainability?

beyond the blast furnace

- ⇒ most metals are found in nature as oxides
- ⇒ *“like dissolves like”*
- ⇒ e^- is the best reducing agent

☞ molten oxide electrolysis:

extreme form of molten salt electrolysis

where pure **oxygen** gas is the by-product



aluminum produced by electrolytic reduction of Al_2O_3
world capacity: ~40 million tons/year

1886

Charles Martin Hall, USA
Paul Héroult, France

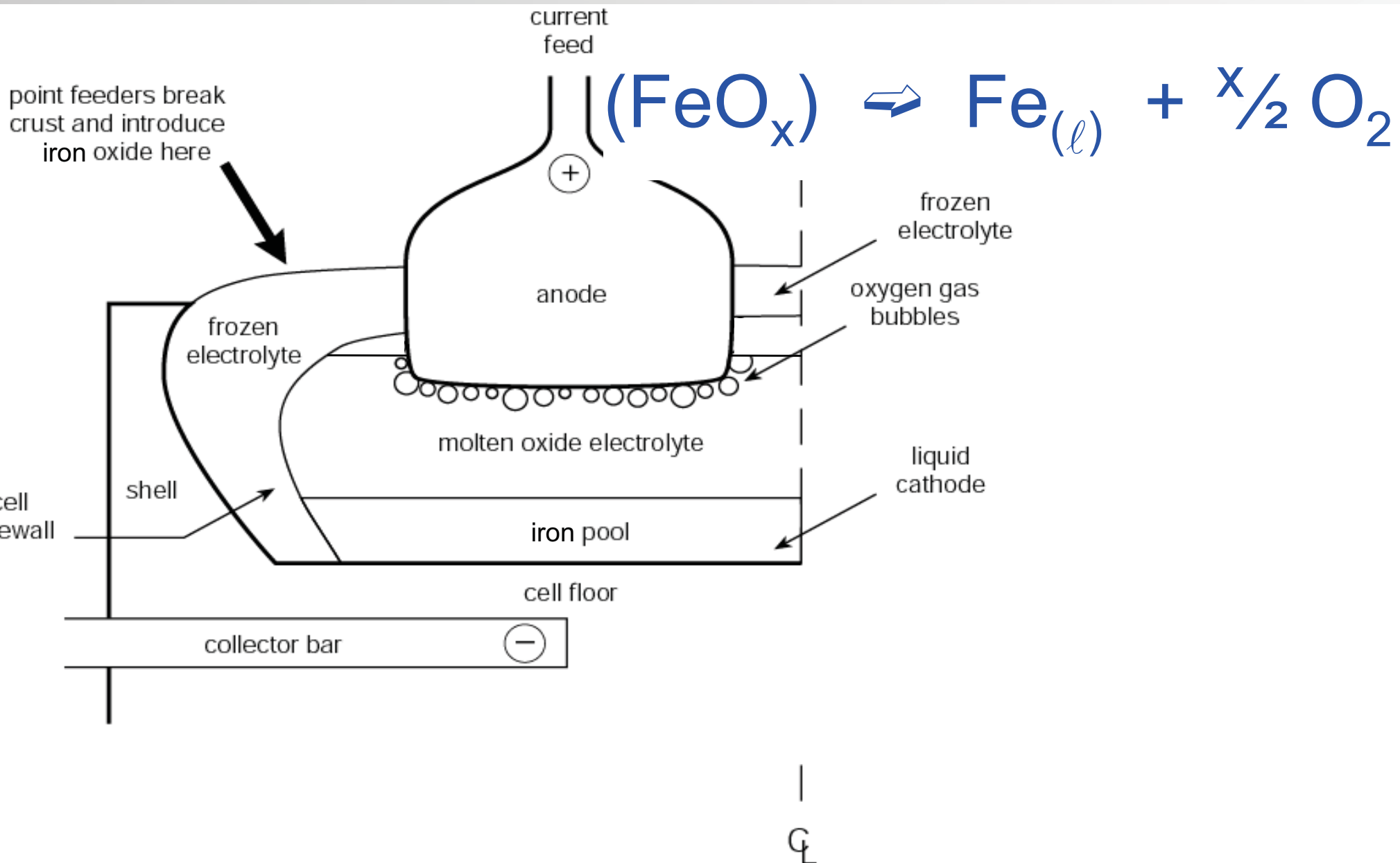


decompose Al_2O_3 dissolved in Na_3AlF_6 ($T = 960^\circ\text{C}$)

☞ liquid Al (-) and CO_2 (+)

☞ find an inert anode & molten oxide electrolyte

green ironmaking: cell schematic



Technology Needs: dateline 2050

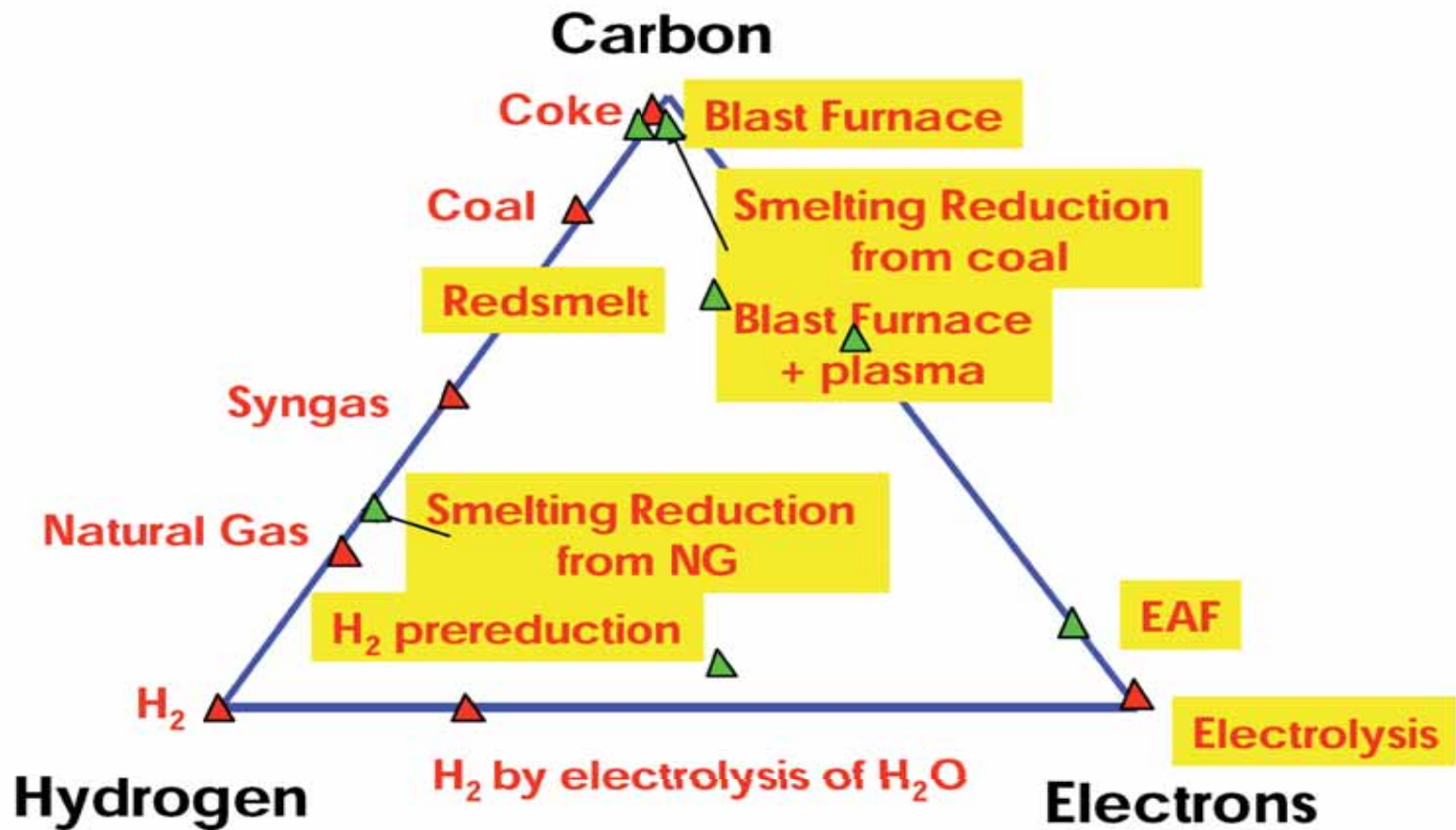


■ *Innovation - IRSID*

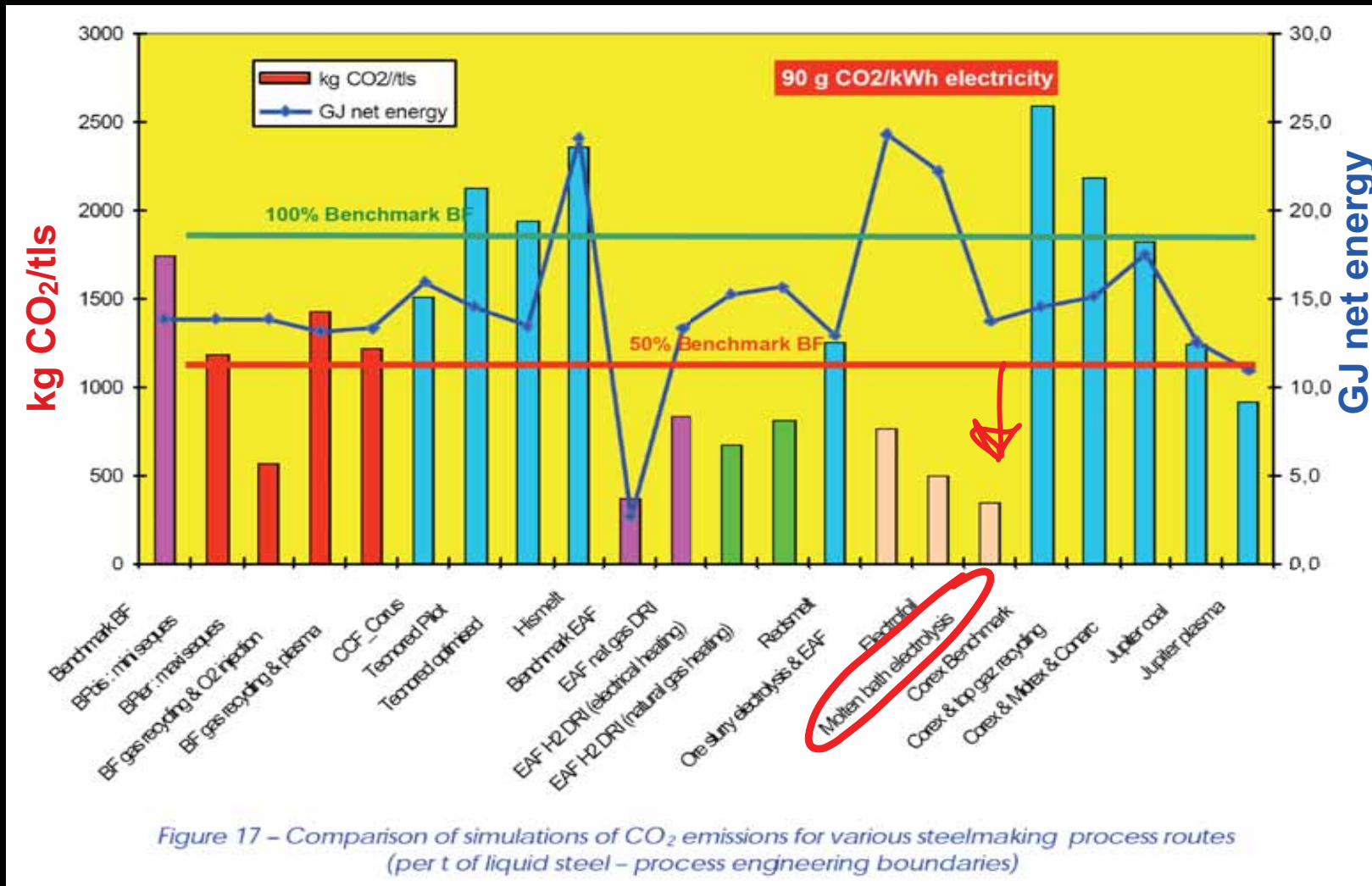
The challenge of Global Warming to the Steel Industry, a European viewpoint

Jean-Pierre Birat, Arcelor Innovation, IRSID, Maizières-lès-Metz, France

Technology Taxonomy: Reducing Agents



Environmental Impact & Energy Savings



Environmental Impact & Energy Savings

- ⇒ CO₂ emissions reduced from 1750 kg/tonne liquid steel for benchmark blast furnace technology to 345 kg/tonne liquid steel: a five-fold reduction
- ⇒ 90 g CO₂/kWh for generation of electric power
- ⇒ equivalent energy consumption: MOE vs benchmark

Other Benefits

tonnage oxygen

scientific and technical challenges

- ⇒ molten oxides of transition metals exhibit electronic conduction
- ⇒ inert anode operable at temperatures as high as 1700°C in an oxide melt

some of the relevant engineering science:

- ☑ electrical conductivity measurements
- ☑ transference number measurements
- ☑ voltammetry → process kinetics
- ☑ electrolysis testing

conductivity measurements

- ⇒ inventing two new techniques for aggressive melts at high temperatures:
 - ① moveable coaxial cylinders
 - ② 4-point crucible

moveable coaxial cylinders

United States Patent [19]

Sadoway et al.

[11] **Patent Number:** **5,489,849**

[45] **Date of Patent:** **Feb. 6, 1996**

[54] **HIGH ACCURACY CALIBRATION-FREE ELECTRICAL PARAMETER MEASUREMENTS USING DIFFERENTIAL MEASUREMENT WITH RESPECT TO IMMERSION DEPTH**

[75] Inventors: **Donald R. Sadoway**, Belmont; **Kevin G. Rhoads**, Andover; **Naomi A. Fried**, Cambridge; **Susan L. Schiefelbein**, Boston, all of Mass.

[73] Assignee: **Massachusetts Institute of Technology**, Cambridge, Mass.

[21] Appl. No.: **212,478**

[22] Filed: **Mar. 14, 1994**

[51] Int. Cl.⁶ **G01N 27/02**

[52] U.S. Cl. **324/447; 324/449; 204/406; 205/81**

[58] Field of Search **324/444, 446, 324/447, 448, 449, 720, 691; 204/406; 205/81-83**

[56] **References Cited**

Jones, Grinnell, et al., "The Measurement of the Conductance of Electrolytes. III. The Design of Cells," *Journal of the American Chemical Society*, pp. 411-419, (Feb. 1931).
Bard, A. J., et al., *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, pp. 316-369. Date unavailable.

Macdonald, J. R., et al., *Impedance Spectroscopy—Emphasizing Solid Materials and Systems*, John Wiley & Sons, pp. 1-29. Date unavailable.

Thomas, J. L., "Precision Resistors and Their Measurements," National Bureau of Standards Circular 470, Issued Oct. 8, 1948.

(List continued on next page.)

Primary Examiner—Kenneth A. Wieder

Assistant Examiner—Christopher M. Tobin

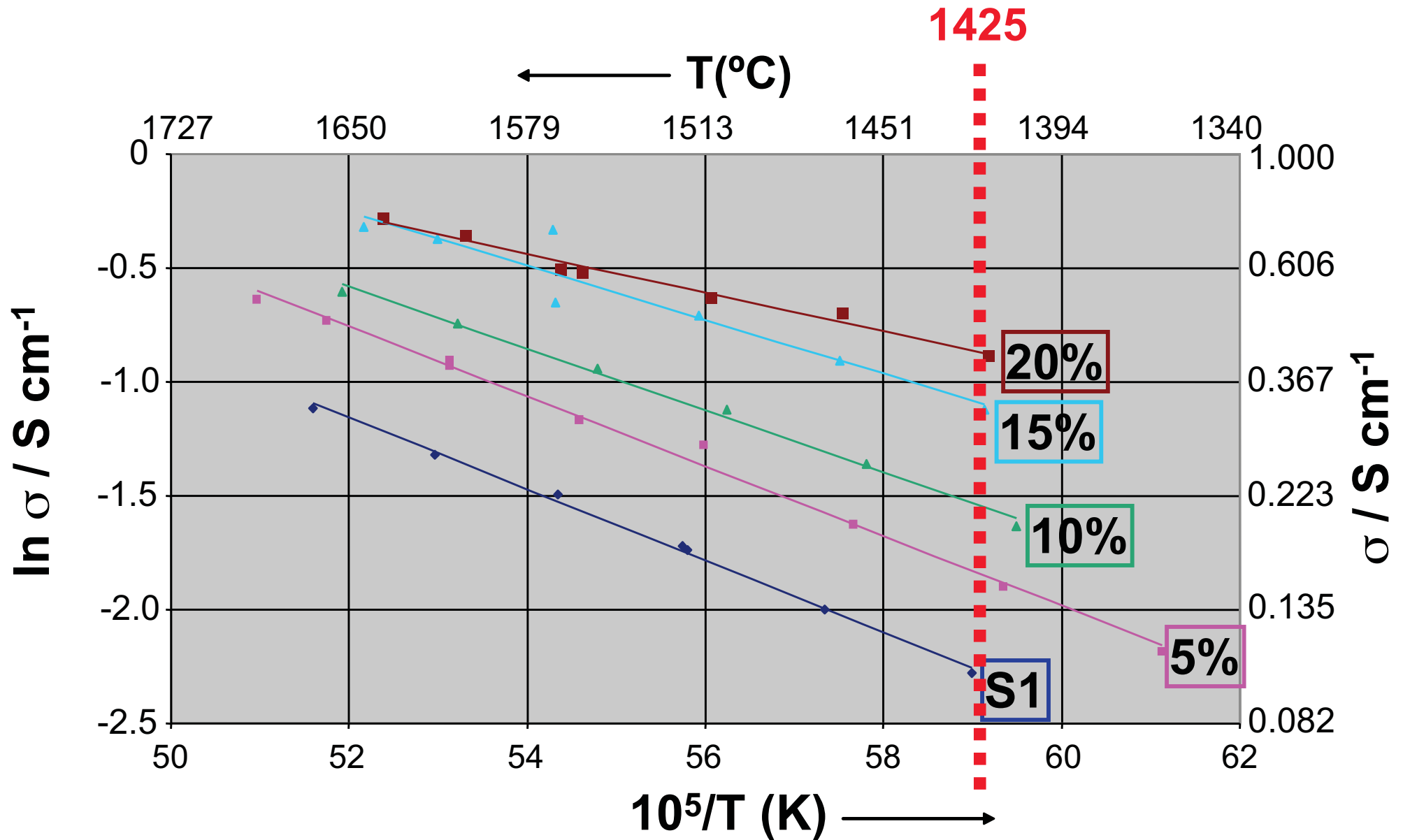
Attorney, Agent, or Firm—Hamilton, Brook, Smith & Reynolds

[57] **ABSTRACT**

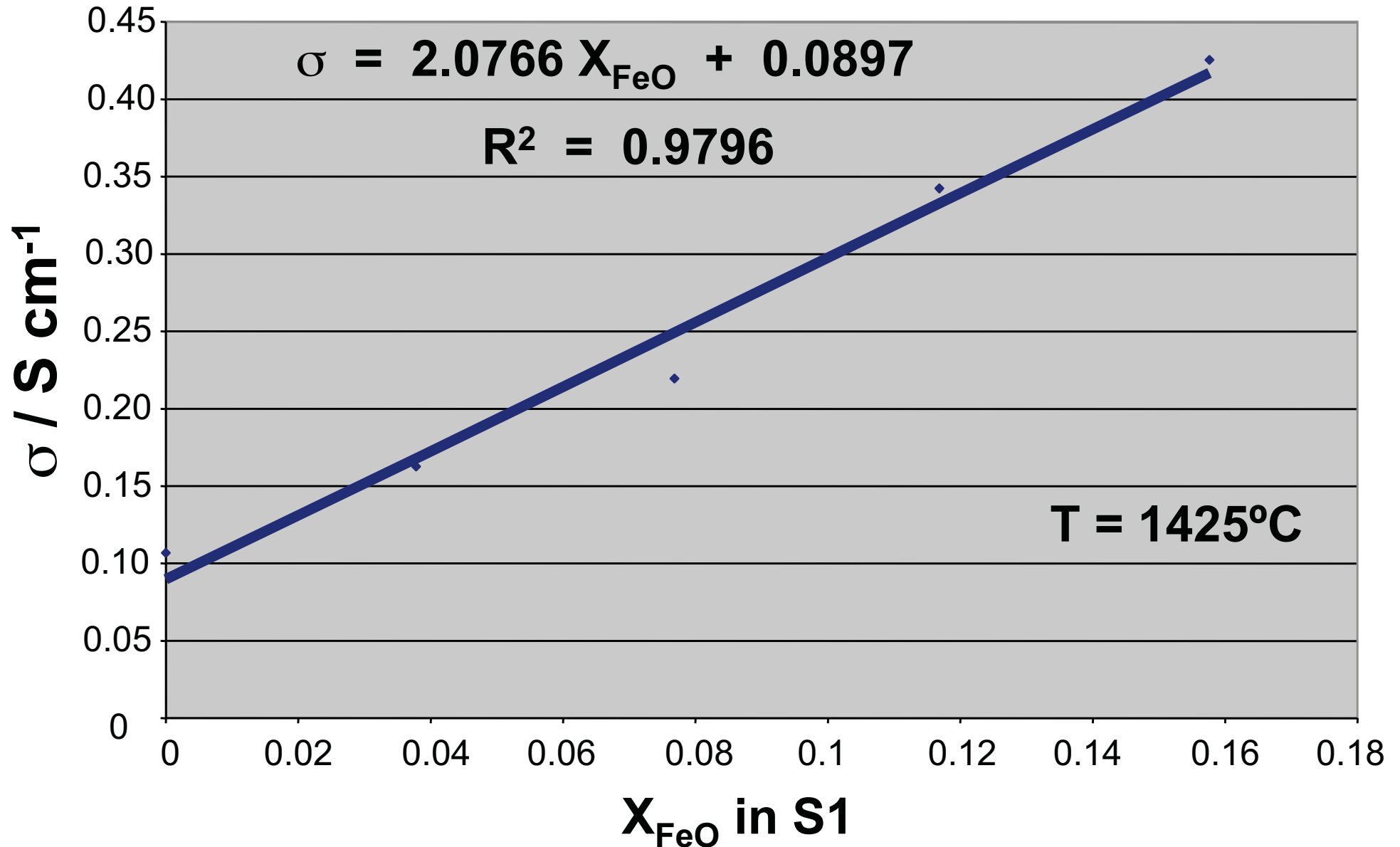
An apparatus and method for measuring electrical parameters of a medium such as electrical conductivity and dielectric constant between a pair of electrodes are disclosed. The medium can be a liquid, gas, powder, etc., and the electrodes can be made of any suitable material.



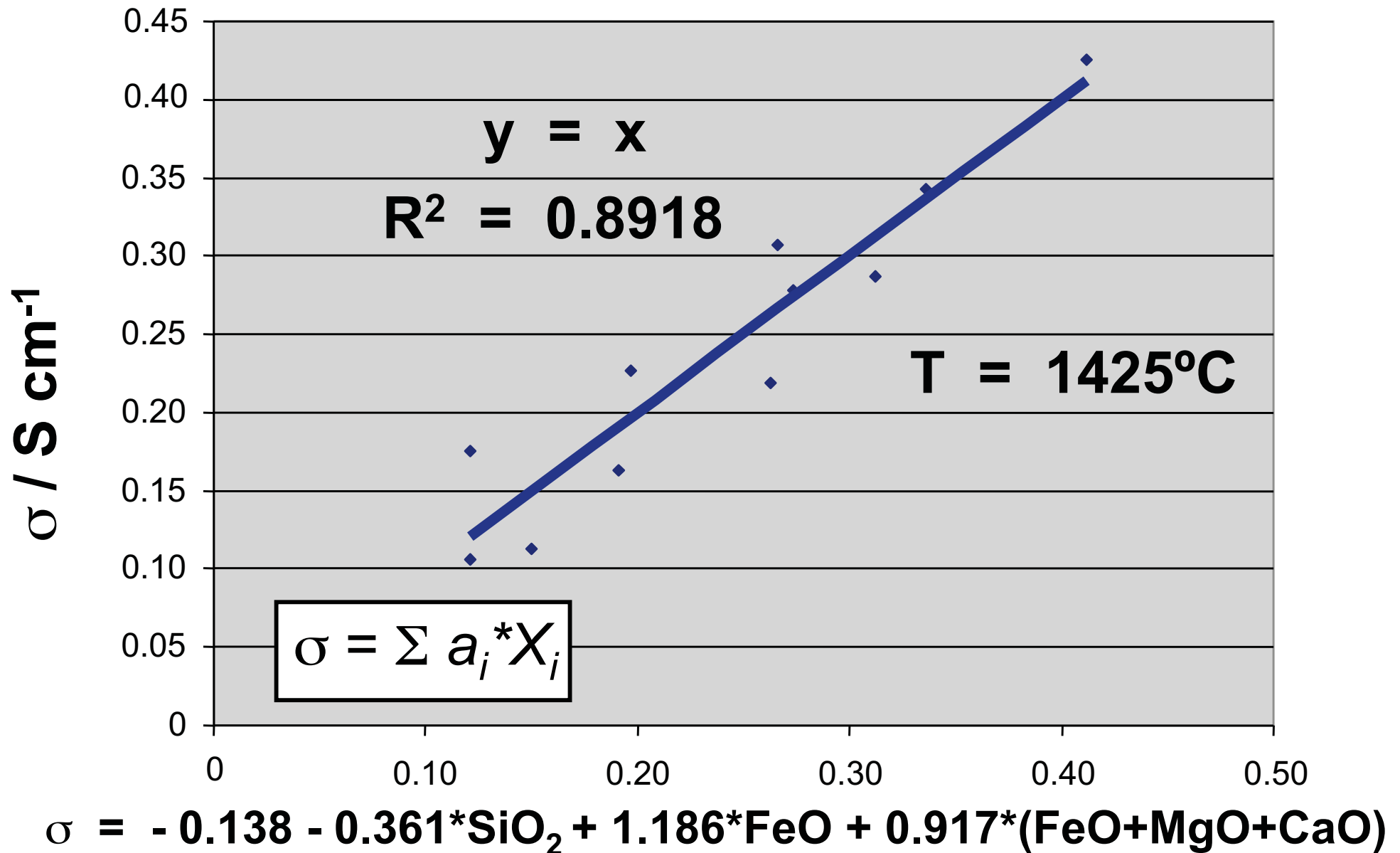
effect of FeO addition: $\sigma = \sigma(T, c)$



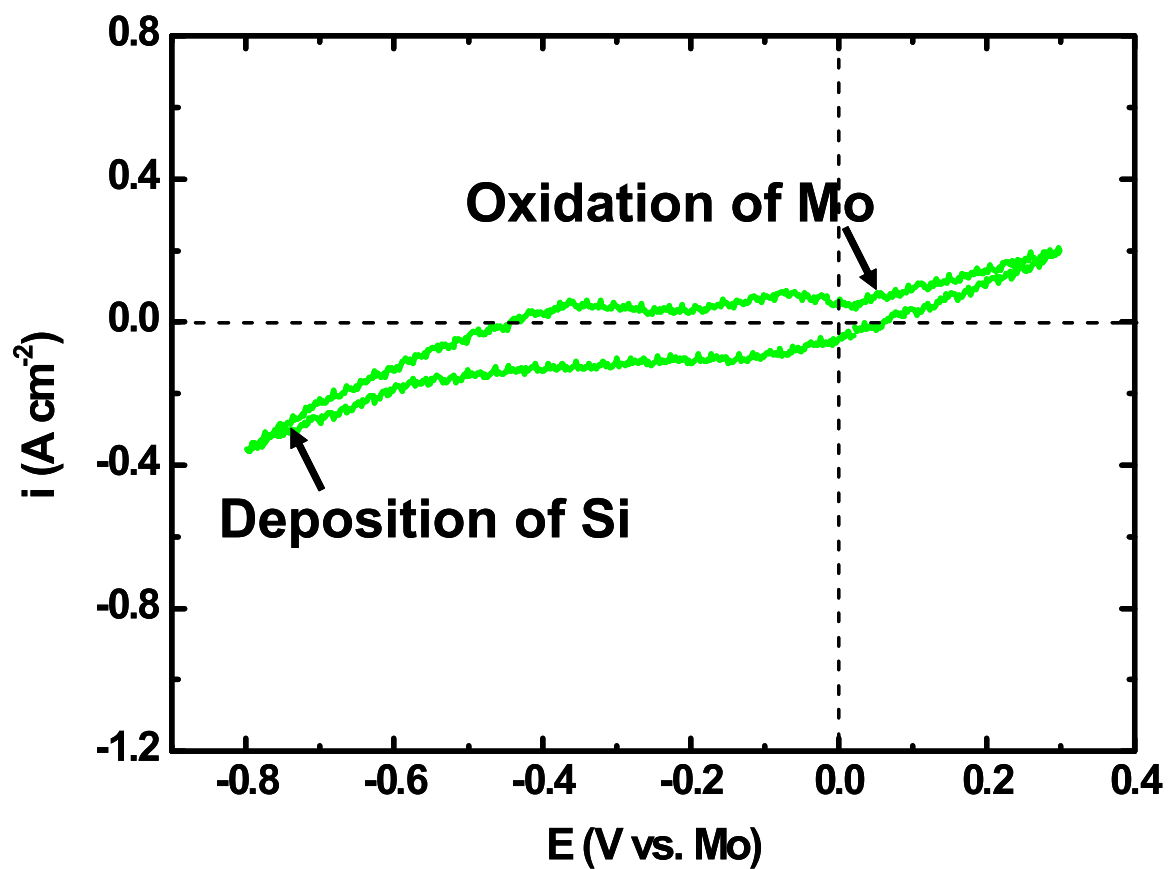
FeO greatly raises conductivity



regression of conductivity data



electrochemistry at white heat

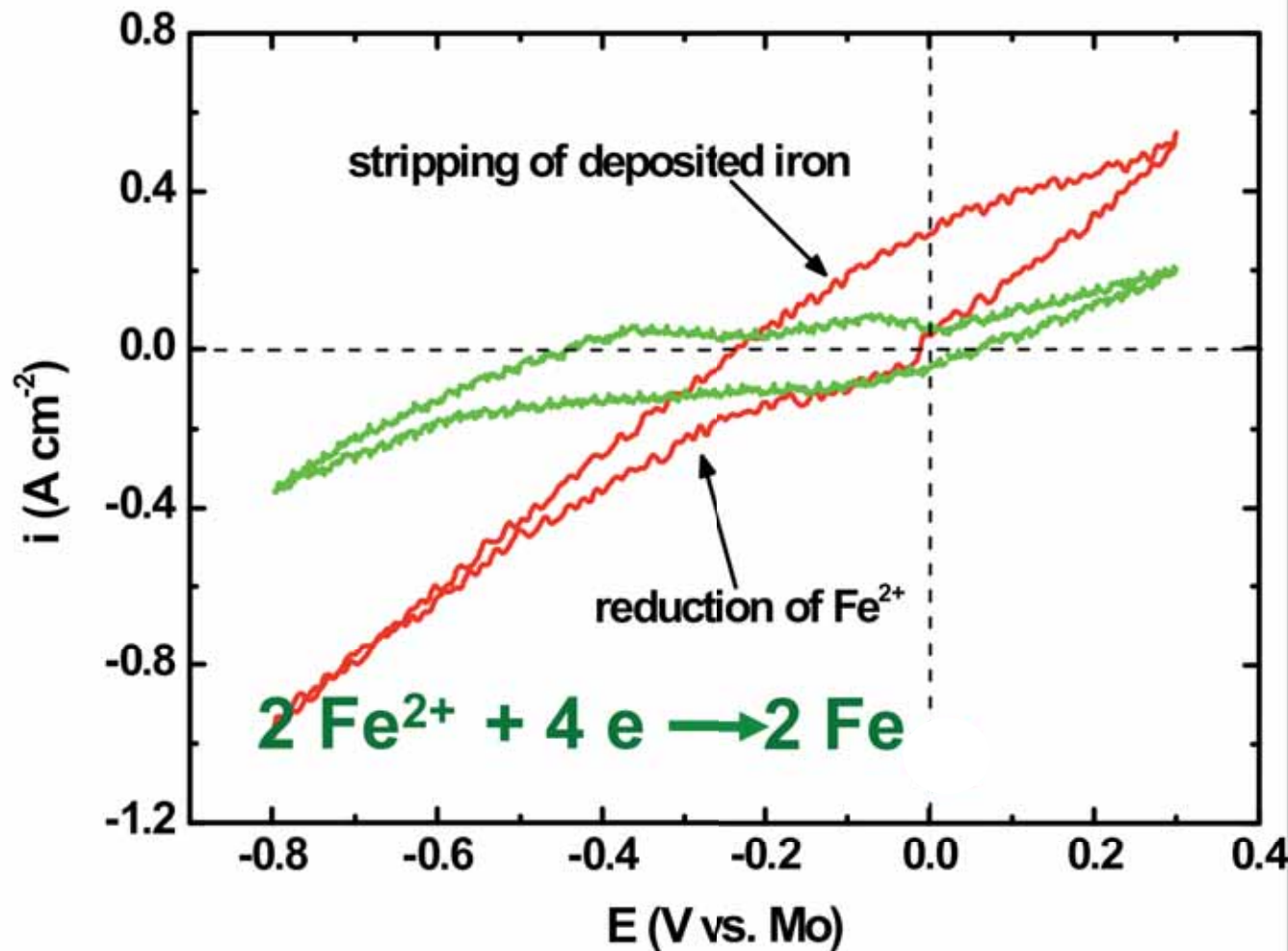


CaO - MgO - SiO₂

scan rate = 50 mV s⁻¹

T = 1575°C

electrochemistry at white heat



add 5% FeO to
CaO - MgO - SiO₂
scan rate = 50 mV s⁻¹
T = 1575°C

--- supporting electrolyte
--- 5 wt% FeO

electrolytic production of molten iron:



cathode: Mo

anode: Pt

electrolyte:

CaO - MgO - SiO₂

feed: FeO

crucible: Mo

reactor tube: Al₂O₃

constant-current electrolysis at 1575°C

current density: $\sim 1 \text{ A cm}^{-2}$

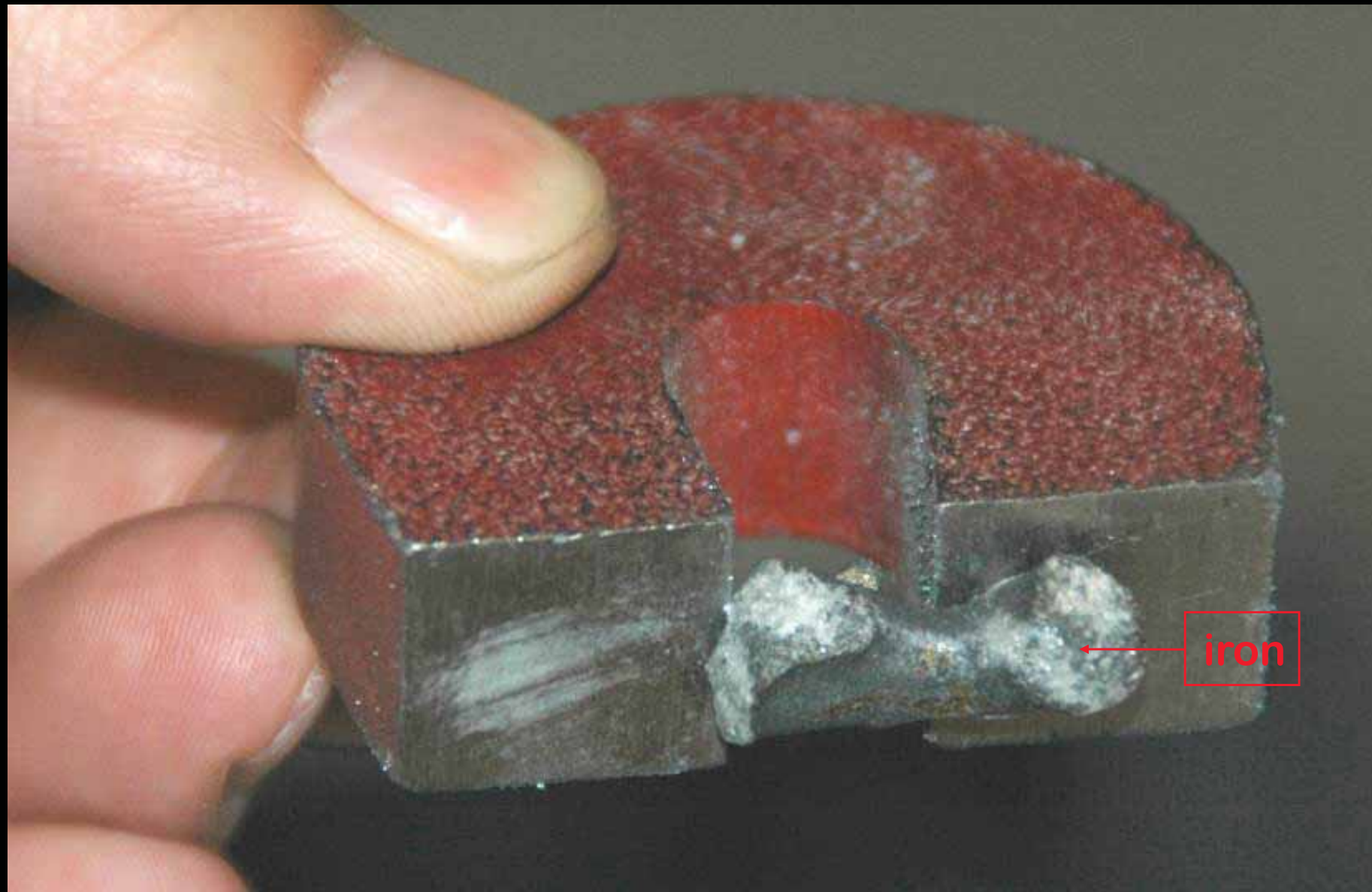
Mo crucible

electrolyte

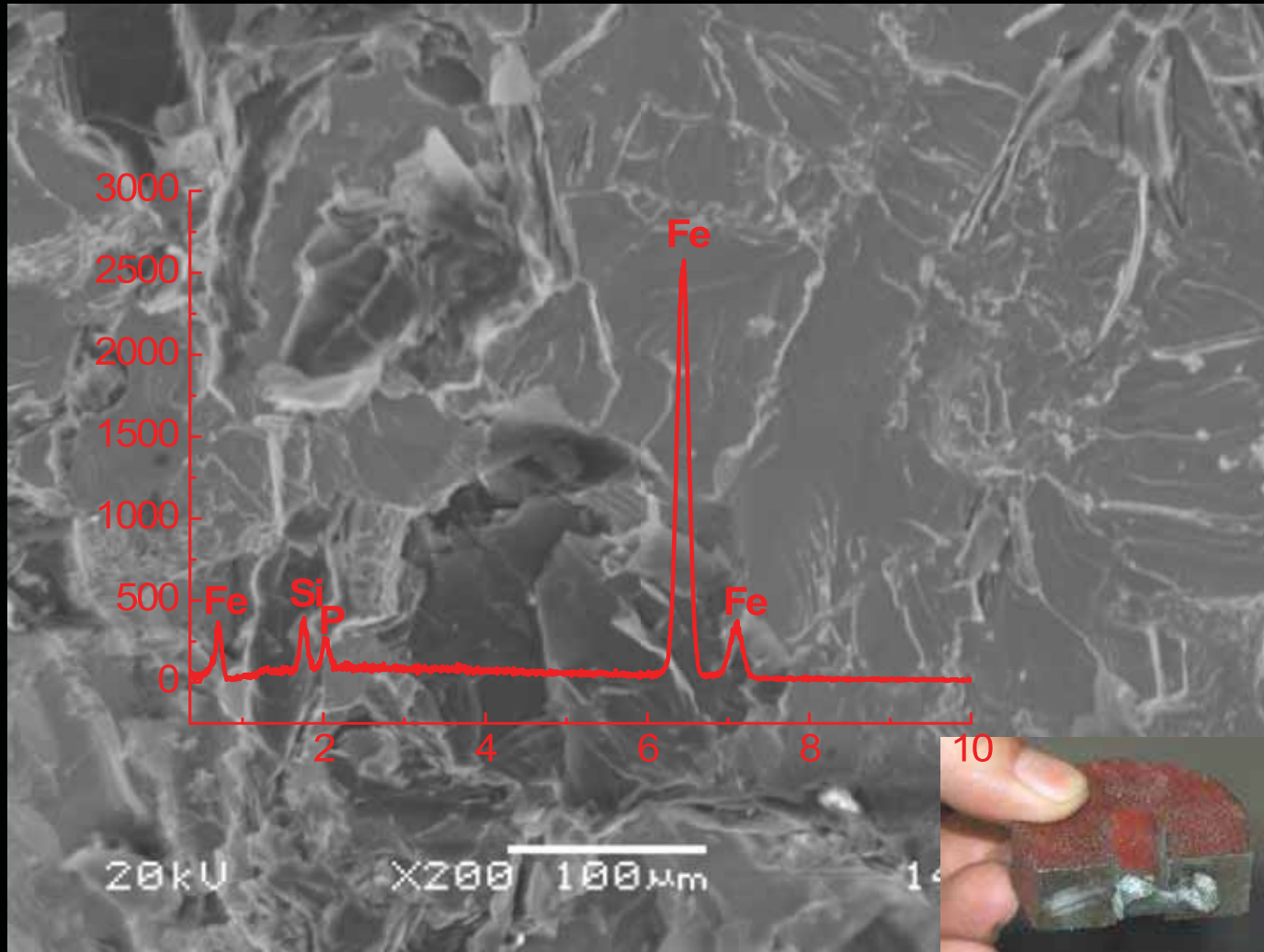
iron



more electrolytic production of molten iron:



SEM and EDX analysis





let's now raise our sights

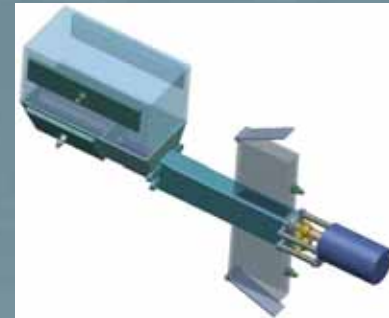
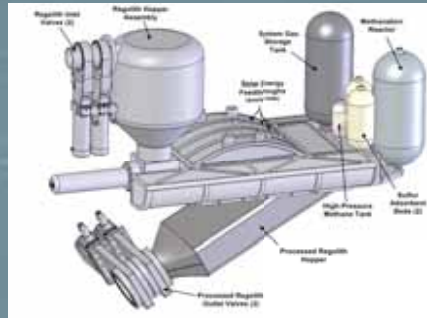
**oxygen generation on the moon
by molten oxide electrolysis:**

- ⇒ sustaining human life**
- ⇒ rocket propellant**

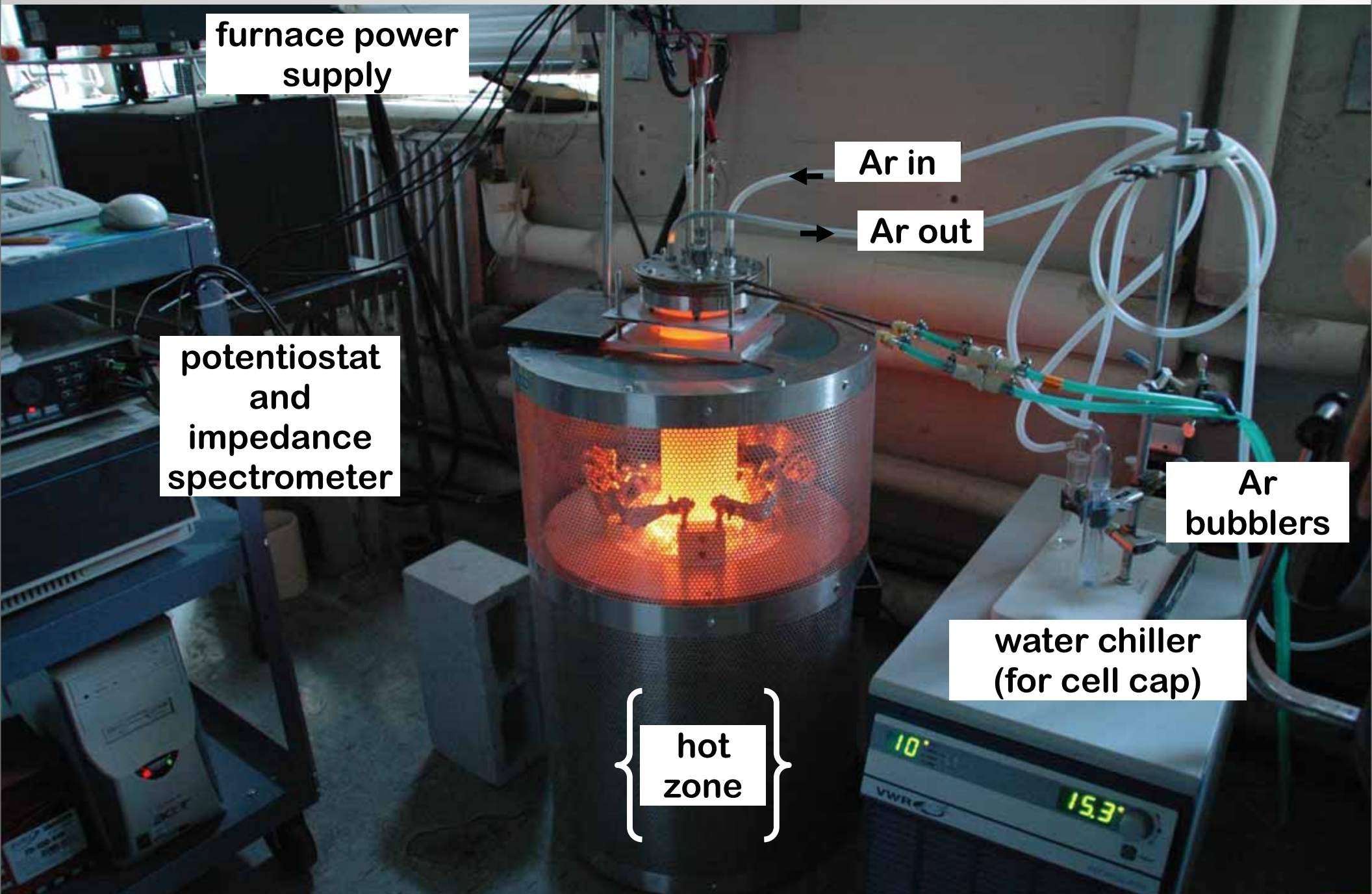


Oxygen Extraction From Regolith

FROM DUST TO THRUST



Lab-scale Cell for Regolith Electrolysis



furnace power supply

Ar in

Ar out

potentiostat and impedance spectrometer

Ar bubblers

water chiller (for cell cap)

hot zone

Lab-so

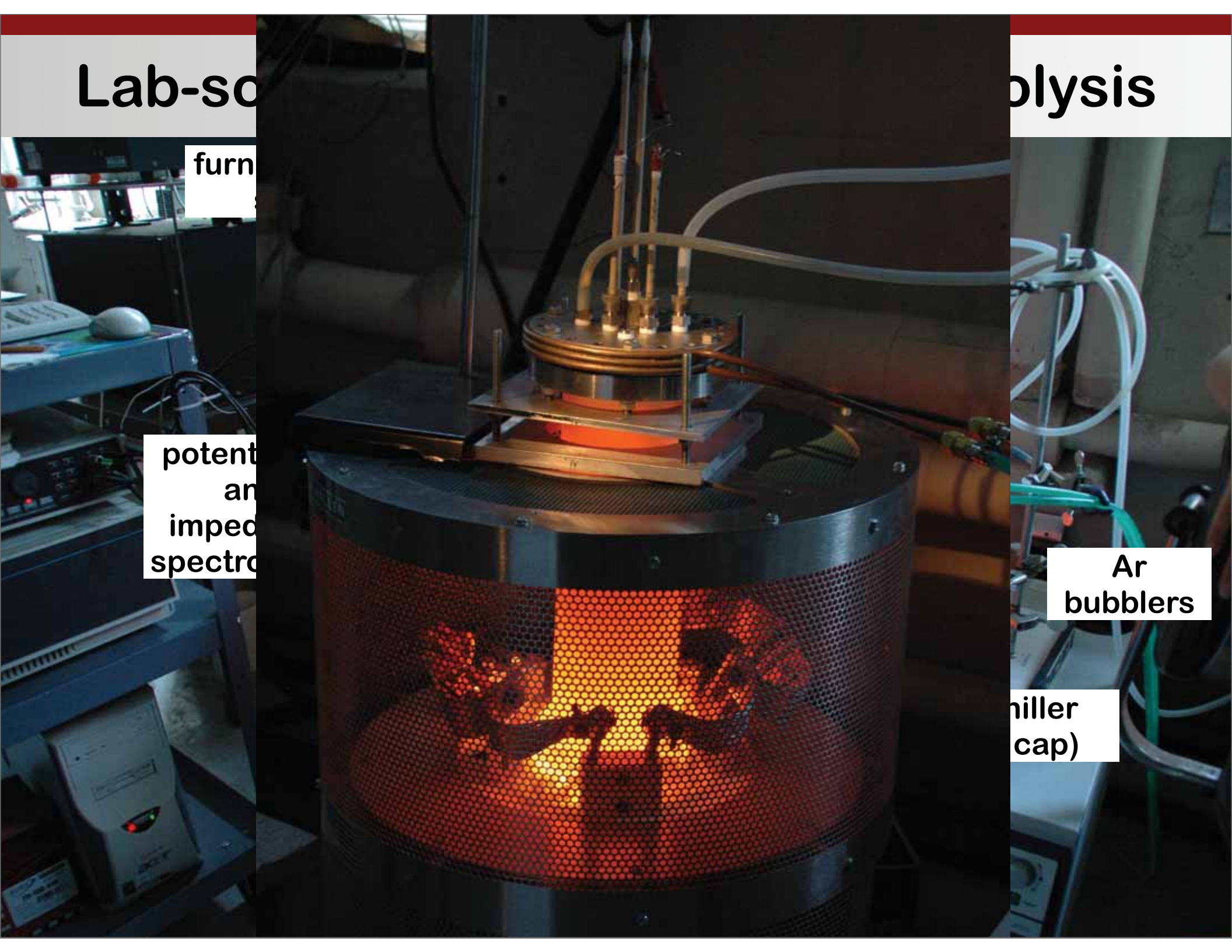
furn

potent
an
impeo
spectro

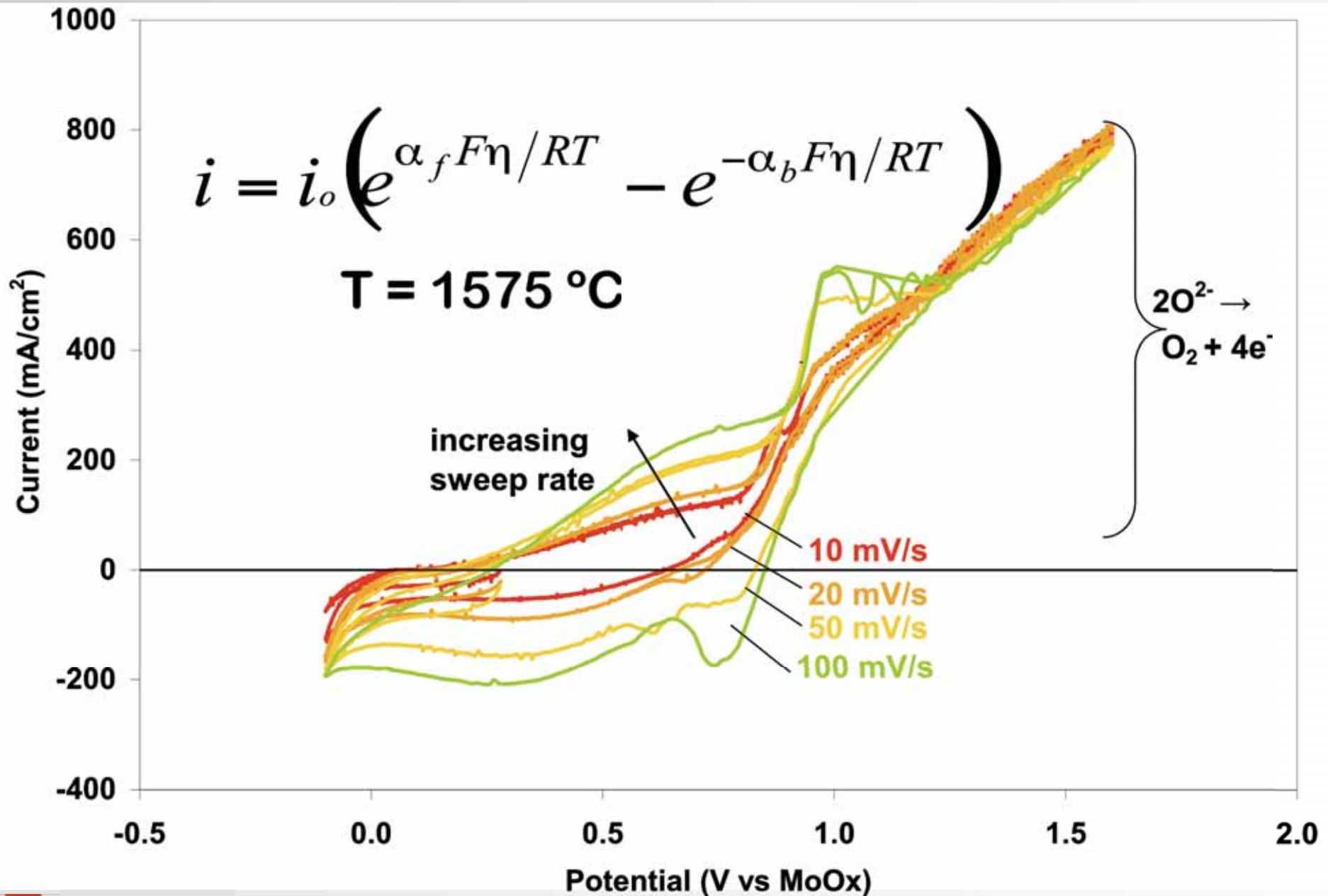
olysis

Ar
bubblers

hiller
(cap)



oxygen evolution kinetics from JSC-1A



Electrochemical Production of Oxygen from Molten Oxides:

Influence of Inert Anode Material and Electrolyte Composition

Presenter: Andrew J. Gmitter

Thesis Supervisor: Prof. Donald R. Sadoway

Masters Seminar

Submitted in Partial Fulfillment for the degree S.M. in

Materials Science & Engineering

December 18, 2007

Optical Basicity: Λ

Oxide	Optical Basicity	Oxide	Optical Basicity
Cs ₂ O	1.7	MnO	1.0
K ₂ O	1.4	ZnO	0.95
BaO	1.15	MgO	0.78
Na ₂ O	1.15	Al ₂ O ₃	0.60
SrO	1.1	SiO ₂	0.48
CaO	1.00	B ₂ O ₃	0.42
FeO	1.0	P ₂ O ₅	0.33
Li ₂ O	1.0		

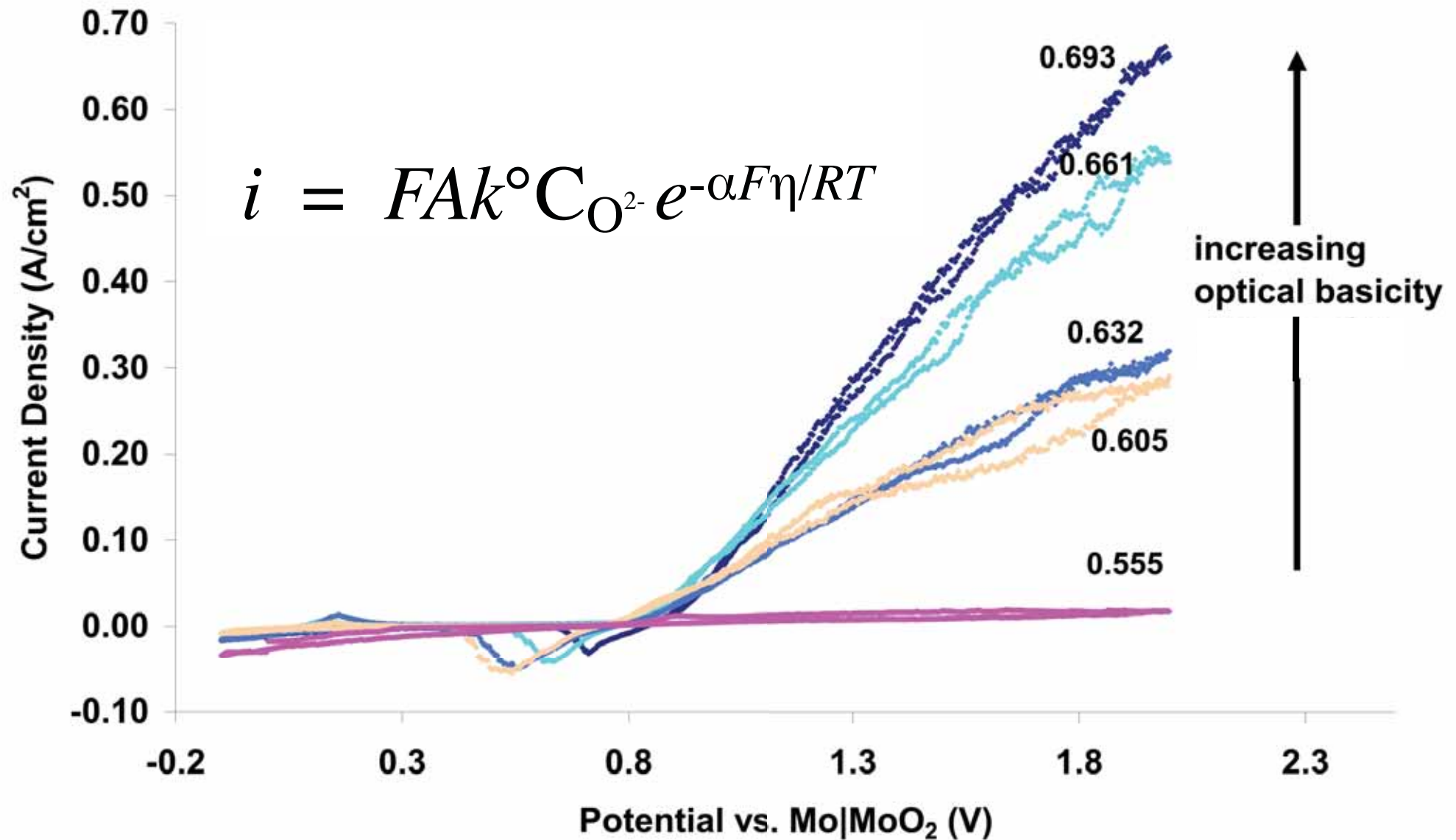
$$\Lambda_{melt} = \frac{\sum_i x_i n_i \Lambda_i}{\sum_i x_i n_i}$$

Λ_i = Basicity for individual oxide

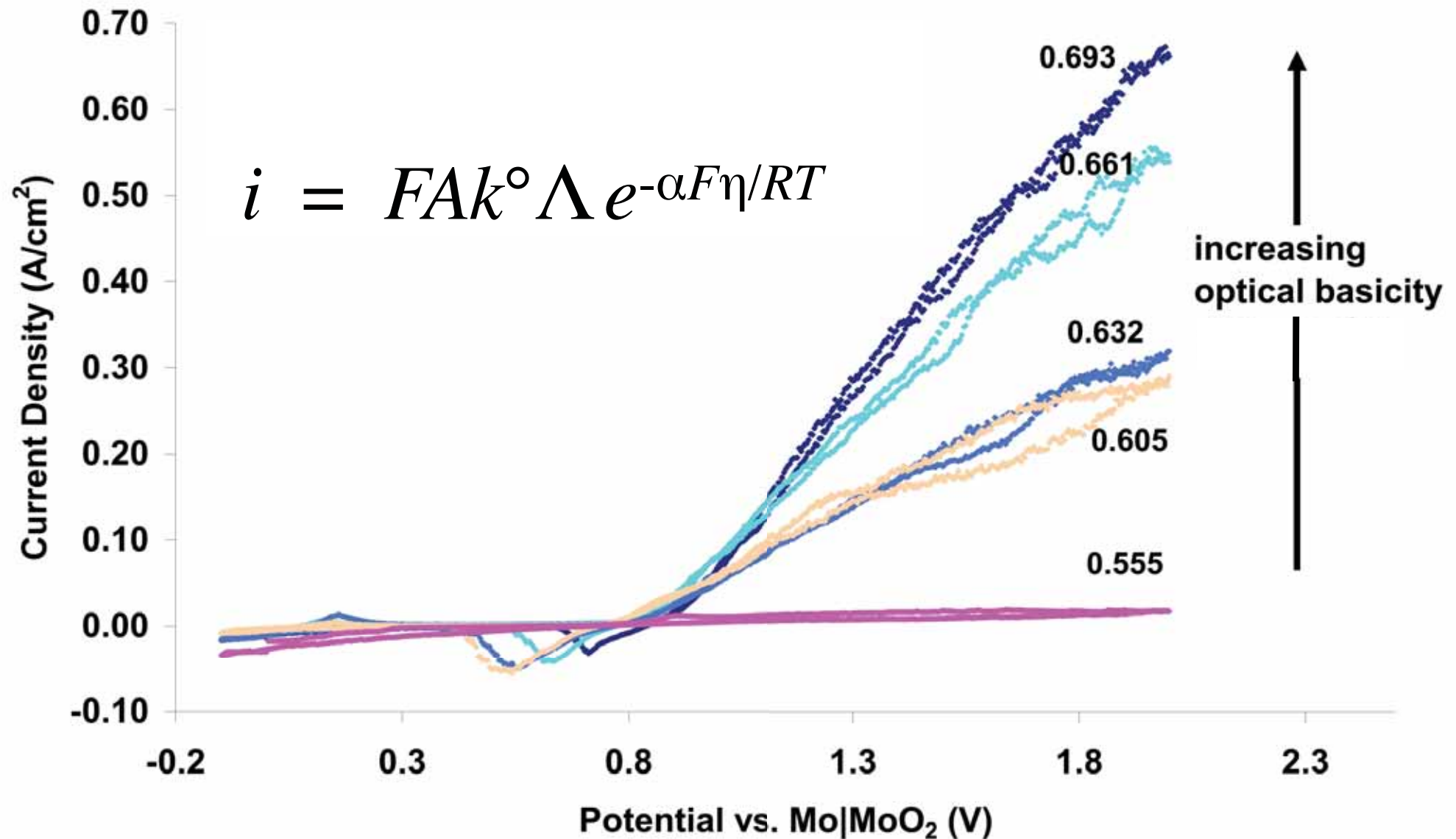
x_i = Mole fraction

n_i = # of oxygen atoms per mole of oxide ($n_{\text{SiO}_2} = 2$, $n_{\text{Al}_2\text{O}_3} = 3$)

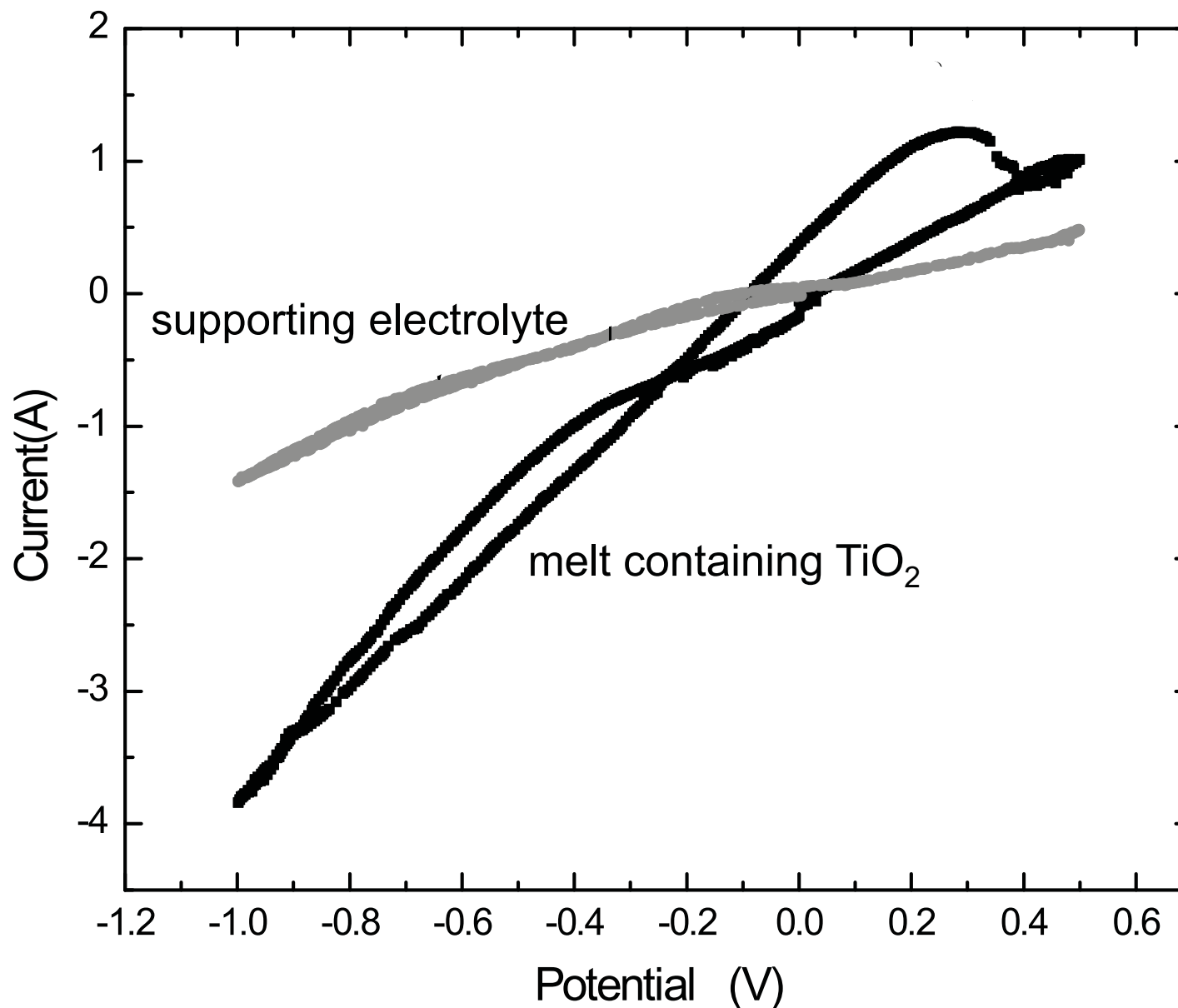
O₂ evolution rate vs. optical basicity



O₂ evolution rate vs. optical basicity



cyclic voltammetry in titanates at 1550°C

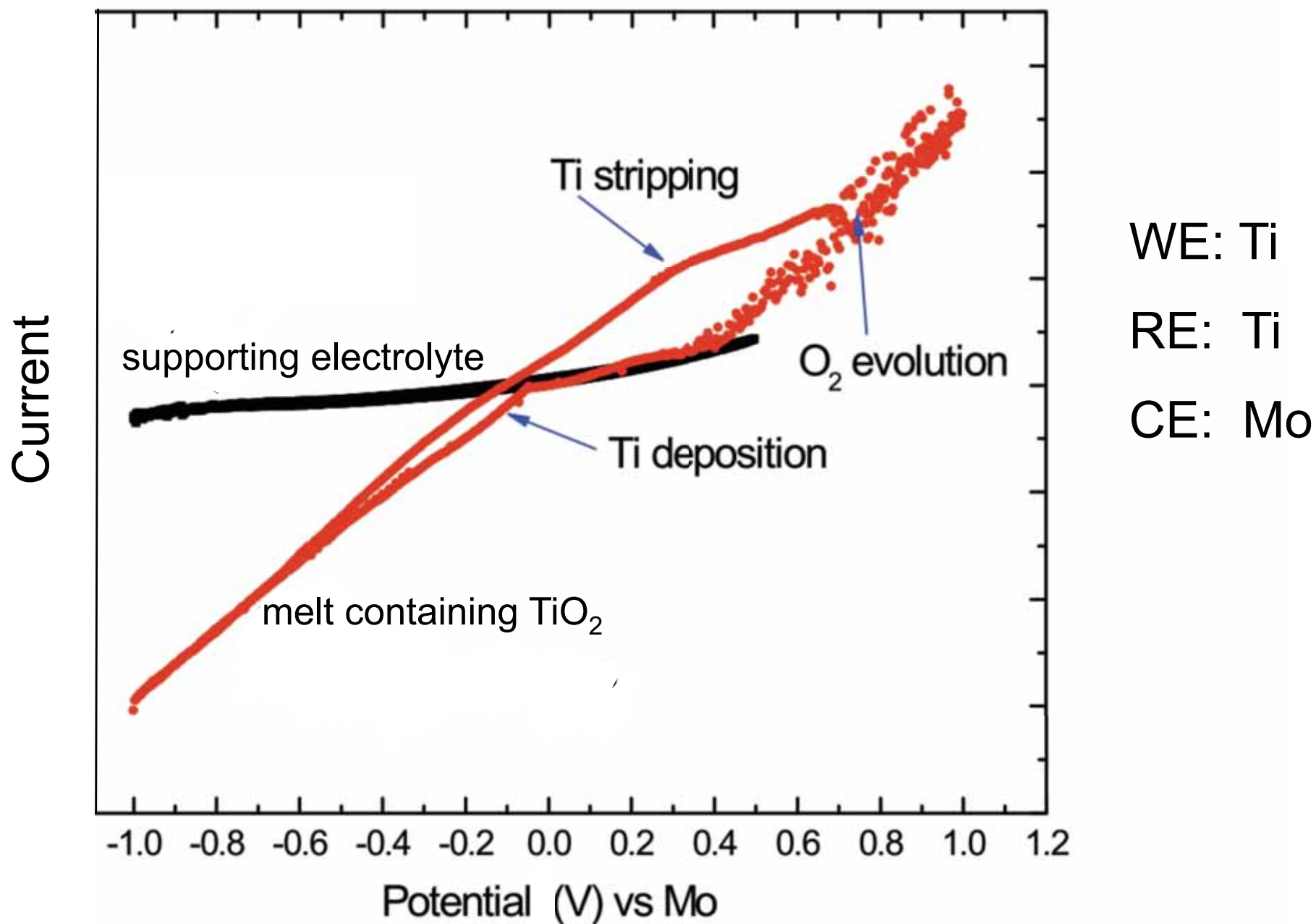


WE: Mo

RE: Ti

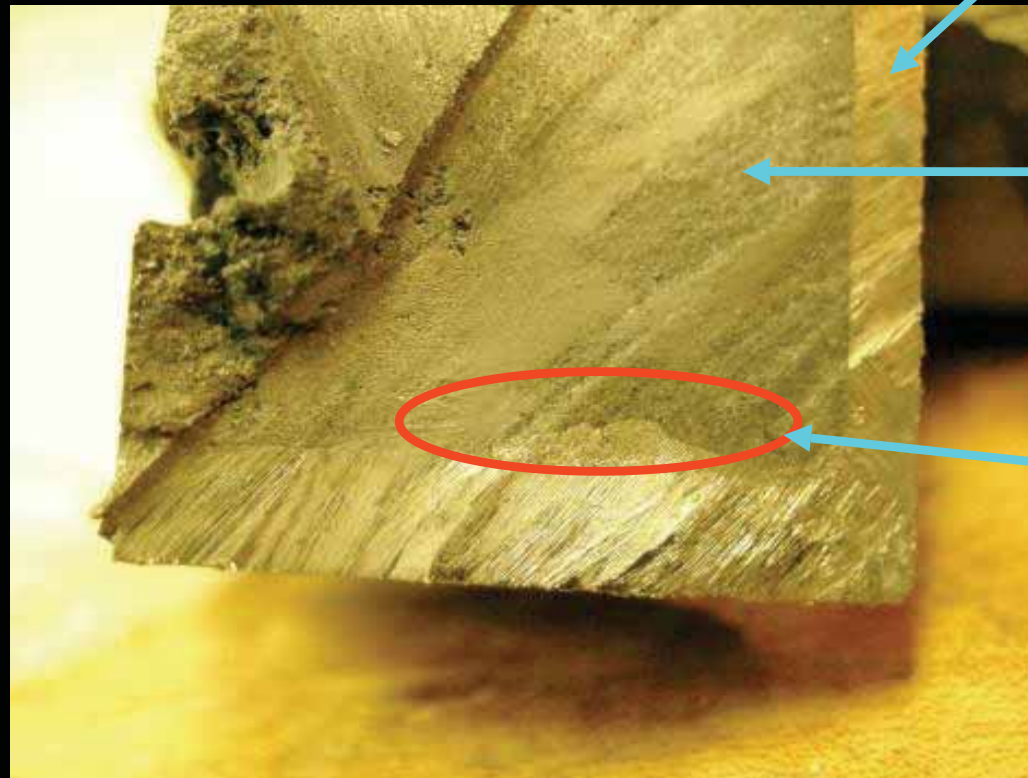
CE: Mo

cyclic voltammetry in titanates at 1550°C



electrolytic production of liquid titanium

$T = 1725^{\circ}\text{C}$ (above m.p. of Ti)



Mo crucible

frozen
electrolyte

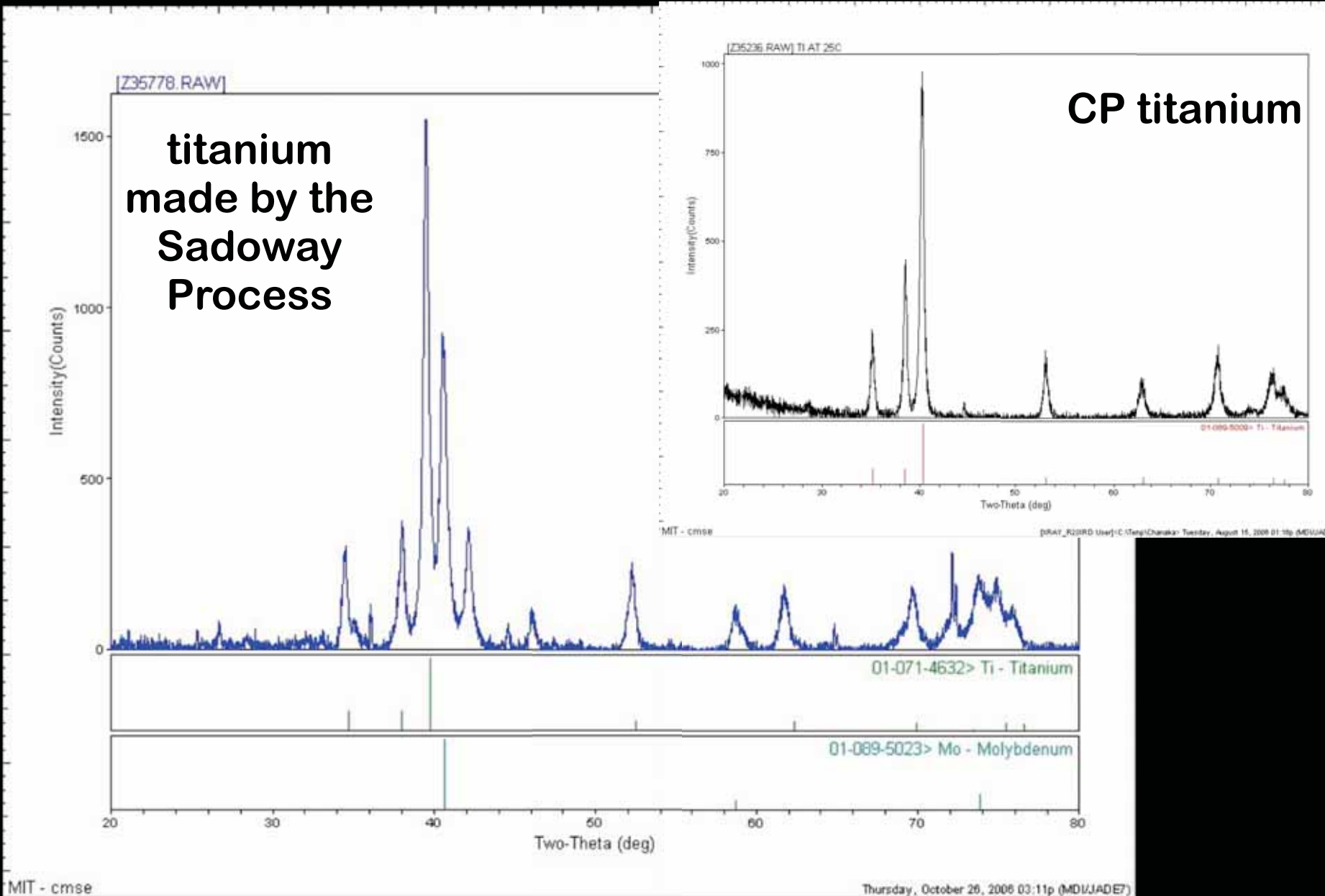
titanium puddle

cathode: Mo

anode: C

current density $\sim 1 \text{ A/cm}^2$

analysis of metal pool indicates titanium



what have we learned?

- ⇒ deposition of Fe, Ti, Ni, & Cr in oxide melts
from oxide feedstock
- ⇒ very high current densities are sustainable
 - ☞ 5 A cm⁻² observed; maybe higher!
c.f. 0.7 A cm⁻² in Hall-Héroult cell
 - ☞ 15× productivity of aluminum smelting
∴ capable of tonnage productivity

what else have we learned?

- first evidence of inert anode
- ☞ full realization of the concept of molten oxide electrolysis
- ☞ carbon-free metal making with tonnage industrial oxygen as by-product

workshop questions

- ① How would low- or zero-cost CO₂ sequestration change the game, and what barriers to separating and capturing carbon would remain?

workshop questions

- ② If carbon-free or carbon-neutral energy carriers were cost competitive with current feedstocks, what technical and economic challenges would prevent the switch to those fuels?

workshop questions

- ③ What are the opportunities for disparate industries to collaborate on carbon management?

workshop questions

- ④ How can industry's specialized knowledge of process engineering and material handling address the grand challenge of reducing carbon emissions?

workshop questions

- ⑤ What are the research priorities in your area of investigation and why?

workshop questions

- ⑥ What barriers exist to successful research and what breakthroughs are needed?

workshop questions

- ⑦ What are the opportunities for fundamental, academic research to develop pathways for technologies to overcome the barriers?

workshop questions

- ⑧ Where do you feel that a contribution by a project such as GCEP could have the most impact?

towards carbon-free metallurgy



The End