

Titanium Extraction by Molten Oxide Electrolysis

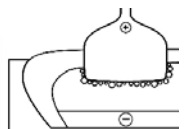
Naomi A. Fried and Donald R. Sadoway

Department of Materials Science & Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts

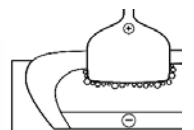
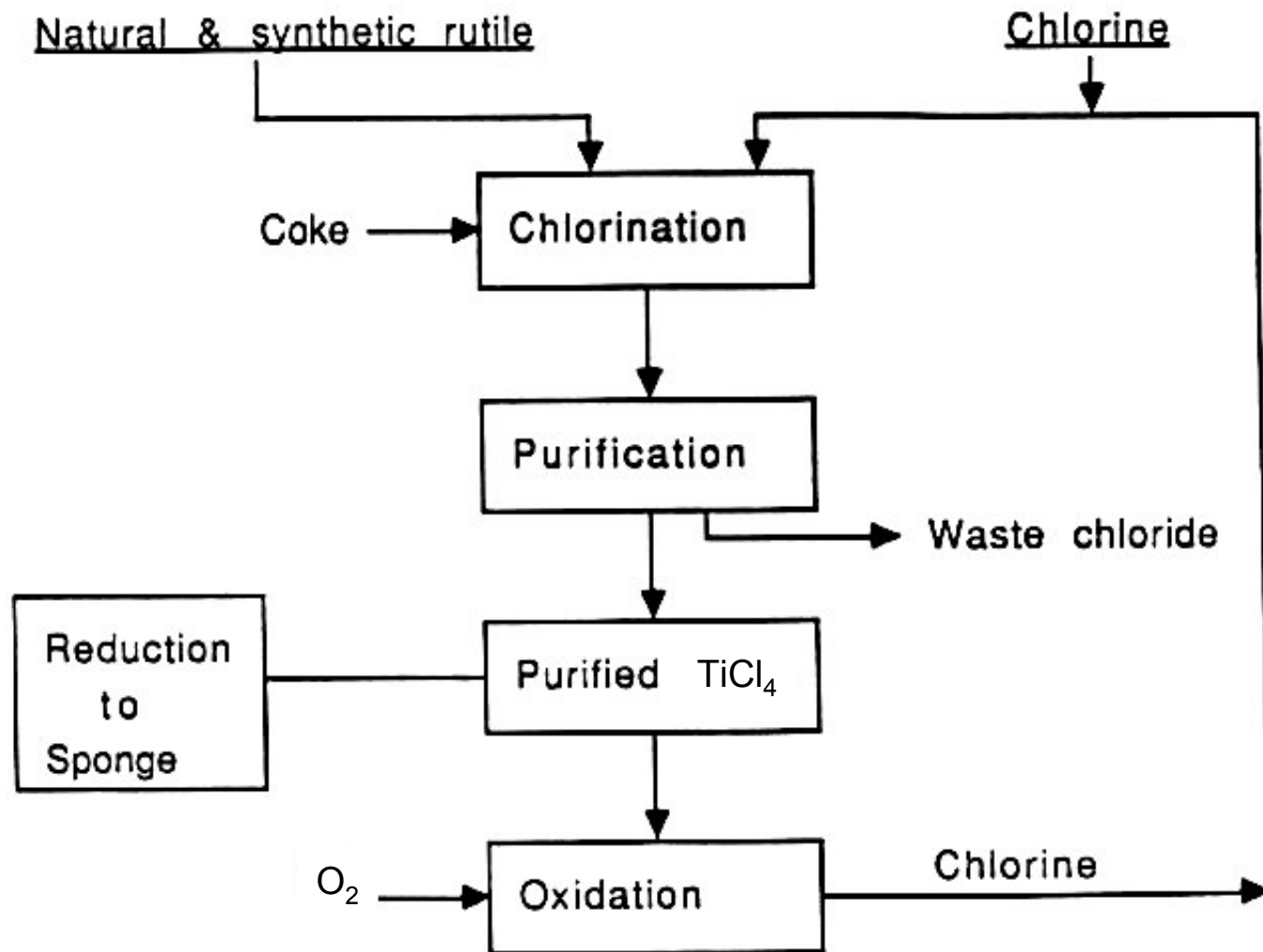
the need for new technology

problems with Ti extraction today:

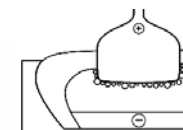
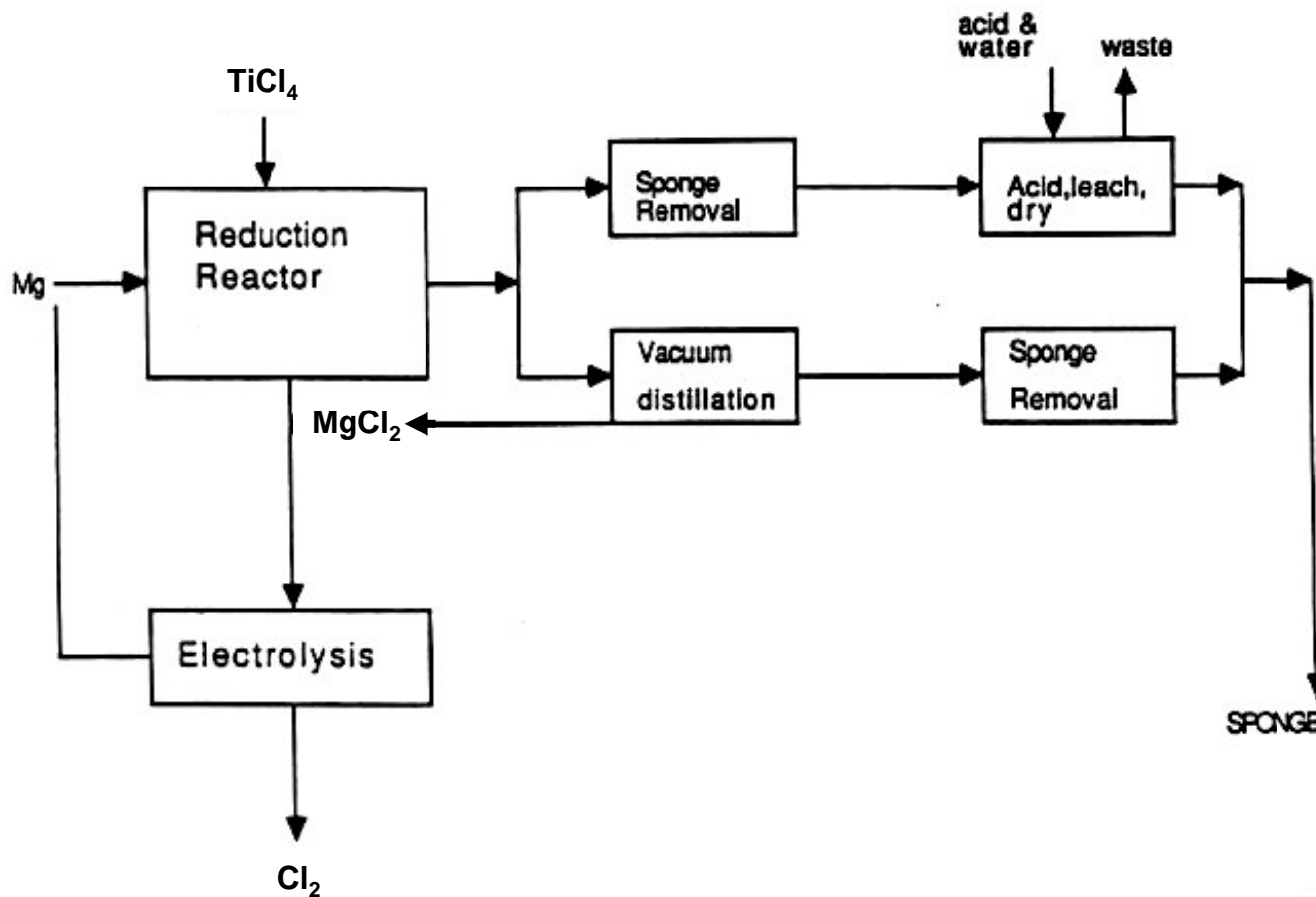
- ❑ many unit operations ☹️
 - ⇒ high capital costs
 - ⇒ high operating costs
- ❑ environmental liabilities ☹️
 - ⇒ C & Cl in presence of O
 - ☞ dioxins? furans? ☠️



Titanium extraction: the front end



Titanium extraction: Kroll reduction



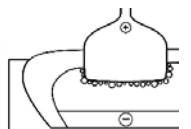
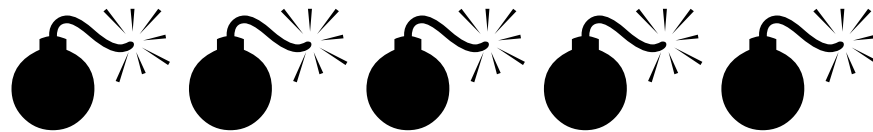
a technological response?

most metals are found in nature as oxides

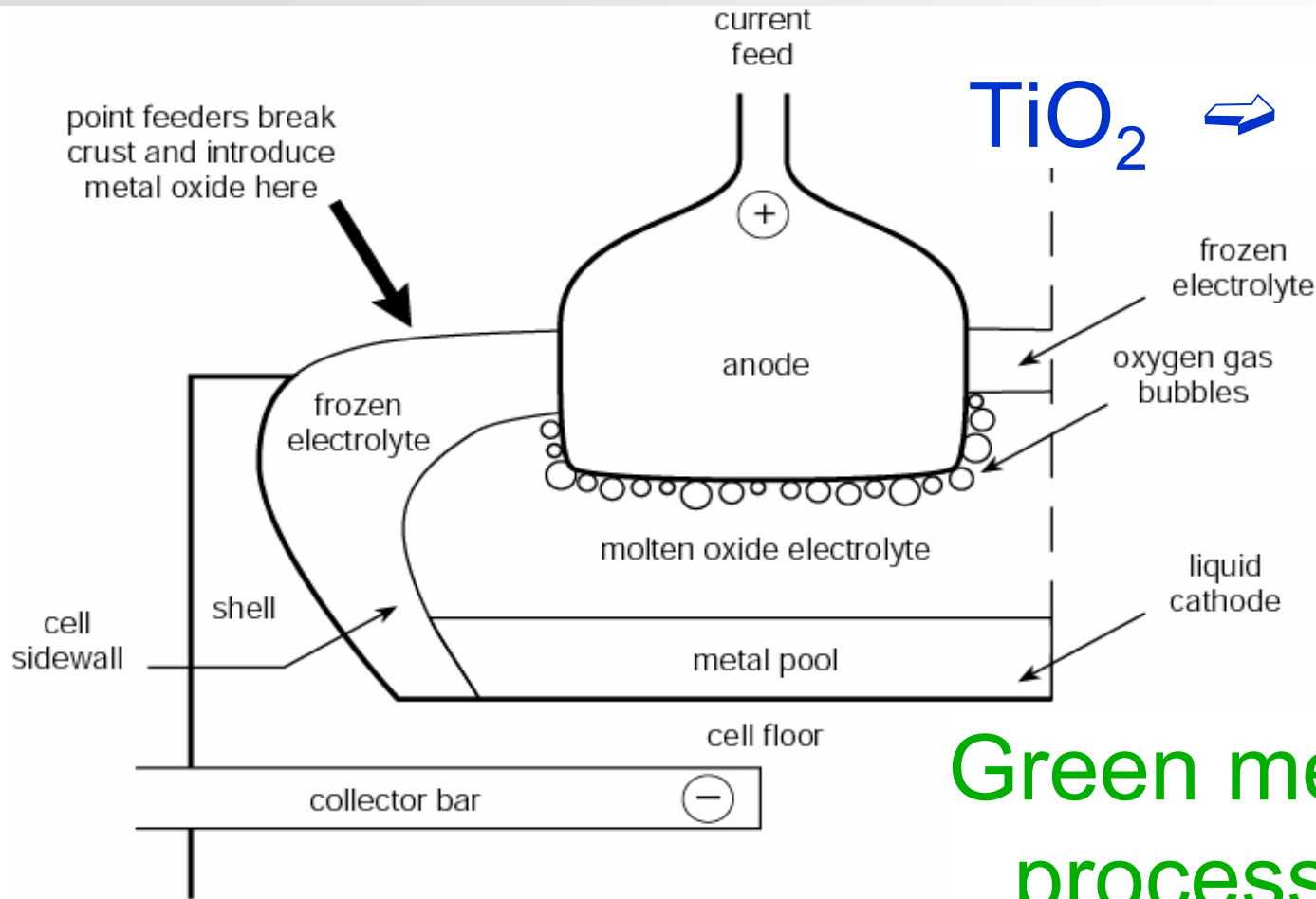
“like dissolves like”

molten oxide electrolysis:

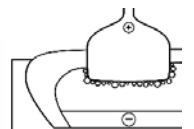
extreme form of molten salt electrolysis
where pure **oxygen** gas is by-product



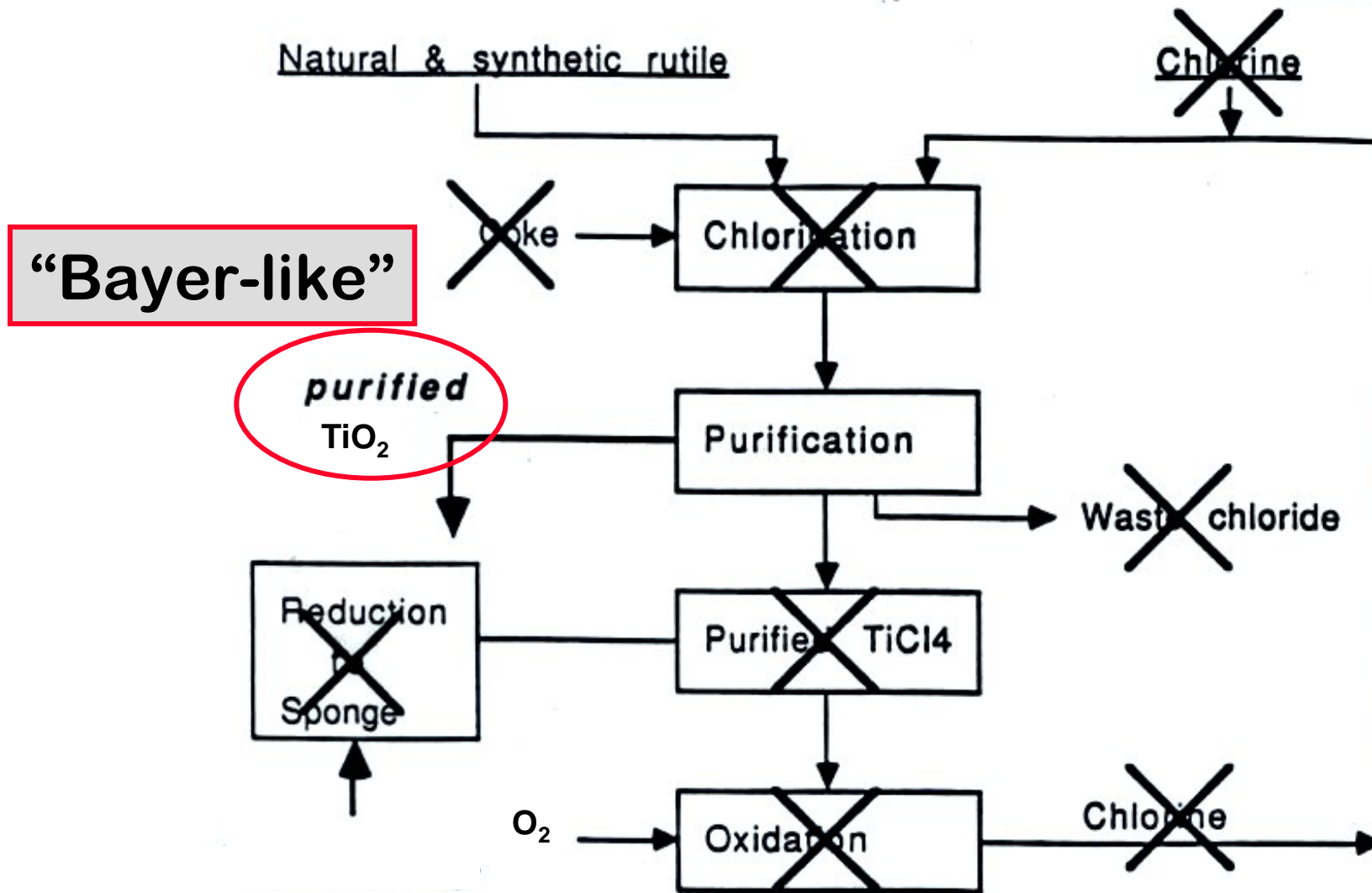
schematic of prototype cell



Green metallurgy:
processes emitting
only products

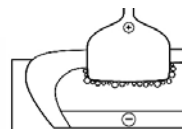


Molten oxide electrolysis: the front end

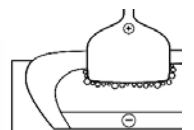
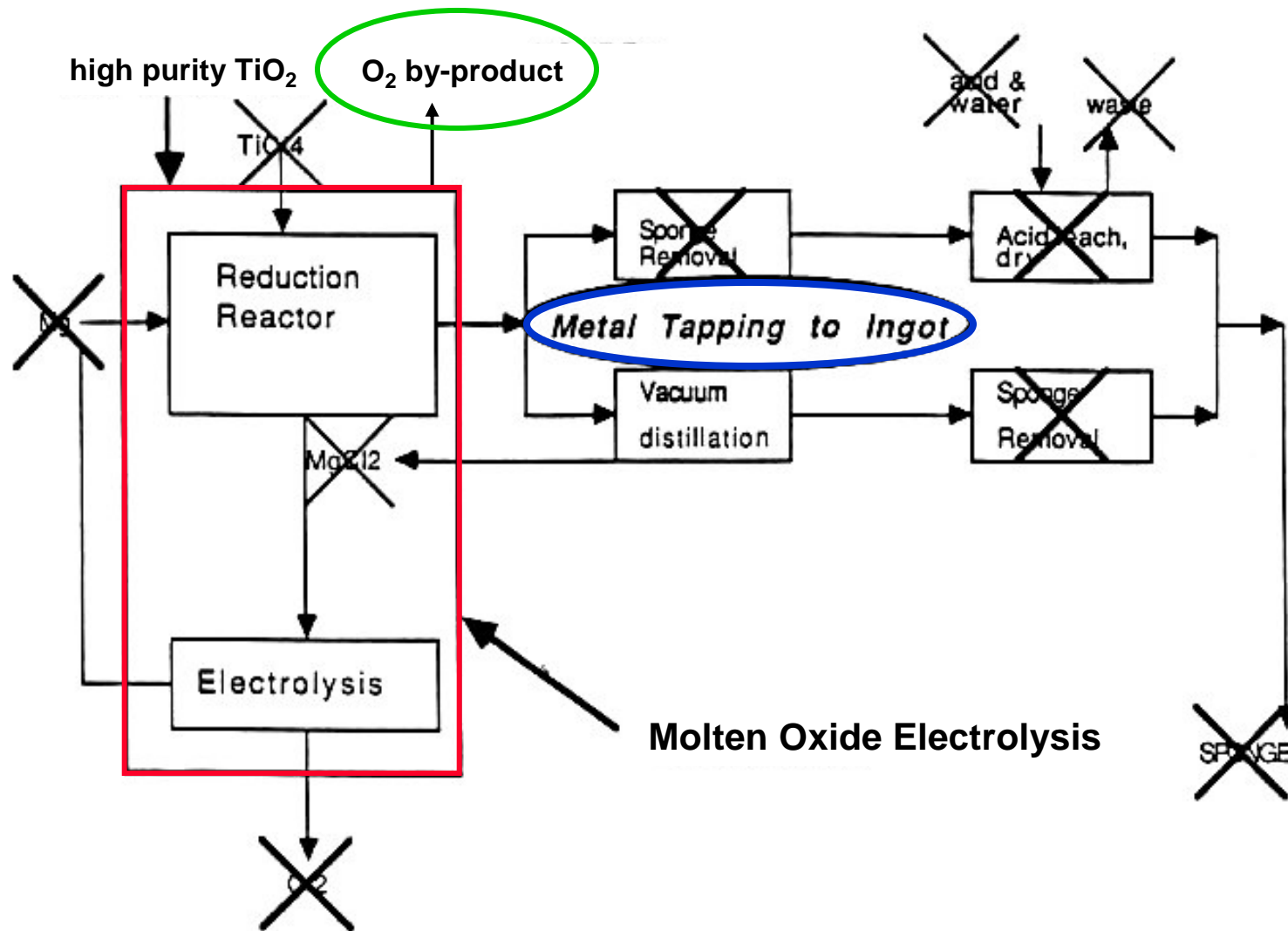


"Bayer-like"

purified
TiO₂

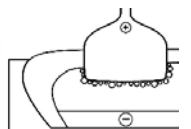


Molten oxide electrolysis:



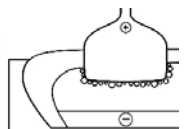
feasibility assessment: issues

- ❑ molten titanates reportedly exhibit electronic conduction
- ❑ inert anode operable at 1700°C



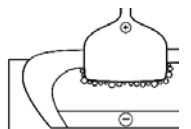
feasibility assessment: current study

- electrical conductivity measurements
- transference number measurements
- modeling electrical properties
- applicability to titanium production



conductivity measurements

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

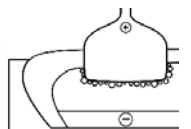
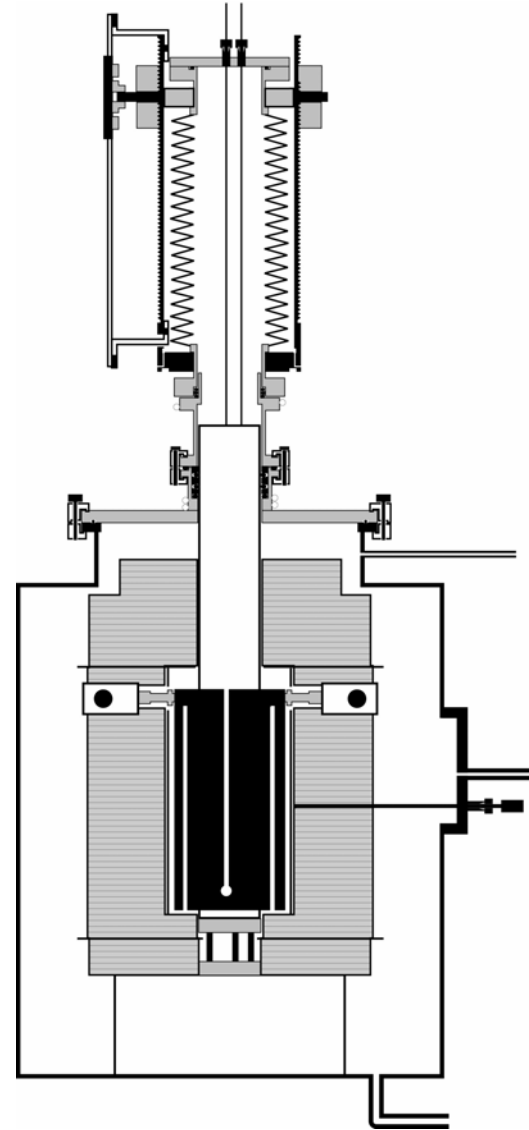


experimental apparatus

conductivity measurements:

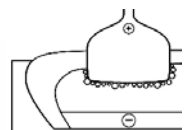
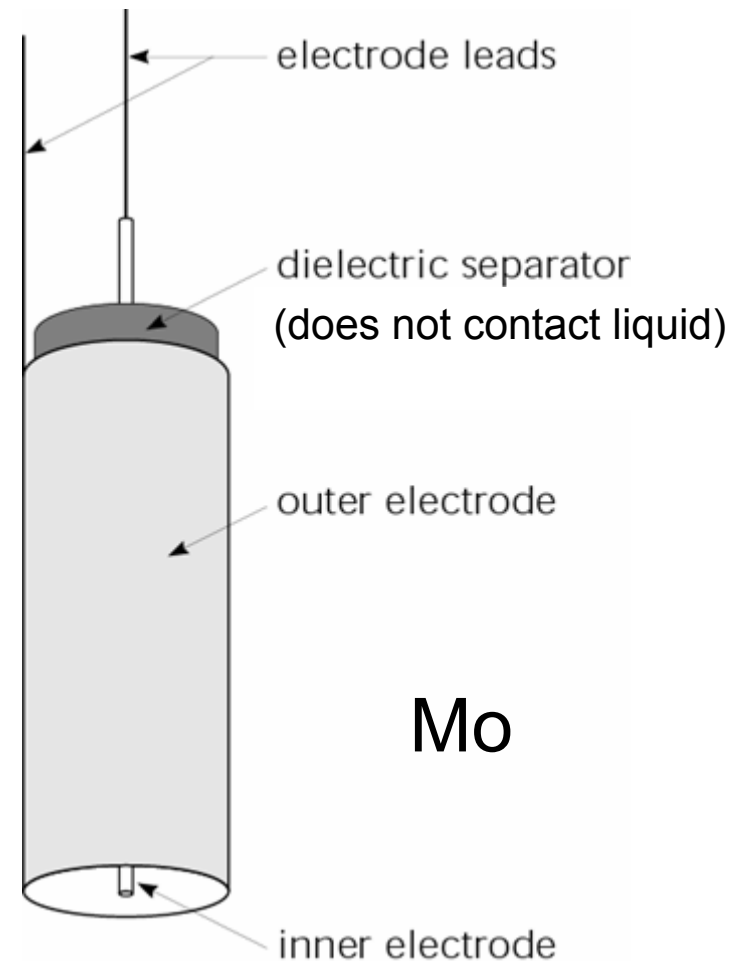
- impedance spectroscopy
- varying immersions or
varying interelectrode gap

☞ isolate melt resistance



all-metal, coaxial-cylinder electrode

enabling high-accuracy
conductivity
measurements in the
most chemically
aggressive melts



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.

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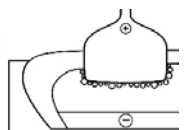
Primary Examiner—Kenneth A. Wieder

Assistant Examiner—Christopher M. Tobin

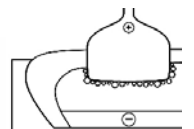
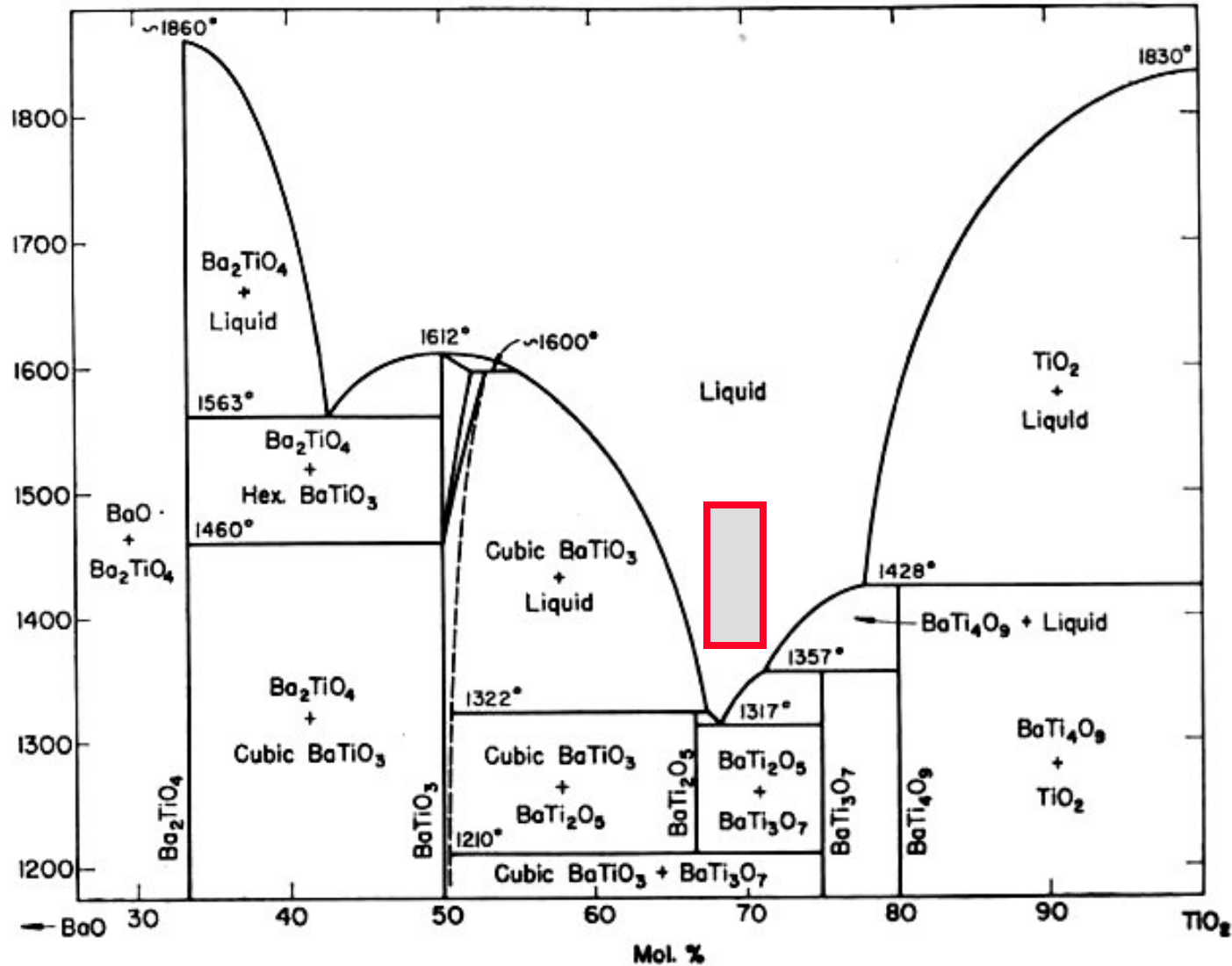
Attorney, Agent, or Firm—Hamilton, Brook, Smith & Reynolds

[57] **ABSTRACT**

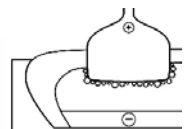
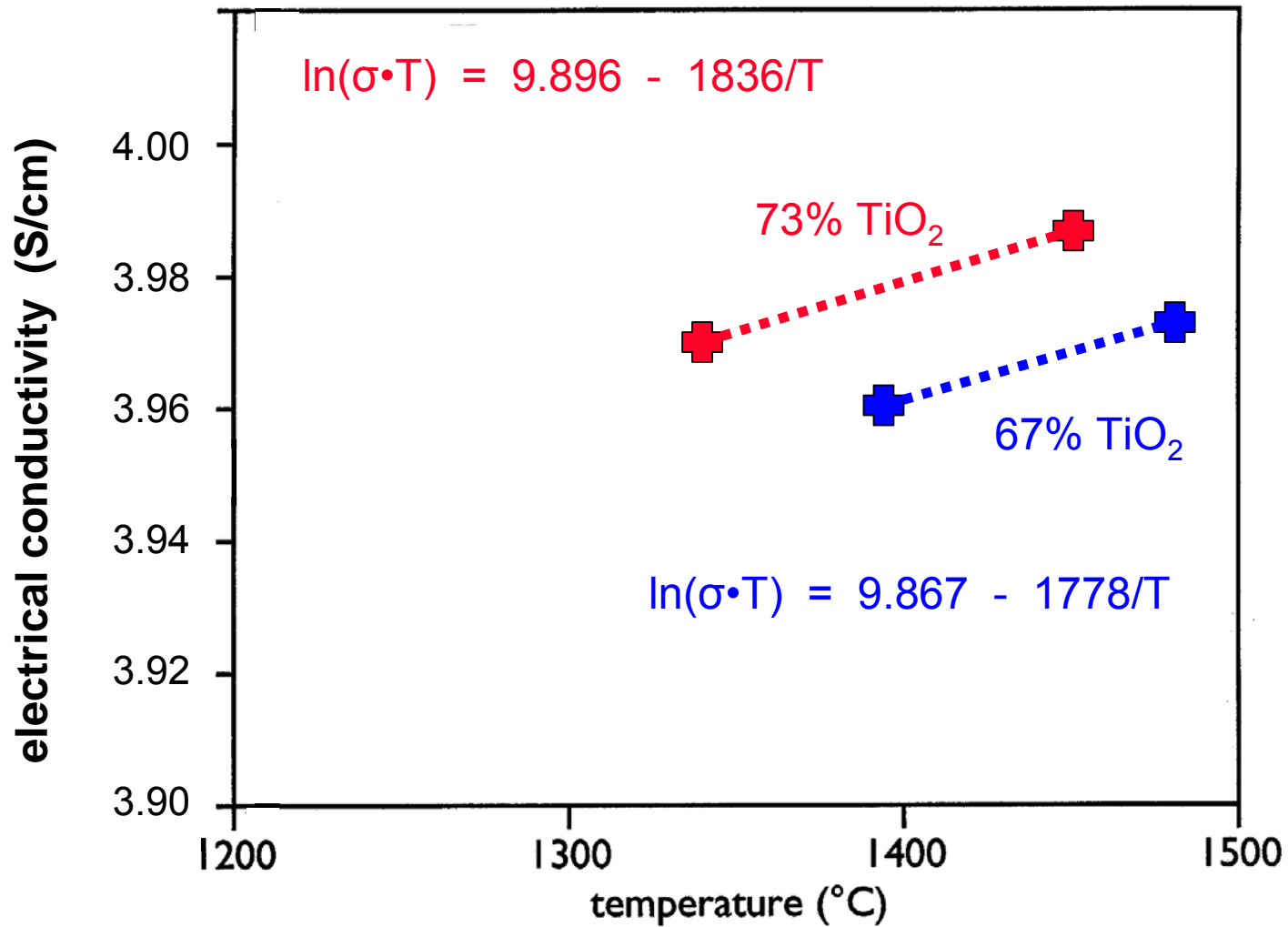
An apparatus and method for measuring electrical parameters of a medium such as electrical conductivity and dielectric constant between a pair of electrodes are disclosed. The medium can be a liquid, gas, powder, etc., and the electrodes can be coaxial metallic circular cylinders. To



TiO₂ – BaO phase diagram

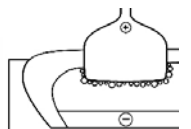
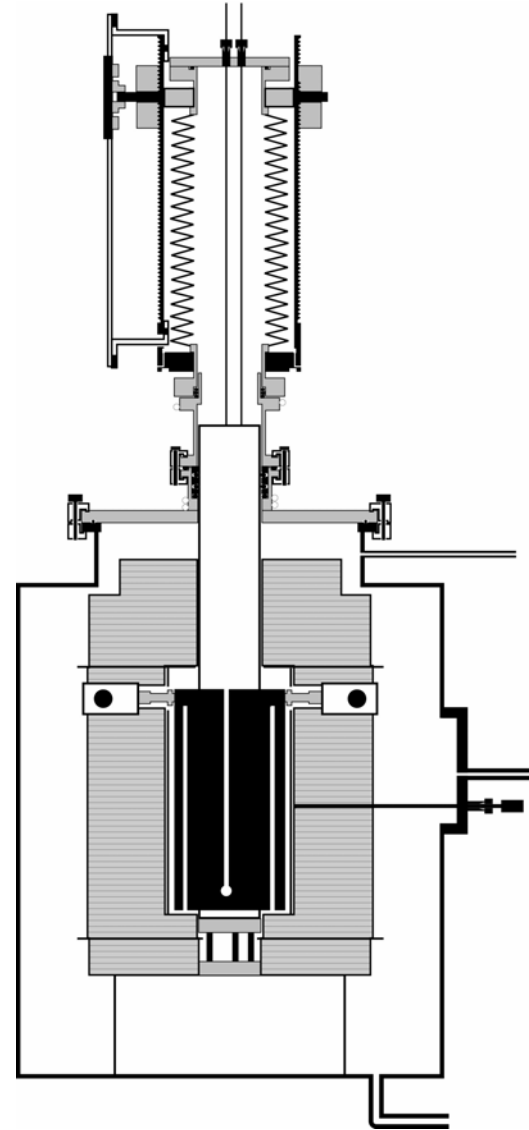


tailoring electrical properties

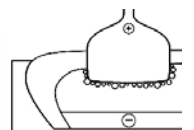
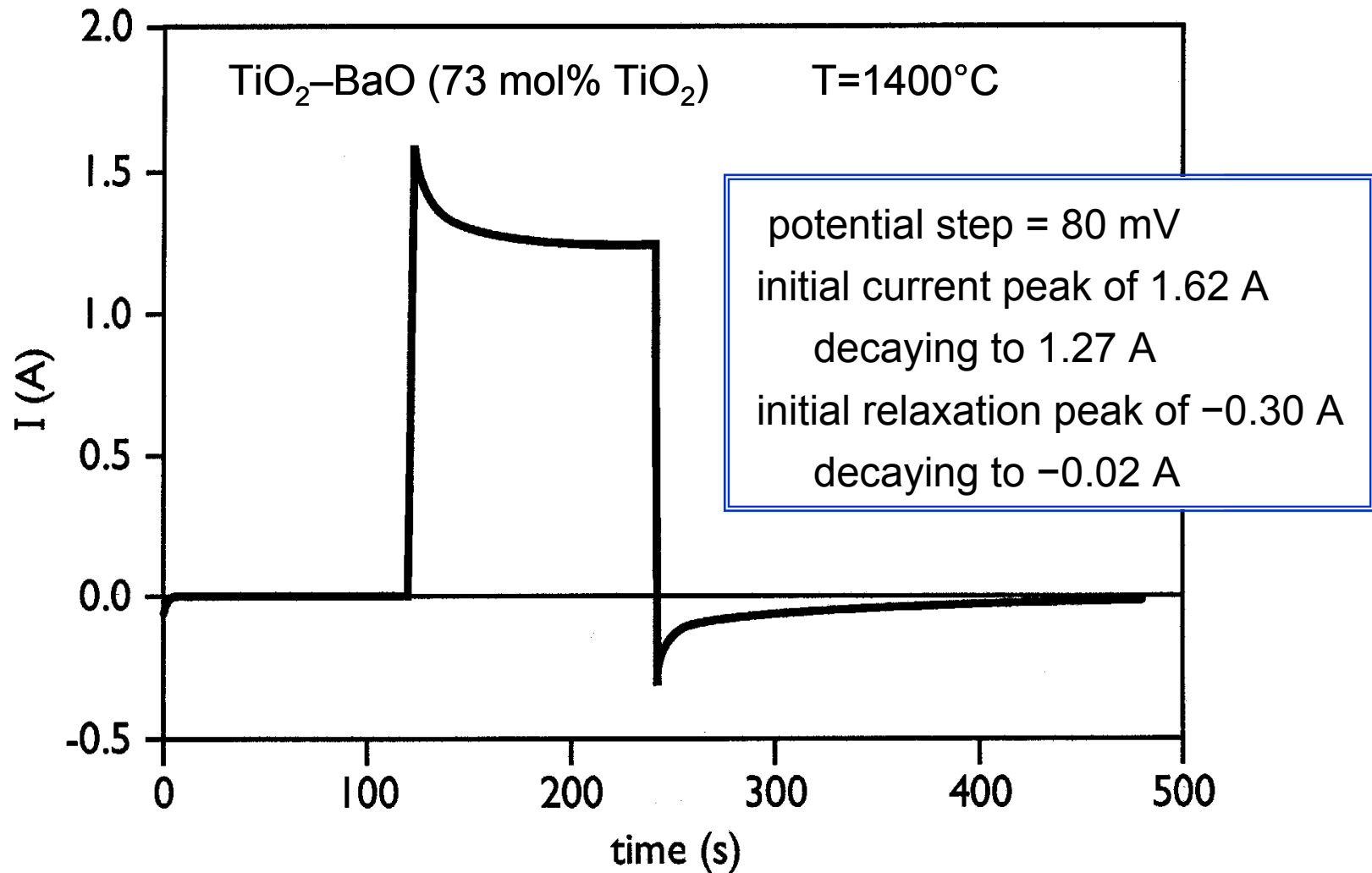


transference number measurements

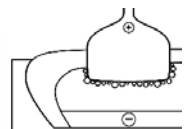
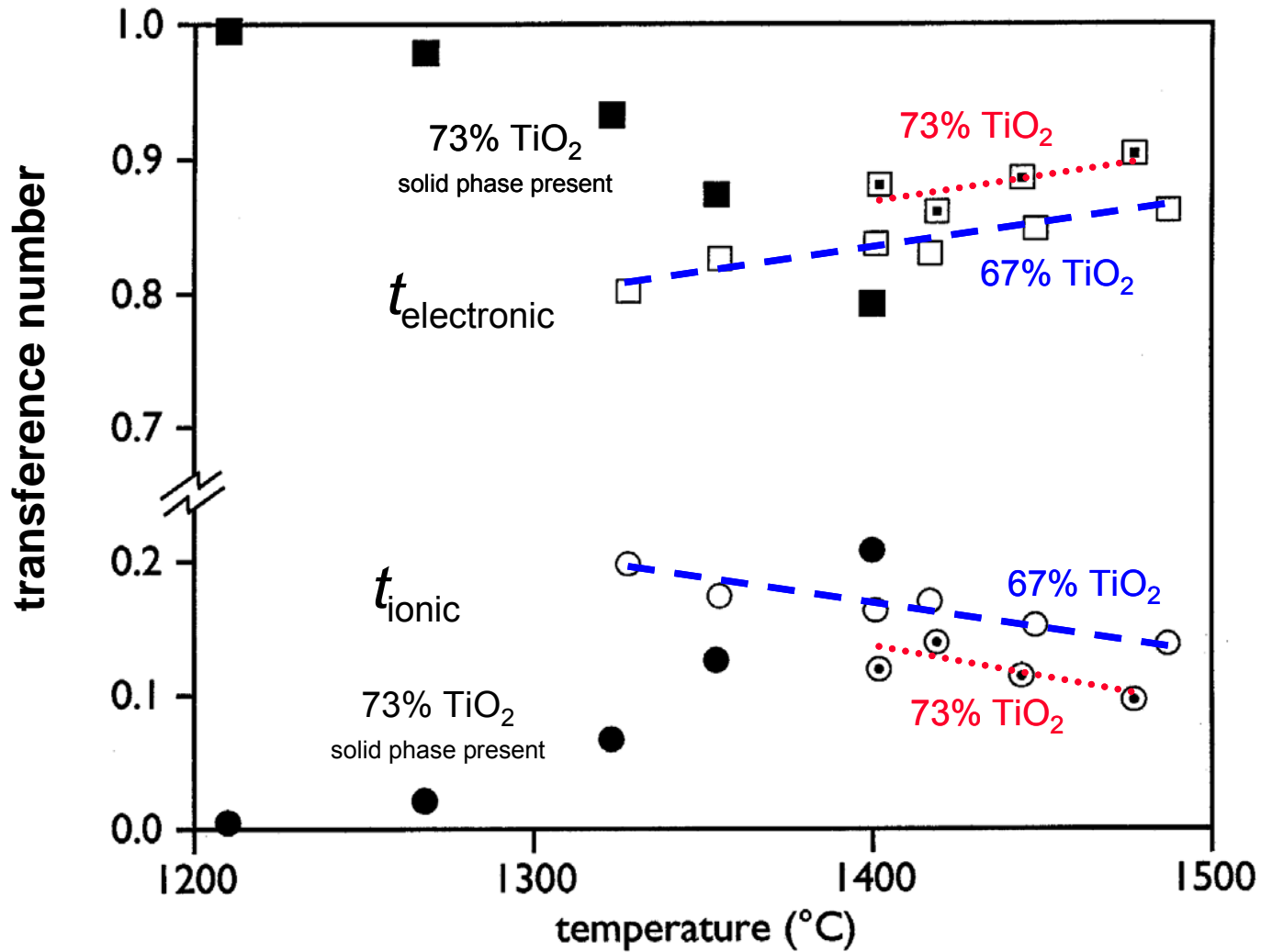
- stepped-potential chronoamperometry with impedance correction
- ☞ isolate electronic and ionic components of conductivity



stepped-potential chronoamperometry



tailoring electrical properties

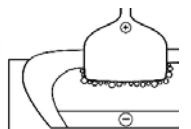


electrowinning experiments

☐ galvanostatic electrolysis at 1450°C

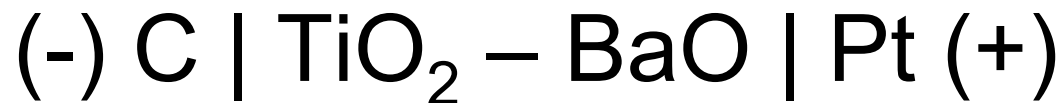


☐ electrolytic generation of oxygen gas confirmed

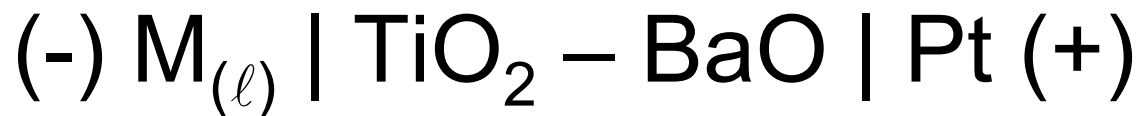


next steps

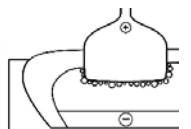
① electrolysis in a fully idealized cell:



② electrolysis in a cell w/ idealized anode:



③ selection and testing of anode materials



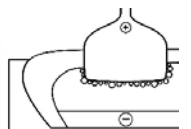
lunar colonization: NASA



oxygen for human life support
and rocket propellant

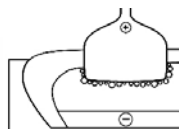


lunar regolith is a
multicomponent silicate rich
in **iron** and **titanium**.



... in closing

- ☑ high-accuracy electrical conductivity and transference number measurements in molten oxides at extreme temperatures
- ☑ electrolytic production of liquid titanium not unviable
- ☑ implications for fluxes and slags, e.g., welding, refining, & metallothermic reduction



acknowledgment

