Electrochemistry and LENR

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ARPA-E LENR Kickoff

ARPA-E Headquarters

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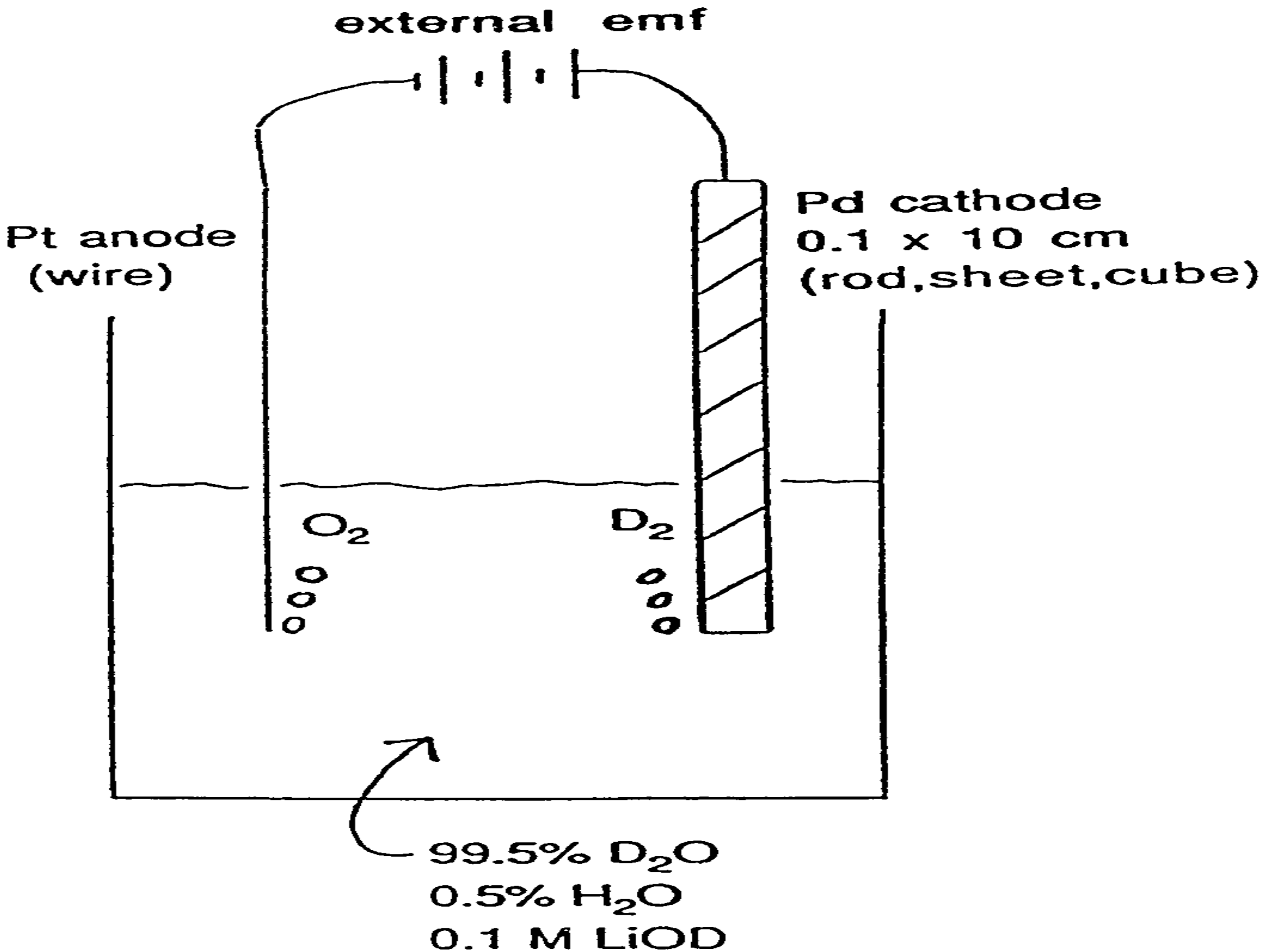
Cold Fusion

- 1989
- Pons, Fleischmann, and Hawkins (PFH)
- Electrolysis of Heavy Water
- Tabletop $500 Apparatus
- Claimed to Achieve Thermonuclear Fusion
- Potential for Limitless Cheap Energy
- How???

Electrolysis of Heavy Water



Electrolysis of Heavy Water

Pd Cathode: $4\ D_2O + 4\ e^- = 2\ D_{2(gas)} + 4\ OD^-$

Pt Anode: $4\ OD^- = 4\ e^- + 2\ D_2O + O_{2(gas)}$

Overall: $2\ D_2O_{(liquid)} \rightarrow 2\ D_{2(gas)} + O_{2(gas)}$

Decomposition of Heavy Water

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PFH Hypothesis

- Kinetic Overpotential is Predominant
- And Large
- Desorption of Deuterium from Palladium
- Is Slow and Rate Limiting

$$D_{(Pd)} + D_{(Pd)} \longrightarrow D_2$$

Cold Fusion

PFH Hypothesis

- 0.8 eV Overpotential
- Causes a High Thermodynamic Activity of Deuterium, of approximately 10^{26} atm
- Within Palladium Lattice
- Allows Atoms to Overcome Electrostatic Repulsions, and Fuse

$$^{2}D + {}^{2}D \rightarrow {}^{3}T\ (1.01\ MeV) + {}^{1}H\ (3.02\ MeV)$$

$$^{2}D + {}^{2}D \rightarrow {}^{3}He\ (0.82\ MeV) + n\ (2.45\ MeV)$$

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Kinetic Overpotential

- **Slow Desorption of D_2 from Pd**
- Butler-Volmer Equation

Boudart (74) has analyzed the P-F-H claim that an applied overpotential of 0.8 eV will lead to a compression of deuterium within the palladium lattice equivalent to 10^{26} atm. If the desorption of deuterium is slow and rate determining, the Butler-Volmer equation predicts that:

$$i_{for}/i_{rev} = \exp(o.p./RT) = r_{des}/r_{ads} = a_{D_2\ Pd}/a_{D_2\ bulk} \quad (5\text{-}10)$$

$$a_{D_2\ Pd} \approx 10^{27}\ a_{D_2\ bulk} \quad (5\text{-}11)$$

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Concentration Overpotential

However, it is unclear whether the overpotential is predominantly due to the slow desorption of D_2 from Pd. It can be seen from eqn (5-8) that mass transfer could be important. The mass transfer overpotential (concentration polarization) could also account for the claimed high activity of deuterium on Pd. A 0.8 volt concentration overpotential leads to an activity of:

$$o.p._{mass\ transfer} = (RT/nF)\ln a_{D_2\ Pd}/a_{D_2\ bulk} \qquad (5\text{-}12)$$

and at room temperature,

$$a_{D_2\ Pd} \approx 3 * 10^{27} a_{D_2\ bulk} \qquad (5\text{-}13)$$

Mass transfer polarization can also cause a large activity of deuterium on palladium. Therefore, the mechanism for building a high activity of deuterium on Pd via the P-F-H scheme is unclear. Because many reaction and transport processes are occurring simultaneously, it is not trivial to identify the origin of the main overpotential.

Cold Fusion

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PFH Experimental Proof

- **Primarily Through Calorimetry**
- **Measured the Temperature**
- **Observed Significant Heat**
- **In Their Electrolysis of Heavy Water**
- **Also Observed Neutrons, Tritium, and Helium**

PFH Calorimeter is Poor

- Open Cells
- Allow Heat & Gases to Escape
- Stirring Affects Thermal Mixing
- If Not Adequate – Hot Spots Within Cell
- Batch Operation
- Losses of Heavy Water Periodically Replaced
- Complicate Heat Balance

Cold Fusion

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Origin of Heat

- Where is it Coming From?
- Open to Debate – Chemical vs. Nuclear
- Both Palladium & Platinum are
- Terrific Oxidation Catalysts For

$$D_{2(gas)} + \frac{1}{2} O_{2(gas)} \rightarrow D_2O_{(liquid)} \qquad \Delta H_{298K} = -286 \text{ kJ/mol}$$

Cold Fusion

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Where are The Nuclear Fusion Products?

- **Helium**
- **Tritium**
- **Neutrons**
- **Are They Found in the Correct Proportions?**

Stoichiometry

$^{2}D + {}^{2}D \rightarrow {}^{3}T\ (1.01\ MeV) + {}^{1}H\ (3.02\ MeV)$

$^{2}D + {}^{2}D \rightarrow {}^{3}He\ (0.82\ MeV) + n\ (2.45\ MeV)$

University of Rochester 1989

- March 1989 PF Announcement
- Great Excitement in Rochester & Around World
- Jacob Jorne Presents Lecture April 1989
- Packed Auditorium
- Evan Granite – Graduate Student
- Working in Decrepit Lab
- Solid Electrolyte Cells and Catalysis
- Suggested Using Closed Solid Electrolyte Cells & Electrochemical Pumping
- Embarked Upon a One Month Side Project

Solid Electrolyte Cell

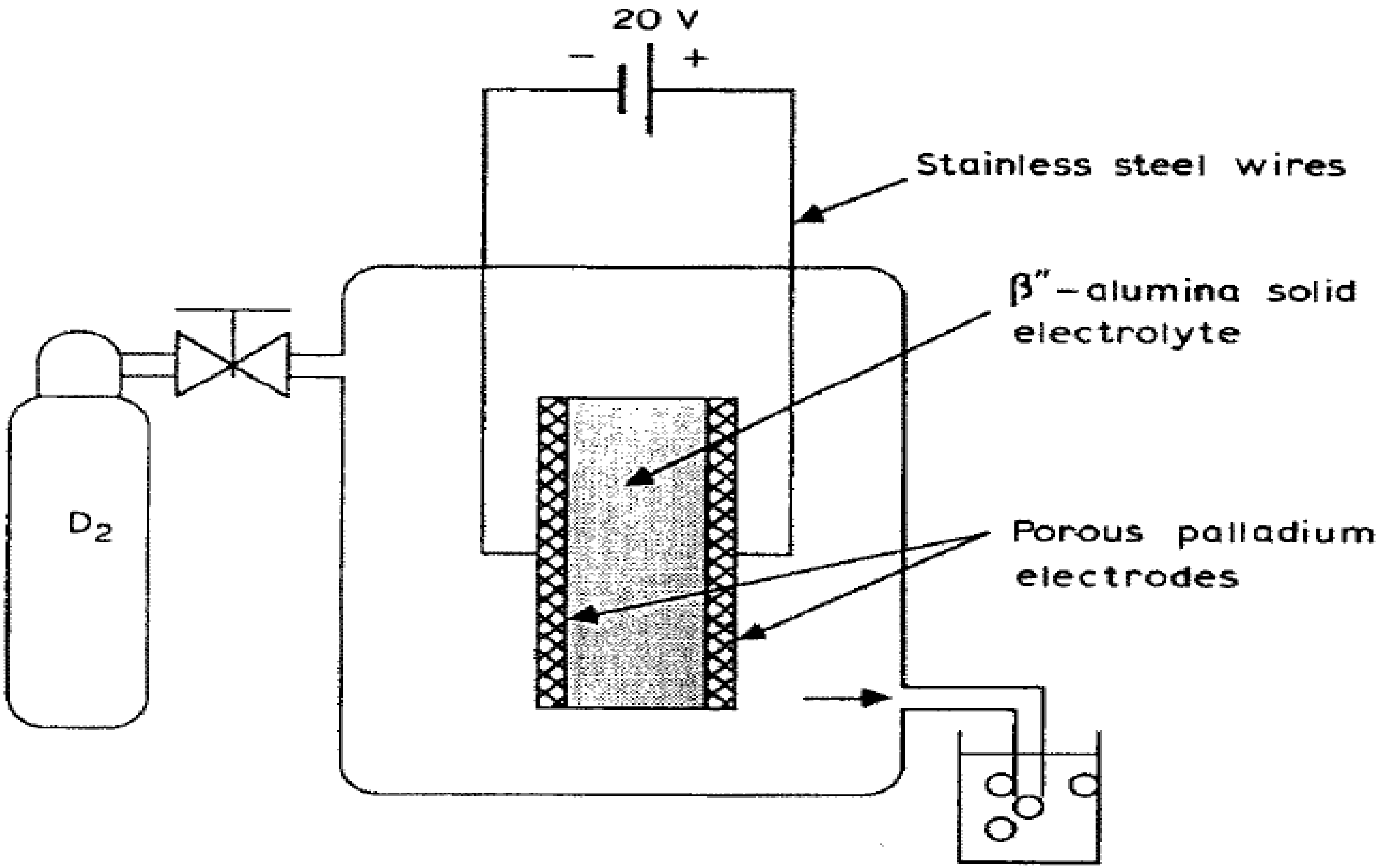

Fig. 1. Solid electrolyte cell for deuterium electrolysis: Pd,D_2 | β''-alumina | D_2,Pd.

Solid Electrolyte Cell

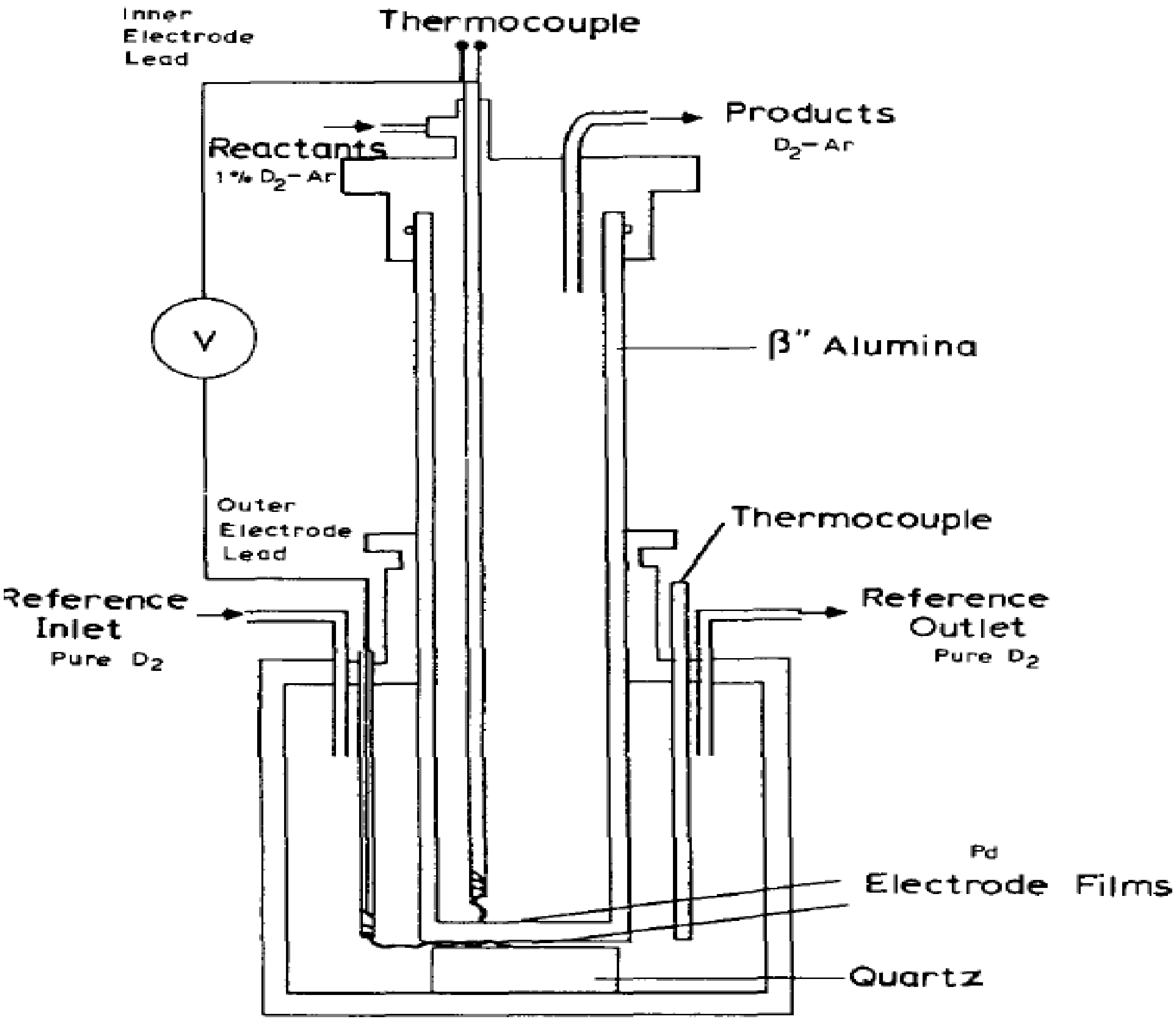

Fig. 2. Solid electrolyte cell for deuterium electrolysis: Pd,D_2 (0.01 atm in Ar) | β"-alumina | D_2 (1 atm),Pd, designed for temperature measurements [15].

Improved Solid Electrolyte Cell

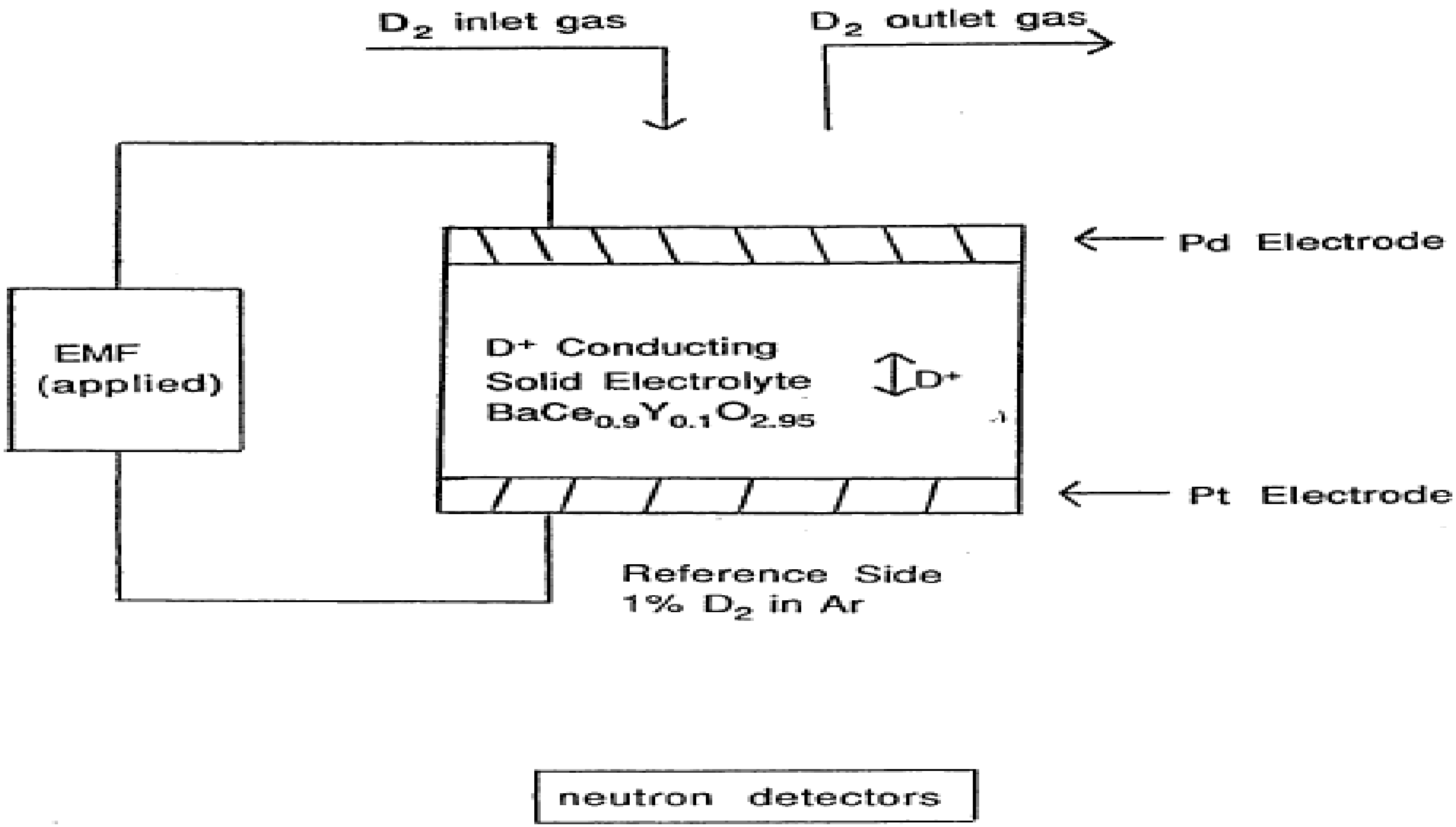

Figure 44: Improved Cold Fusion Apparatus

Results

- Electrochemically Pump D^+ to/from Pd
- Closed Cells, Thermocouple Touching Pd Film
- No Thermal Evidence of LENR
- Calorimetry Substantially Improved vs. PFH Cell
- Mass Spectrometer – Searching for Helium
- Neutron Detectors – "Spikes" - Likely Noise

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Cold Fusion

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Epilogue: Part I

- Martin Fleischmann Passed Away in 2012
- Expressed Regret Over March 1989 Press Conference
- To Announce Results to the World
- University Pressured P&F to Call Press Conference
- Worried about IP Royalties & Being “Scooped”
- Groups Today Working on Cold Fusion and LENR
- John Huizenga, University of Rochester, Book 1992
- DOE Reports in 1989, 2004
- Bubble Fusion and Recent Google Efforts
- ARPA-E Meetings 2021 and Today

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Epilogue: Part II

- Highly Imaginative Idea
- Using ChE Mass & Kinetic Resistance Concepts
- Granite Employs as Lesson in Graduate Catalysis Course
- To Be Applauded

Lessons

1. Reproducibility
2. Calorimetry and Open Cells
3. Interpretation of Data – Nuclear vs Chemical Reactions
4. Venues for Reporting Results – Journals, Conferences, etc - Not Press Conferences
5. Civil Discourse in Science
6. Never Inhibit Imagination and Creative Efforts

Future Research Opportunities

1. Other Mass or Kinetic Transfer Limited Systems

- Catalysts
- Sorbents
- Electrochemical Cells
- Many Elements “Love” Hydrogen & Deuterium
- Nickel, Rhodium, Platinum, Iridium - Catalysts
- Hydride Forming Pollutants
- Hg, As, Se, and P – Catalysis Poisons - “Skid Row”
- “Promoted” Pd using Hydride Forming Poisons
- Screen Pd-Alloys using Composition Spread Films

Future Research Opportunities

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2. Meaning & Origin of High Deuterium Activities

- Thermodynamic Activity of Deuterium
- Monotonic Function of Concentration

Possible Origins

- Slow Desorption of Deuterium from Pd
- Concentration Overpotential
- Sticky Bubbles

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Questions

- evan.granite@hq.doe.gov
- LENR and Palladium References
- Suggestions for Future Research
- Potential 35th Anniversary Review

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Palladium Sorbents and Catalysts

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Palladium Sorbents and Catalysts

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Appendix

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I. Seven Sacred Steps in a Catalytic Reaction

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- 1. Mass Transfer (Diffusion) of Reactants from Bulk Fluid to Surface of the Catalyst Pellet (External MT)
- 2. Diffusion of Reactant from Pore Mouth through Catalyst Pores to Immediate Vicinity of Internal Catalyst Surface (Internal MT)
- 3. Adsorption of Reactant(s) onto Surface
- 4. Reaction on Surface of Catalyst

I. Seven Sacred Steps in a Catalytic Reaction

- **5. Desorption of Product(s) from Surface**
- **6. Diffusion of Product(s) from the Interior of Pellet to the Pore Mouth at External Surface**
- **7. Mass Transfer of Product(s) from External Pellet Surface to the Bulk Fluid**

Courtesy of Fogler

I. Seven Sacred Steps in a Catalytic Reaction

"The Seven Commandments"

- **Analogous Steps for Other Reactor Systems**
- **Sorbent Packed Bed Reactors**
- **Electrochemical Systems (Electrolysis, Fuel Cells)**
- **Bioreactors (Immobilized Enzymes)**

Introduction to Electrochemical Reactors

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A Beautiful & Electrifying Subject

- **Batteries**
- **Fuel Cells**
- **Electrolysis**
- **Electroplating**
- **Electrochemical Separations**
- **Electrochemical Sensors**
- **NEMCA Effect & Catalysis**
- **Cold Fusion and LENR**

Introduction to Electrochemical Reactors

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A Beautiful & Electrifying Subject

- Batteries – Electrochemical Batch Reactors
- Fuel Cells – Electrochemical Flow Reactors
- Electrolysis – Electrochemical Decomposition
- Electroplating – For Appearance & Corrosion
- Electrochemical Separations – Pumping
- Electrochemical Sensors – Concentration Cells
- NEMCA Effect & Catalysis – Spillover of Ions
- Cold Fusion and LENR – Limits of Imagination

Introduction to Electrochemical Reactors

Beauty of Electrochemistry

- Extraordinary Energy Efficiencies
- High Selectivity for Separations
- A Wide Array of Selective Sensors
- Can be Relatively Simple & Cheap! (At Lab-Scale)

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Beauty of Electrochemistry

- Extraordinary Energy Efficiencies

- Relationship Between EMF & $\Delta G_{reaction}$

$$\Delta G_{reaction} = -nFE_{therm}$$

Where: n is the number of electrons transferred

F is Faraday's constant 96,487 coulomb/equivalent

E is the EMF (volts, or joules/coulomb) from thermo

Beauty of Electrochemistry

- Extraordinary Energy Efficiency

$$\Delta G_{reaction} = -nFE_{therm}$$

- Can Attain 80% Energy Efficiency by Electrochemistry

By Comparison

- Coal-Burning Power Plant: 33% Thermal Efficiency
- Automobile – 20% Thermal Efficiency ?

→ Batteries & Fuel Cells are Magical Devices

Beauty of Electrochemistry

- Extraordinary Separations
- Ionic Conductors: Ions Carry Charge
- Examples: YSZ, CSZ, $BaCeO_3$, AgI……
- Exclusive Ionic Conductors
- Near 100% Selectivity for Separation

YSZ Solid Electrolyte

O^{2-} O^{2-} O^{2-} O^{2-} O^{2-} O^{2-}

Y^{3+} $Zr^{4+}Zr^{4+}Zr^{4+}Zr^{4+}$ Y^{3+}

O^{2-} O^{2-} O^{2-} $V_{O^{2-}}O^{2-}$ O^{2-}

$\Leftarrow$ Vacancy motion

O^{2-} motion $\Rightarrow$

Oxygen Anion Solid Electrolytes

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O^{2-} Conductors	Composition
Yttria-stabilized zirconia	6-10 mol% Y_2O_3 in ZrO_2
Calcia-stabilized zirconia	5-15 mol% CaO in ZrO_2
Yttria-doped thorium oxide	15 mol% Y_2O_3 in ThO_2
Yttria-doped cerium oxide	5 mol% Y_2O_3 in CeO_2
Yttria-doped bismuth oxide	25 mol% Y_2O_3 in Bi_2O_3
Iron-molybdenum oxide	$3MoO_3 \cdot Fe_2(MoO_4)_3$
Yttrium-barium-copper oxide	$YBa_2Cu_3O_{6.8}$

Proton Conducting Solid Electrolytes

H^+ Conductors

exchanged ß" alumina	$H_{1.74}Mg_{0.74}Al_{10.26}O_{17}{\cdot}1.98H_2O$
Strontium cerium oxide	$SrCeO_3$
Barium cerium oxide	$BaCeO_3$
Ytterbium doped SrCeO	$SrCe_{0.95}Yb_{0.05}O_{2.975}$

Sodium Ion Conducting Solid Electrolytes

Na^+ Conductors

ß alumina	$Na_2O \cdot 11Al_2O_3$
ß'' alumina	$Na_2O \cdot MgO \cdot 5Al_2O_3$

Electrolysis

Electrochemical Decomposition

- Through Electrical Energy
- Most Famous Example: Electrolysis of Water
- $\Delta G_{reaction} = -nFE_{therm}$
- From Thermodynamics – Require 1.23 Volts
- EMF Calculated from Thermo at Room Temperature

Electrolysis: Non-Idealities

Will 1.23 Volts Be Sufficient to Decompose Water?

Electrolysis: Non-Idealities

- **No!**

- **Why?**

Overpotentials

In Order to Pass Current & Continually Evolve Oxygen and Deuterium Gas, Must Overcome The Following Resistances:

1. Kinetic Resistances

Kinetic Overpotential

- **Adsorption**
- **Electron Transfer**
- **Desorption**
- **On Electrode Surfaces**

Overpotentials

In Order to Pass Current & Continually Evolve Oxygen and Deuterium Gas, Must Overcome The Following Resistances:

2. External Mass Transfer

External Mass Transfer Overpotential

- **Diffusion of Reactants and Products**
- **Through the Boundary Layer of Electrodes**
- **Even Have to Account for Gas Bubbles**
- **That Like to Stick on Electrode Surfaces in Solution**

Overpotentials

In Order to Pass Current & Continually Evolve Oxygen and Deuterium Gas, Must Overcome The Following Resistances:

3. Internal Mass Transfer

Internal Mass Transfer Overpotential

- **Diffusion of Reactants and Products**
- **Through Porous Electrodes**

Overpotentials

In Order to Pass Current & Continually Evolve Oxygen and Deuterium Gas, Must Overcome The Following Resistances:

4. Electrical Resistance

<u>IR Drop Overpotential</u>

- **Electrical Resistance of Solution**
- **To Pass Current**
- **IR Drop**

Overpotentials

Total Overpotential is Sum of All of These Resistances:

Kinetic Resistances + External Mass Transfer +Internal Mass Transfer + Electrical Resistance

$$op = E_{applied} - E_{therm}$$

with:

$$op = op_{kinetics} + op_{ext\ mass\ transfer} + op_{internal\ mass\ transfer} + op_{IR\ Drop}$$

So we typically need 1.5 - 2 volts to decompose water

(op between 0.3 and 0.8 volts)

Overpotentials

Sound Familiar?

- Our Model from Heterogeneous Catalysis!!
- Provides a Sound Framework
- To Understand Numerous Physical Processes
- Sorbents, Electrochemistry, Supported Enzymes
- To Better The World!