ChevronTexaco

Materials Issues in Alkaline Fuel Cells

Analytic Energy Systems, LLC

D.Bloomfield

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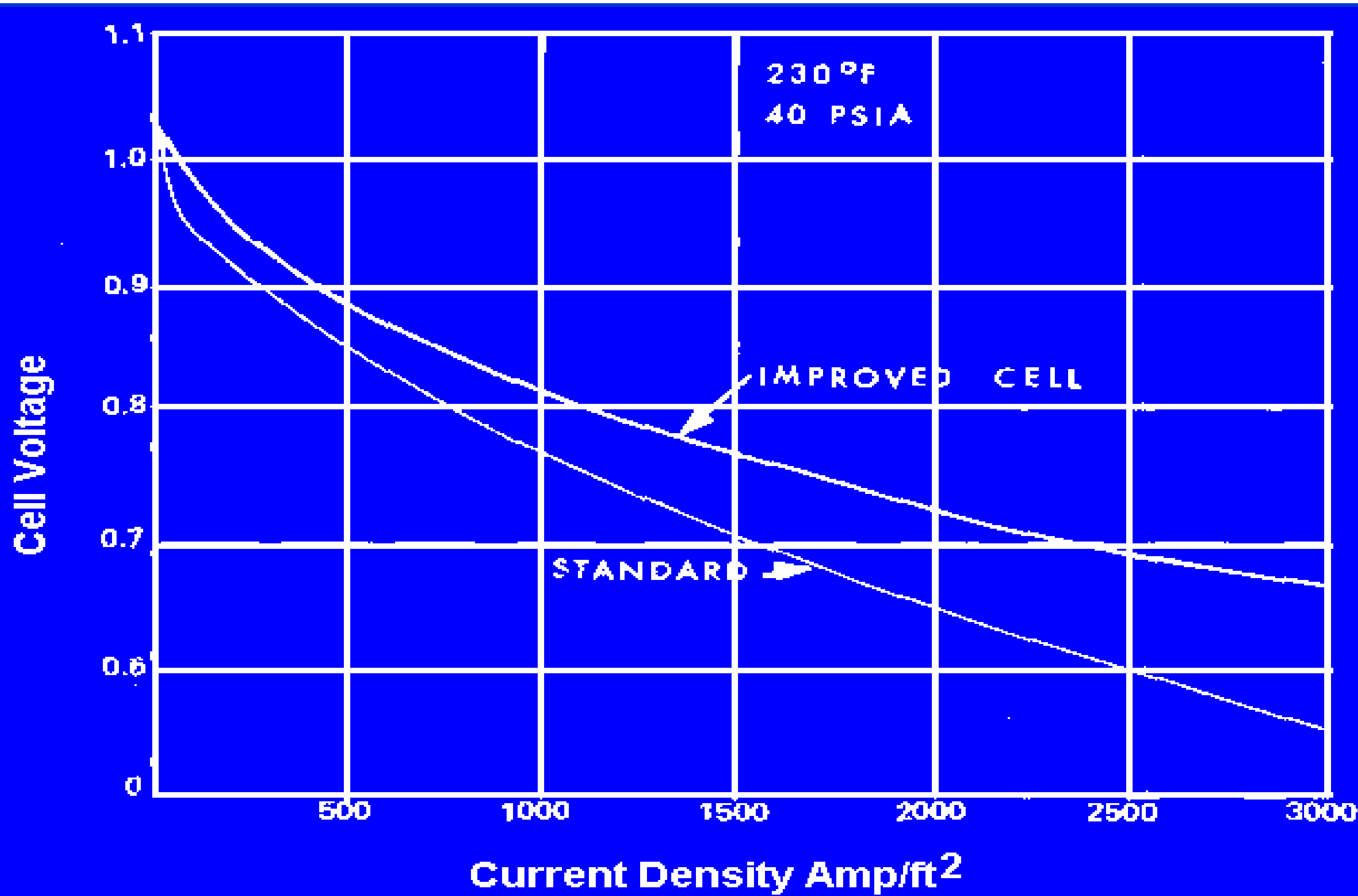
Introduction

- **Performance**
- **Carbonates**
- **Concentration Polarization**
- **Circulating Electrolyte**
- **Material Degradation**
- **Monopolar Cells**
- **Conclusions**
- **Recommendations**

AFC (5cell) Substack Performance (circa 1969)

Precious Metal 20 mg/cm2 Cathode 10 mg/cm2 Anode



Ref.AFAPL-TR-69_106

Figure 21 Cell Performance

Companies that Left AFC

Gulzow, Journal of Power Sources, 61 (1996) 99-104

Allis Chalmers 1959

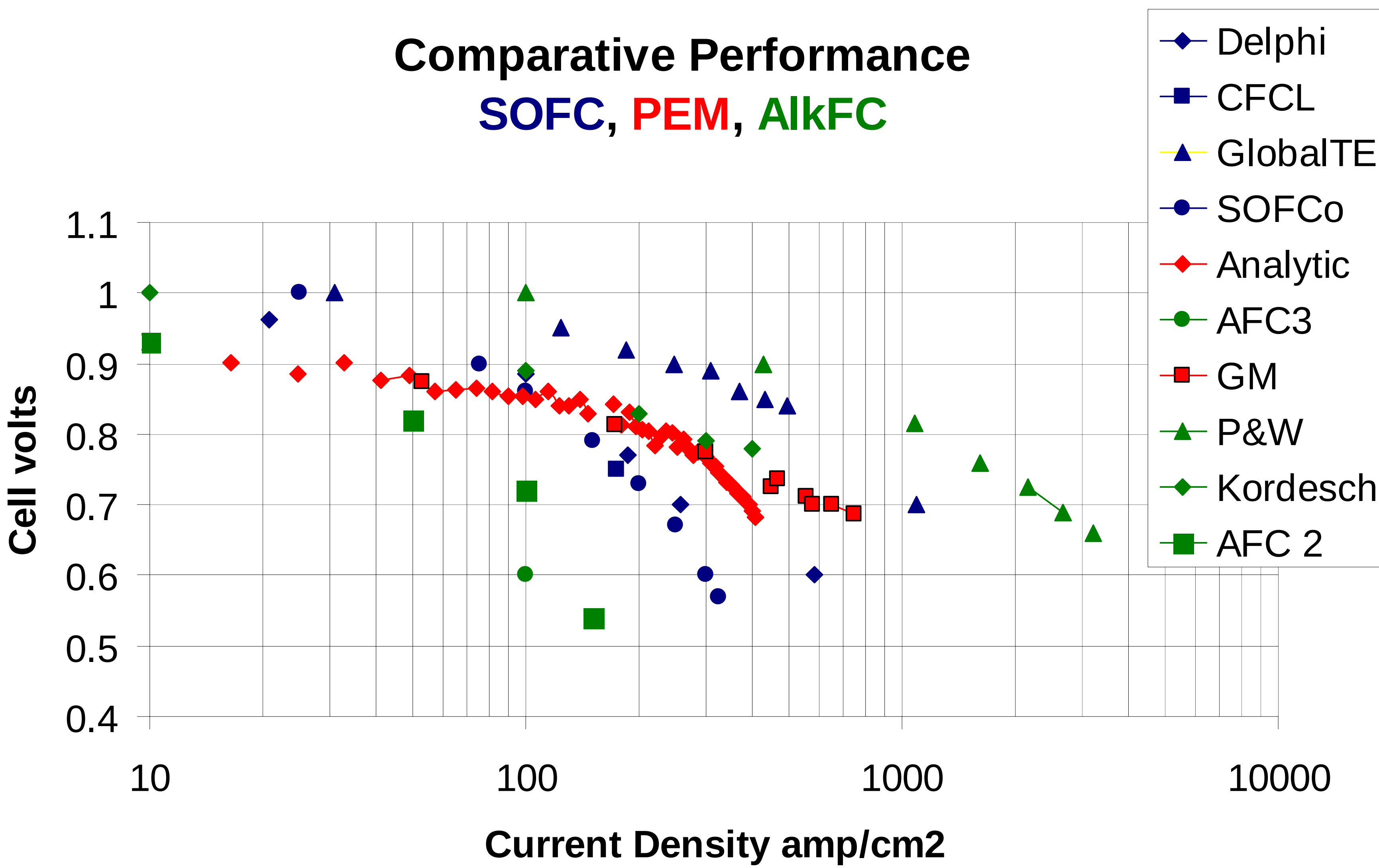
UTC – Apollo, LEM, Commercial PC10, Military PC3, Shuttle
– Left 1970's

Terminated - Siemens, Varta (1993), GH (1994),
ISET (1994), DLR (1994), ELENCO(1995),
Hoechst, Zetek (2002)

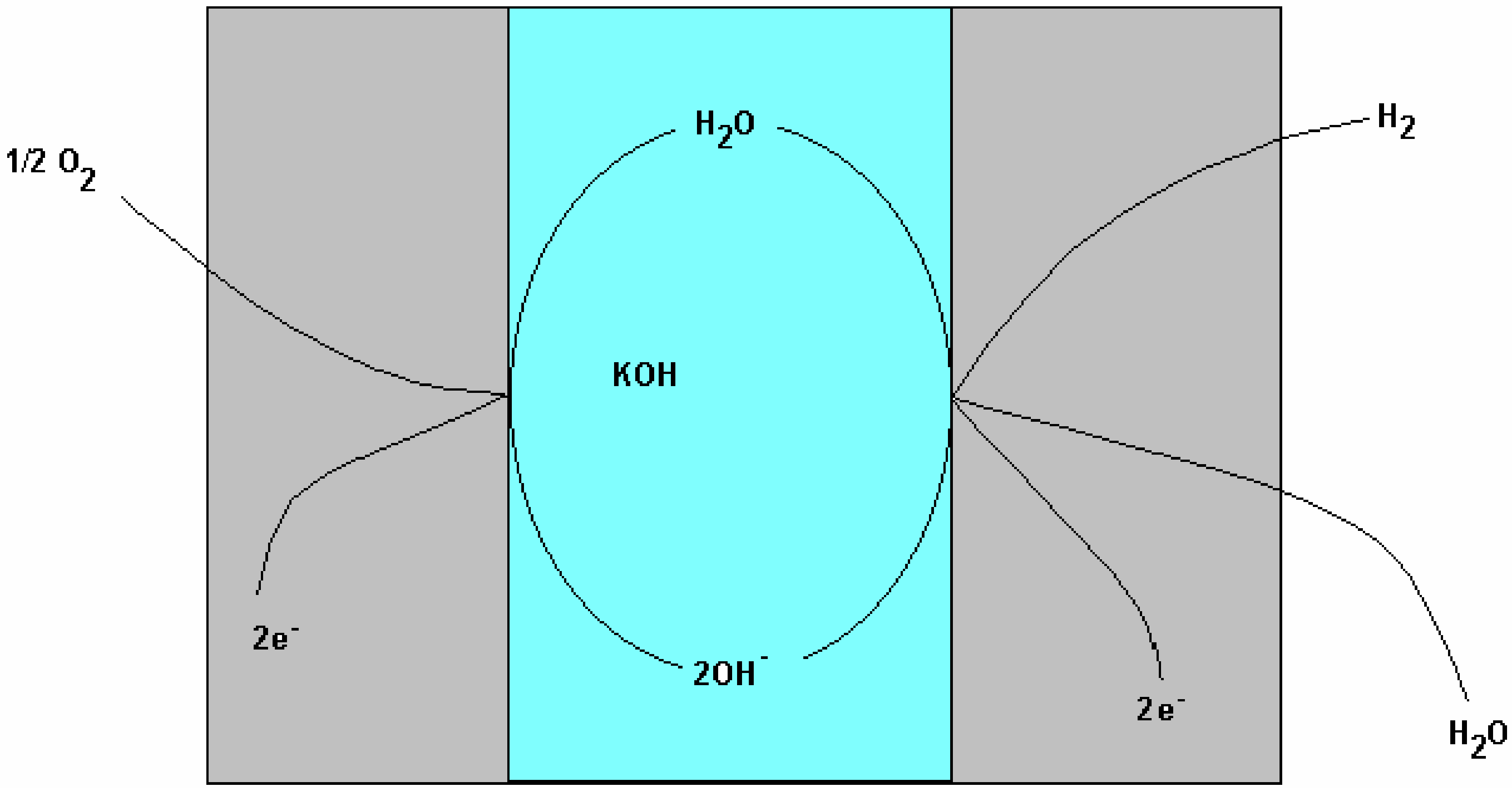
Examine Old Conclusions in Light of New Technology

Where is the New Technology?

Relative Fuel Cells Performance Varying Operating Conditions



AlkFC Chemistry
Molten Alkali (300C) & Aqueous Alkali (120C)



Trapped vs Circulating electrolyte
Circulating Electrolyte

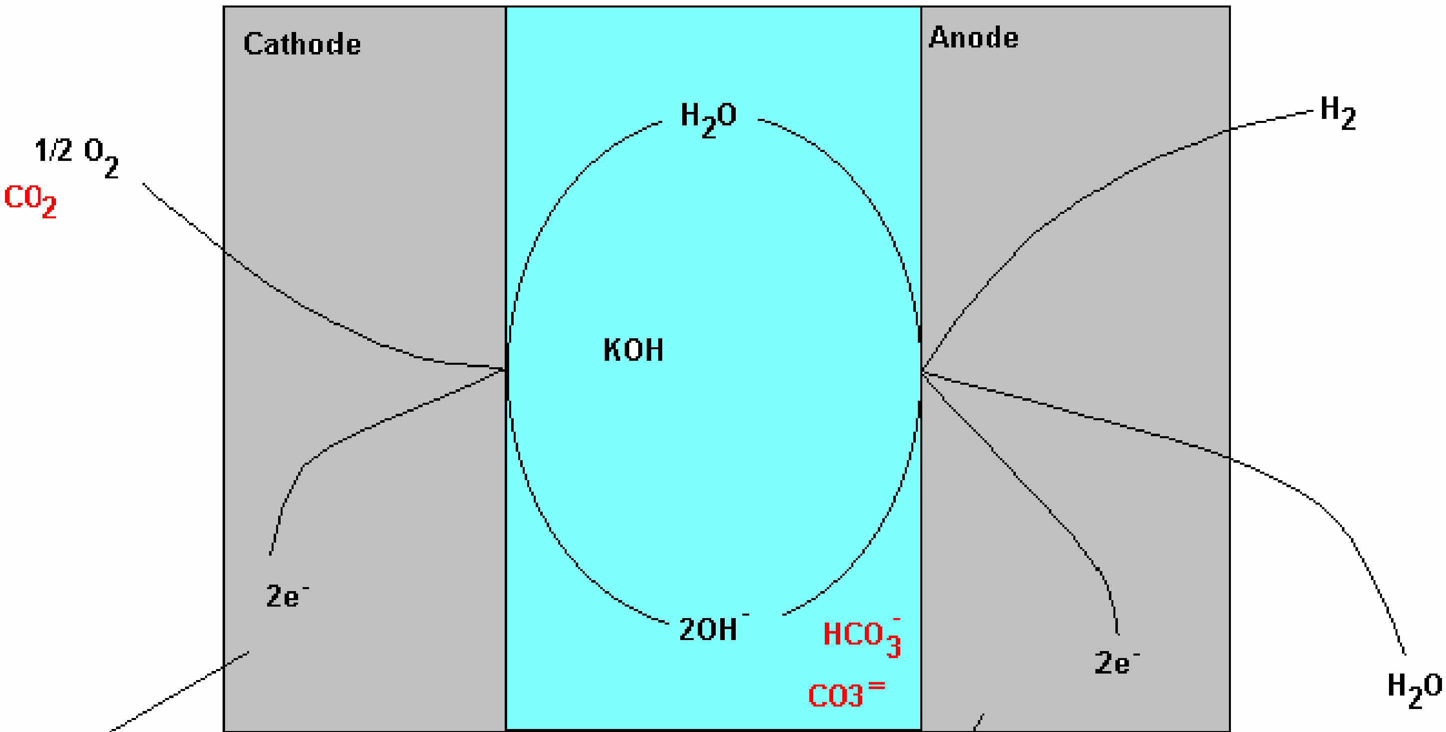
Problems

- Thick Films Offsets High Ionic Conductivity
- Pressure Drop Along Cell Matrix Contributes to Flooding
- Electrolyte Flow Maldistribution
  - — Contributes to Carbonate Problems
  - — Concentration Polarization

Advantage

- Permits draining electrolyte to limit corrosion
- Electrolyte Serves as Coolant

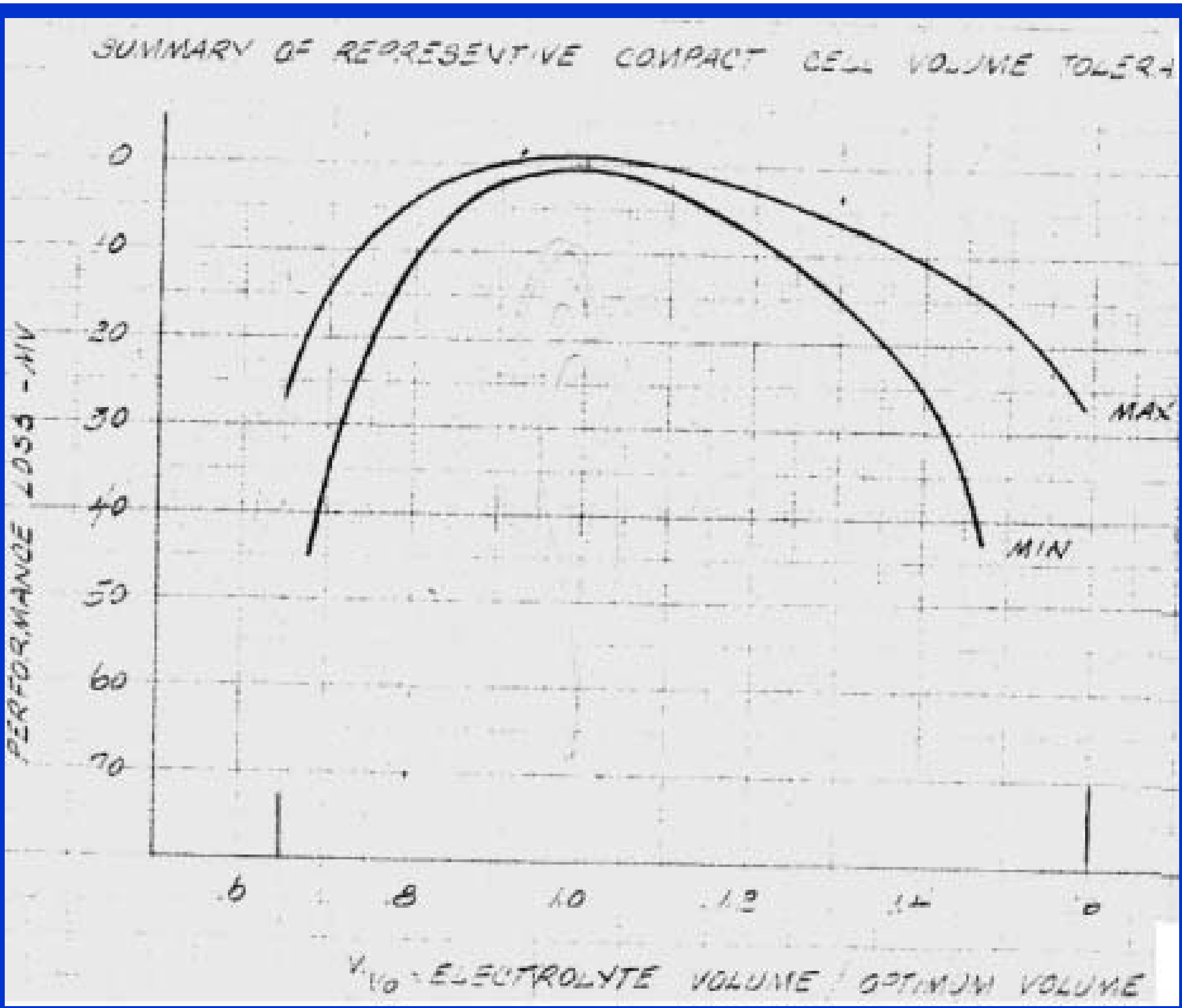
Effect of Carbon Dioxide



Alkaline-Earth Ruthenates
Lithium Doped Lanthanum Nickelate
Ni-Co Spinel
Pb-Ru Pyrochlore
Na-Pt Bronze
Ag/AgHg

Pt/Au
Ni (Raney)

Controlling Electrolyte Distribution Within Trapped Matrix

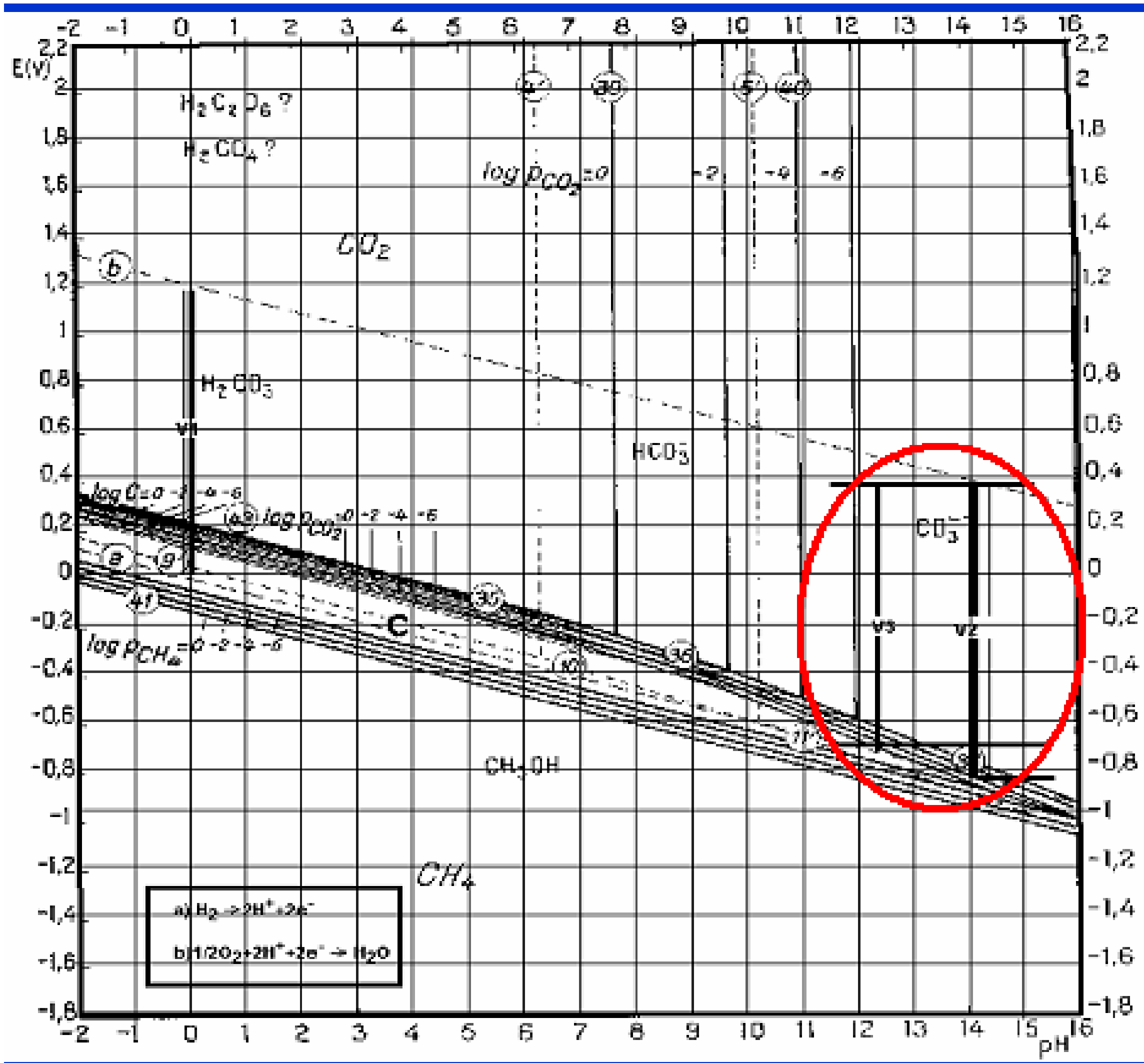


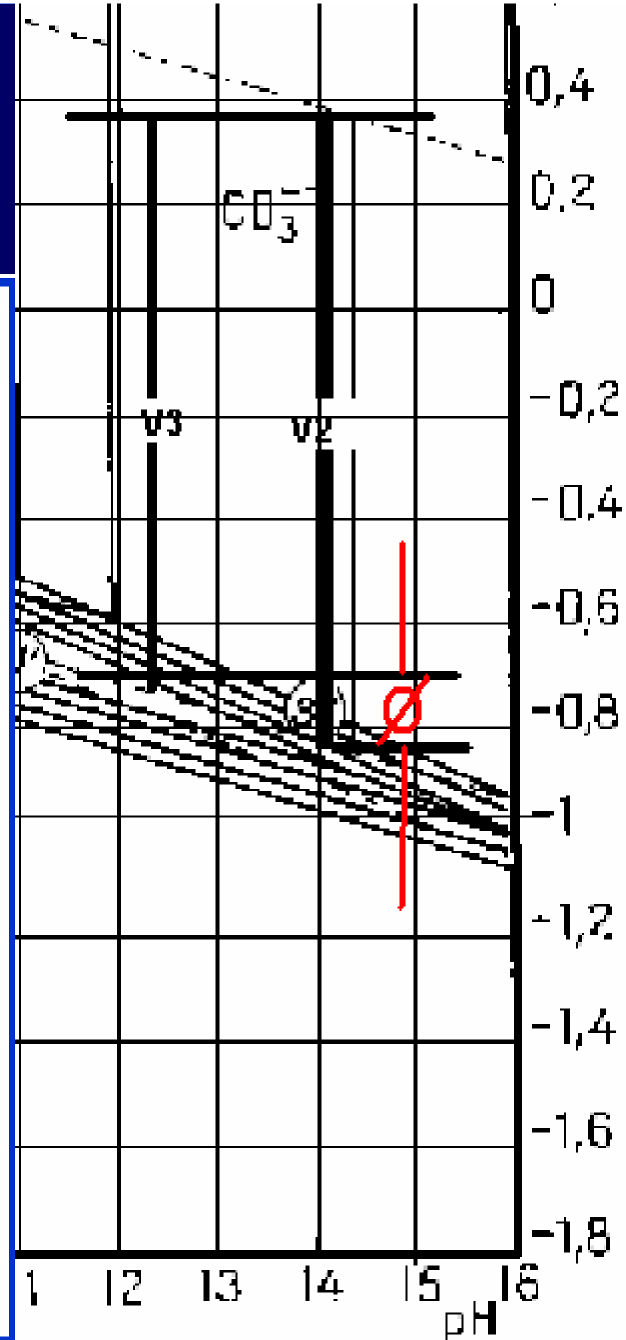
Deviations from the optimum fill volume leads to significant performance losses

Carbonate alters Density and saturation Properties

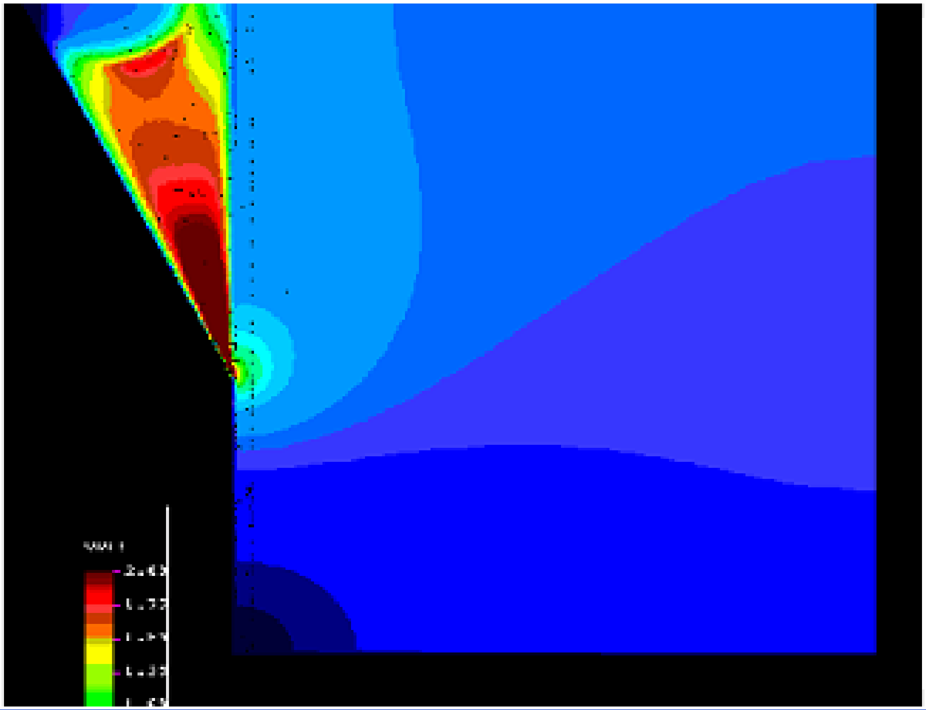
Concentration Polarization
Bigger Effect Than Resistance

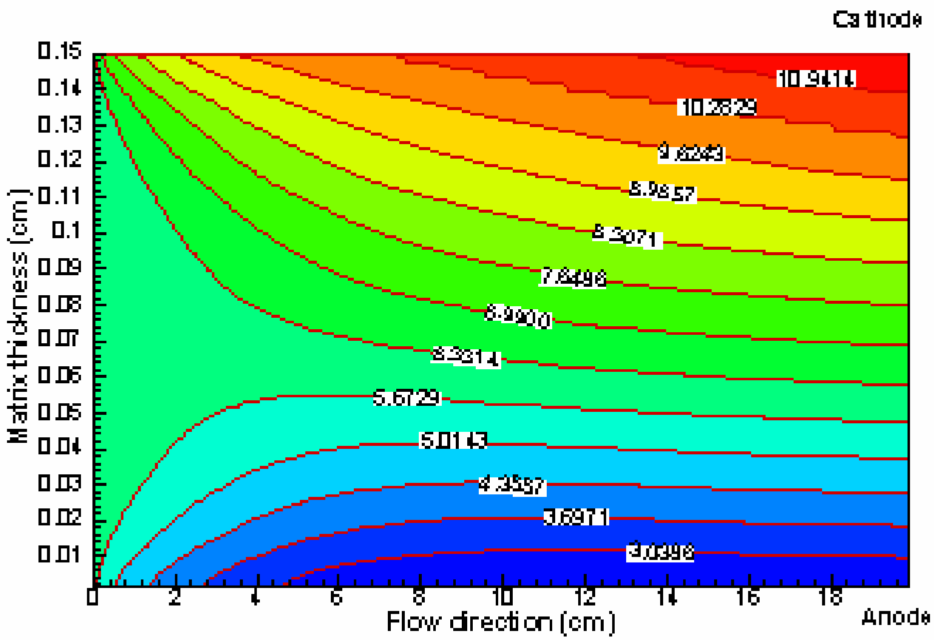
Pourbaix





Circulating Electrolyte Modeling
Flow Maldistribution and Concentration Gradients





Flow Distribution

Concentration Distribution

Material Degradation

- Carbon Corrosion
  - Catalyzed by precious metal
- Catalyst Corrosion
  - Nickel Powder, Raney Ni /Particulate/Cu [9]
- Plastic Decomposition
  - Teflon
  - Cell Frame Materials
- Ceramics (electrolyte matrix)

Effect of KOH on Supported Pt Catalyst

Tomantschger, Findlay, Hanson, Kordesch, Srinivasan.-Journal of Power Sources, 29 (1990) 443 - 450

- KOH exposure to platinum supported carbon catalyst drastically affects noble metal.
- Platinum particles Agglomeration starts with exposure to KOH
- Agglomerates size increased logarithmically over 48 h.
- Particle size increased from <50 to over 200 microns

Has Anyone Tried Non-Carbonaceous Support ?

- **Carbides**
- **Borides**

Carbon Corrosion

Tomantschger, Findlay, Hanson, Kordesch, Srinivasan.-Journal of Power Sources, 29 (1990) 443 - 450

- Pt (1 mg/g carbon) increases corrosion rate in first 50 h
- Corrosion levels off in first 200 h (outer surface is wetted).
- Rapid increase in the corrosion rate after 500 h
- Electrolyte penetrates and corrodes inside of the carbon agglomerates

Observations confirm noble metal acts as a carbon corrosion catalyst.

Nickel Alternatives - Cathode Catalyst Corrosion

Singer & Fielder Journal of Power Sources, 29 (1990) 443 - 450

Corrosion test screening of alkaline fuel cell oxygen reduction electrode candidates

Pyrochlore ($Pb_2Ru_20_{6.5}$)

Short Term Stability

Long Term Stability Questions

Spinel $NiCo_20_4$

Unstable

Comparisons made with long term performance tests

Catalysts Should be tested for Peroxide Decomposition

Anode Instability& Corrosion

E. Gulzow, M. Schulze, G. Steinhilber Journal of Power Sources 4656 (2002) 1–10

Nickel/TFE/Copper Variations Tried

Anode Problems Due More To TFE Instability

Than Catalyst Activity

– Resistance & Concentration Polarization (Carbonation)

– Loss of Hydrophobicity (TFE instability)

– Capillary Structure   (carbonation)

– Flooding (Teflon instability)

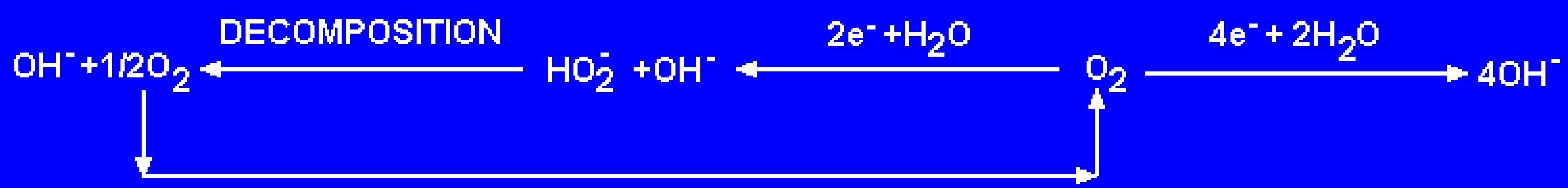
Peroxide Mechanism & Cathode Reaction

Chantenet et al JES 150 (3) D47-D55 (2003)

Pt is Good Peroxide Decomposition Catalyst

Pt Catalyzes the Oxidation of Carbon Support

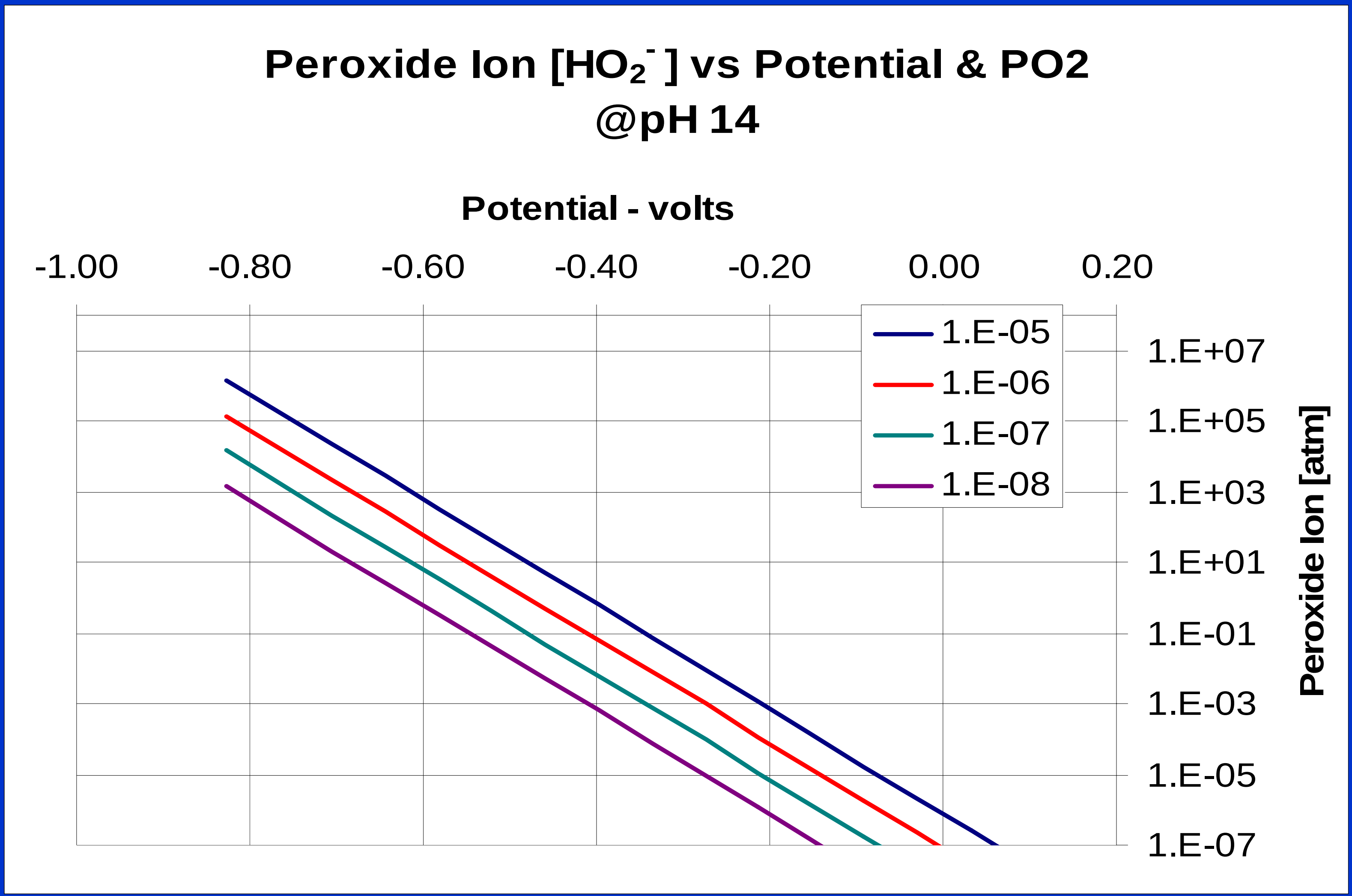
Ni is Not a Good Decomposition Catalyst



Cathode Mechanism

Peroxide Concentration

Pourbaix



PTFE Physical & Chemical Stability

Tomantschger, Findlay, Hanson, Kordesch, Srinivasan.-Journal of Power Sources, 29 (1990) 443 - 450

- KOH exposure alters surface properties of PTFE
  - — Decreased contact angle
  - — Surface energy
- PTFE SEM Surface Examination
  - — Roughening Caused by KOH Electrolyte.
  - — Function of PTFE Types and Particle Sizes
- PTFE Changes Under Fuel Cell Operating Conditions Contributes to Electrode Degradation,
- PTFE Chemical Degradation
  - — Caused by Electrolyte Access
  - — Accelerated by Peroxide Presence

Materials Properties Variation Summary

Physical Properties

- Wettability
- Surface Tension
- Viscosity
- Conductivity
- Water Saturation Properties

Chemical Reactivity

- Carbonate formation
  - Reactants
  - Cell materials (Frames)

How many problems are Peroxide Related?

Monopolar vs Bipolar Design

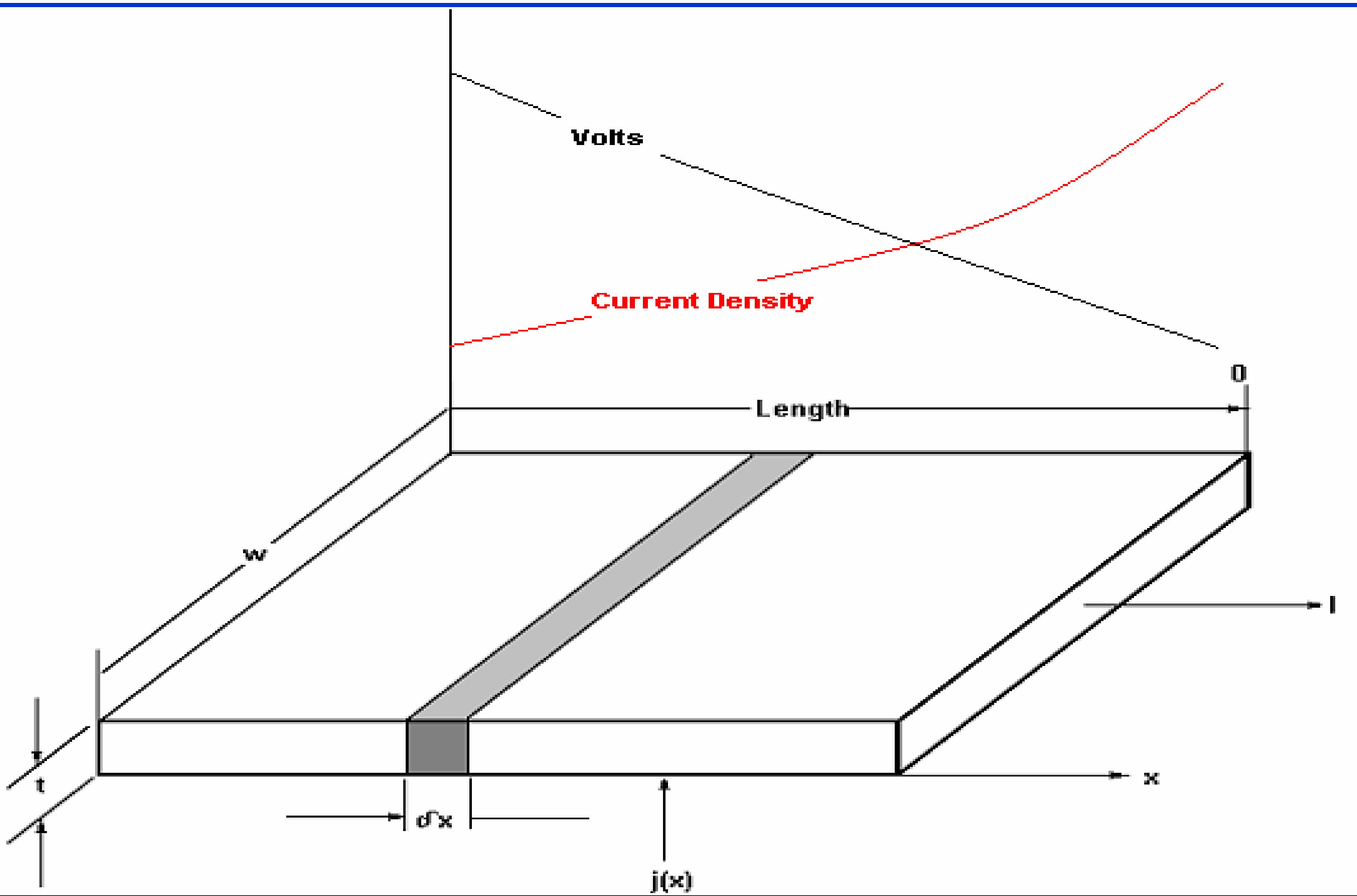
Monpolar Design

- **Resistivity Φ_{Ω} (resistance loss)**

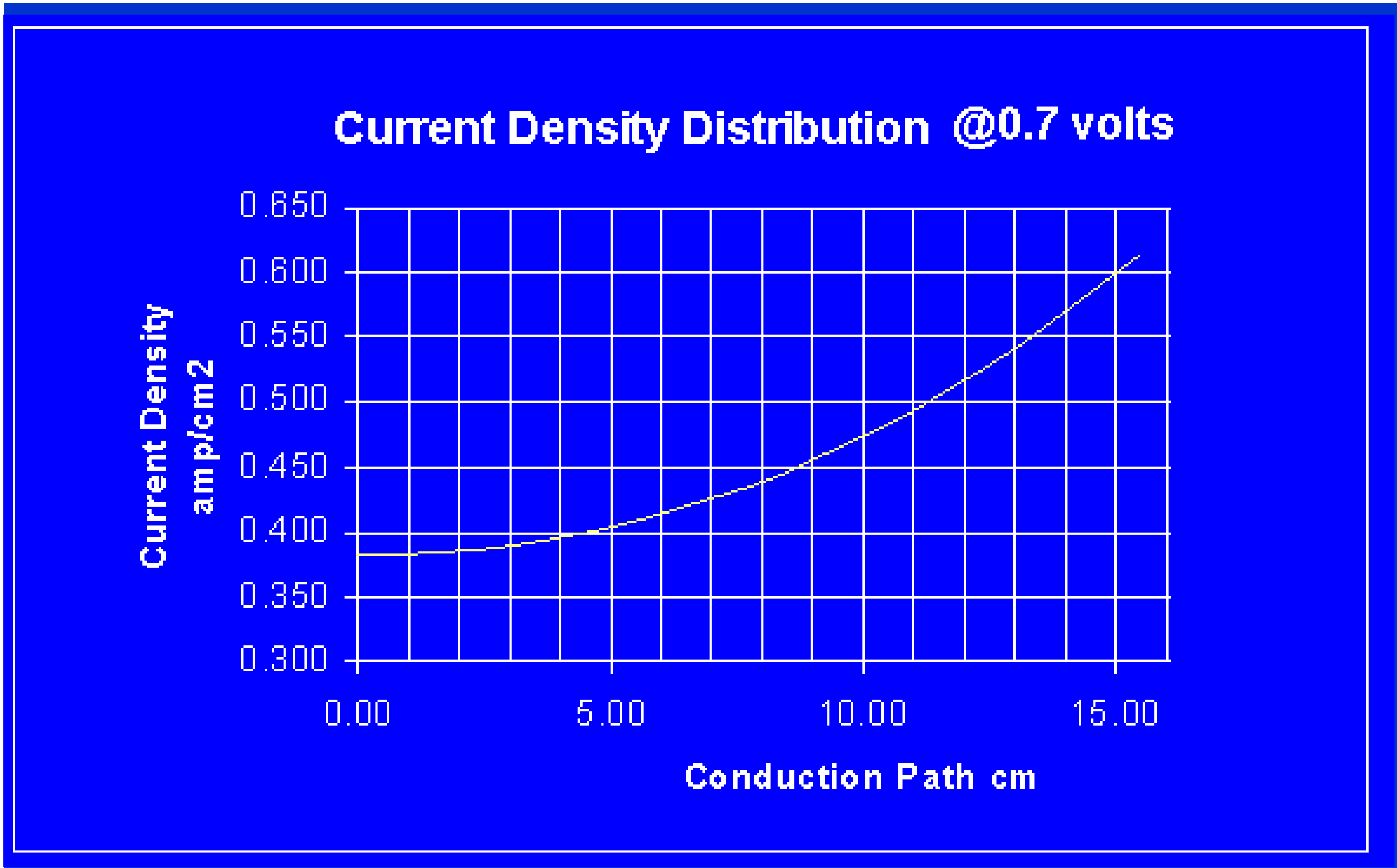
  $=f(x^2)$ x=conduction path

- **Poor catalyst utilization**
- **Cell Stiffness Tenting & Structure**
- **Follow up Systems**
- **High Part Count**

Design
Monopolar vs Bipolar



Monopolar Current Collection
Effect of Resistance in Electrode Plane



Conclusions

Alkaline Fuel Cell Challenge

Many Symptoms Linked to Peroxide Effects

Good Peroxide Decomposition Catalysts are

Poor Reduction Catalyst or Corrosion Catalysts

Circulating Electrolyte is used because

Catalyst Corrodes in Presence of Electrolyte

Carbonate Formation

Monpolar Design is bulky and has poor catalyst utilization

Directions for Alkaline Fuel Cell Material Development

Performance/Life

- Run Full Cells for Performance & Durability
- Half Cells don't have the Same Problems

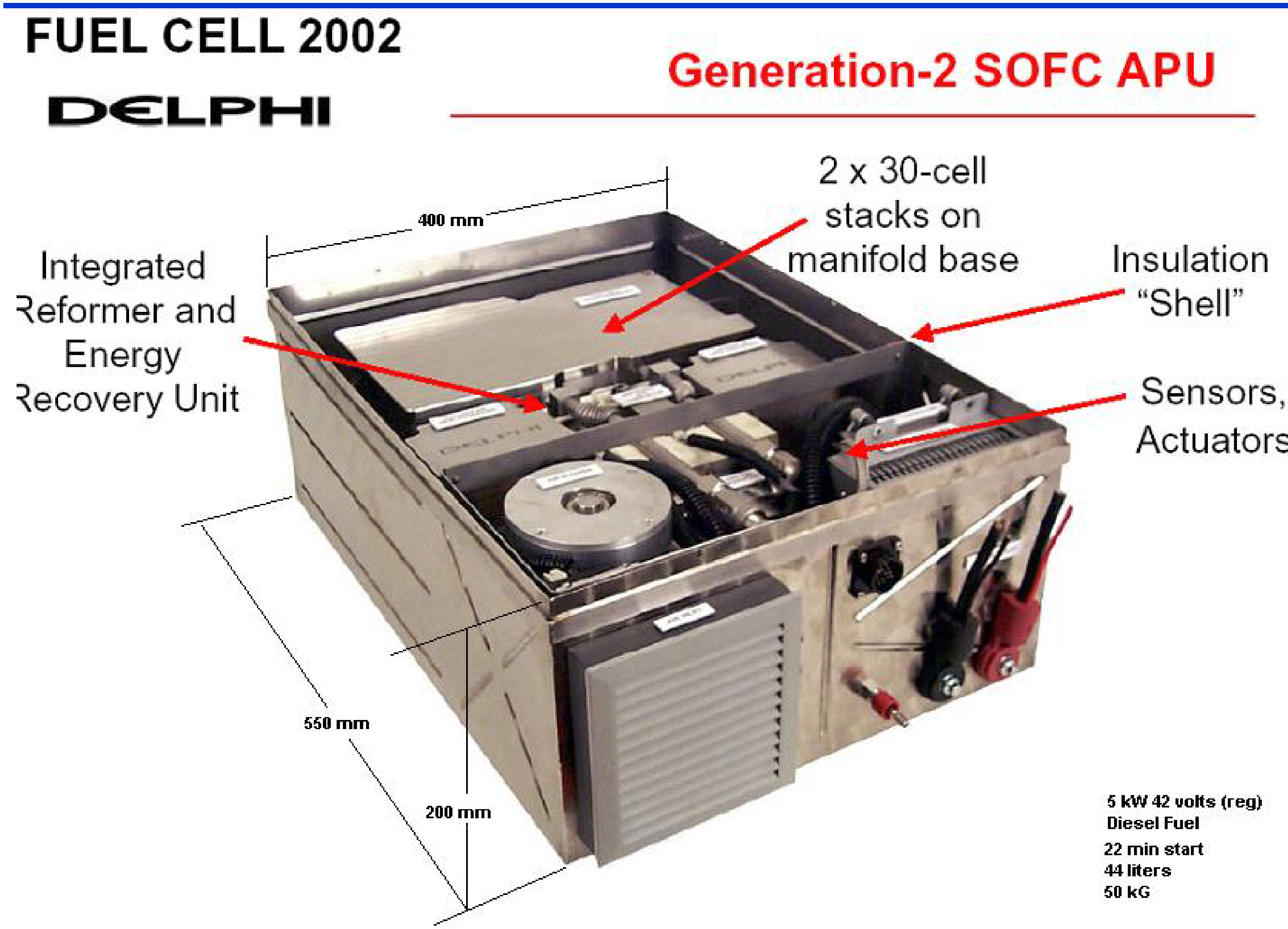
Materials Degradation Forced Design Compromise

PTFE	Electrocatalysts
Carbon	Cell Frame
Matrix	Electrolyte

Design

Bipolar Cells	Trapped Electrolyte

Competition From SOFC



Competition from PEM

	L x H x W
Size:	**472 x 496 x 251 mm**
	(18.6" X 19.5" X 9.9")
Weight:	**100 kg (220 lbs.)**
Design power:	**94 kW**
Peak power:	**129 kW**
Number of cells:	**200**

Internal Combustion Engines Run on H_2

Honda Scooter & ECD Hydride Storage