OXIDATION OF DRY AND NEAR-DRY HYDROCARBONS AT HIGH-POWER-DENSITY ANODES

K. Krist, O. Spaldon-Stewart, R. Remick
Gas Technology Institute
J. Jewulski,
Technologix Corporation

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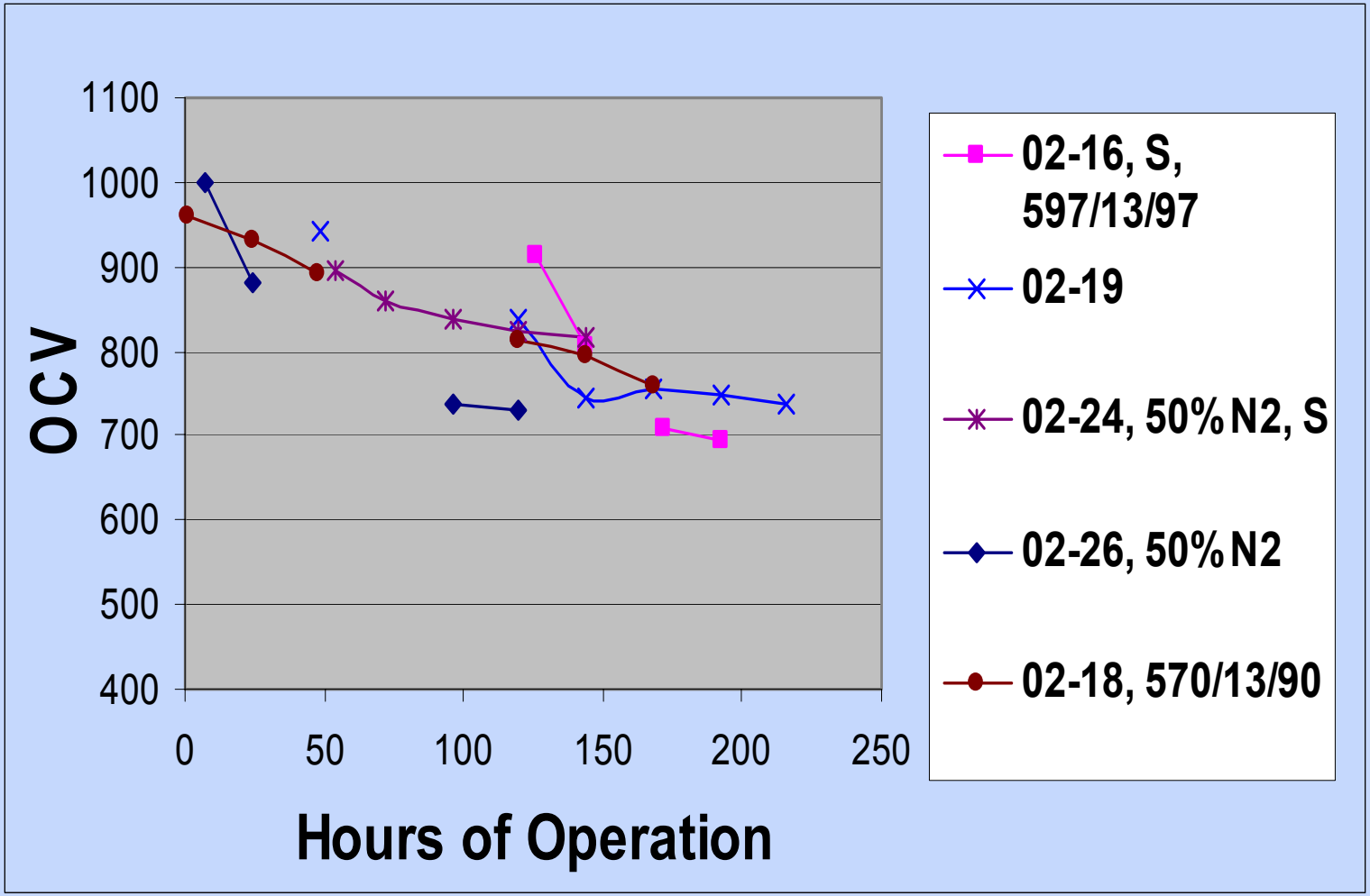
Overall Objective and Approach

- High-power-density anode able to operate on as-received HC fuels
  - To reduce or eliminate need for fuel processing and contaminant removal upstream of the FC stack
- By fabricating anode bi-layer that has an active interlayer
  - Within the constraint of low melting point of Cu oxide

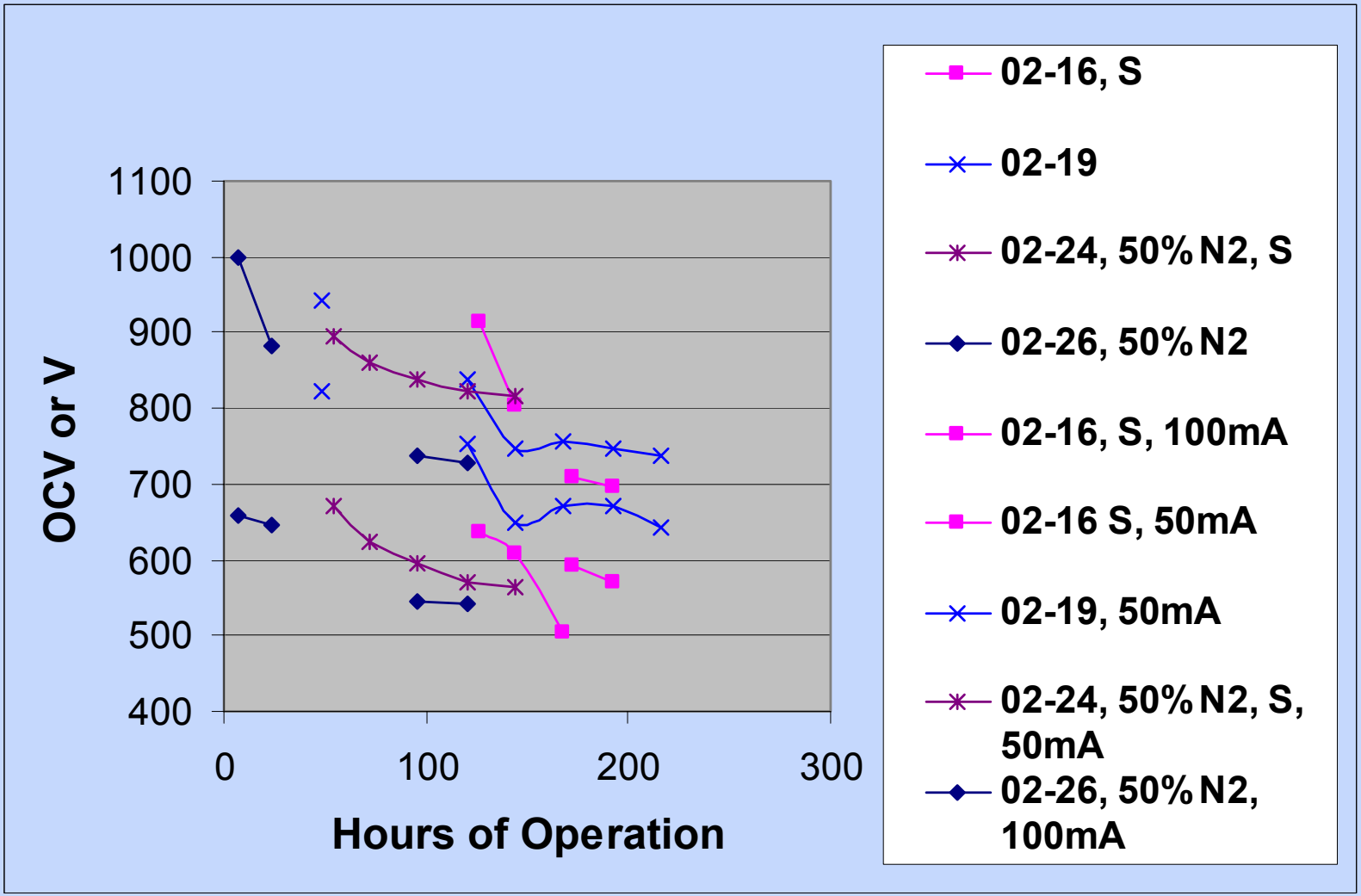
Interim Objective I

- **Eliminate or reduce carbon deposition so that it does not compromise cell operation.**

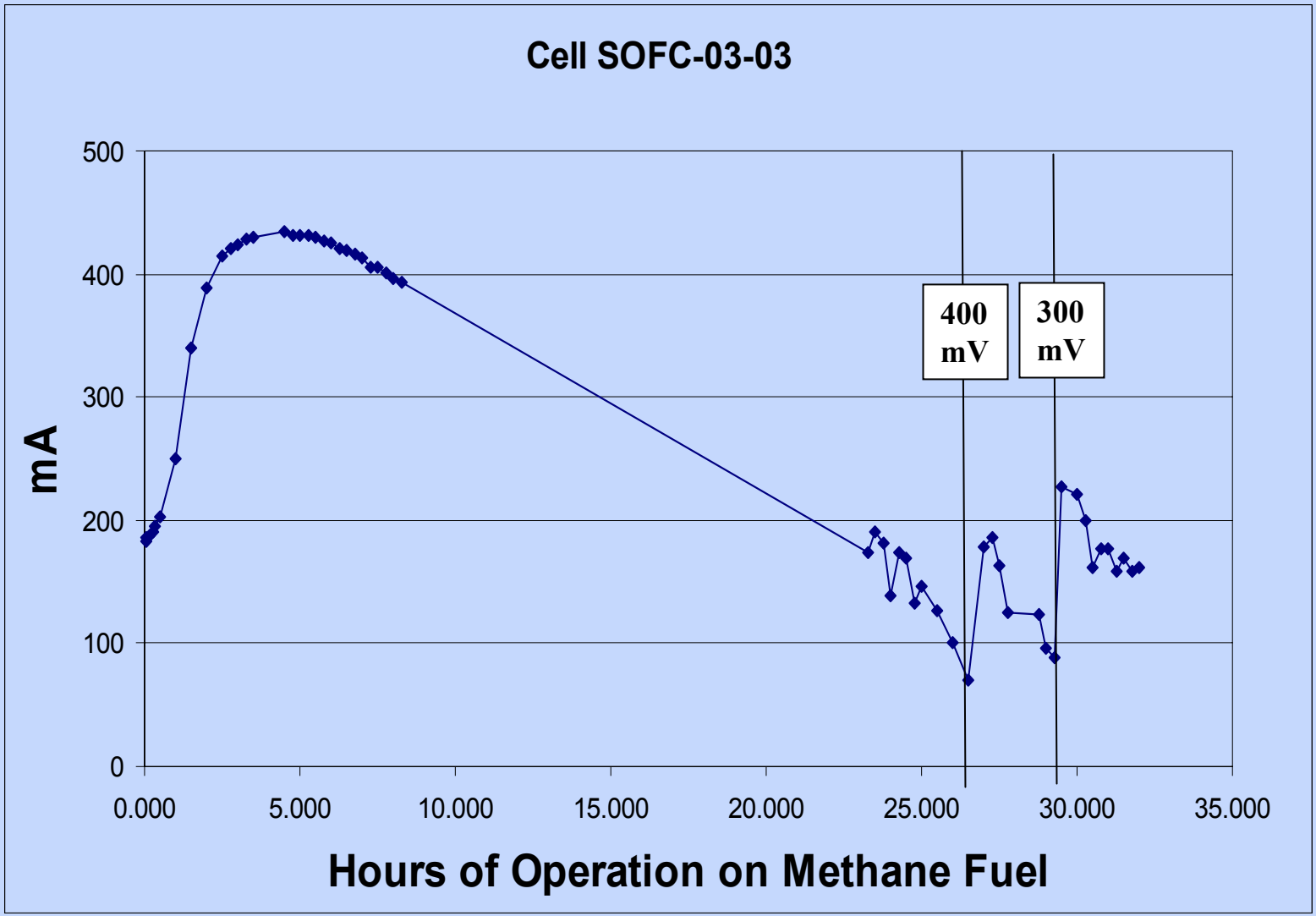
Dry CH_4 OCV at 800°C with ~600µ Anode, 13µ Electrolyte, ~100µ Cathode



Dry CH_4 Performance at 800°C (~600µ Anode, 13µ Electrolyte, ~100µ Cathode)



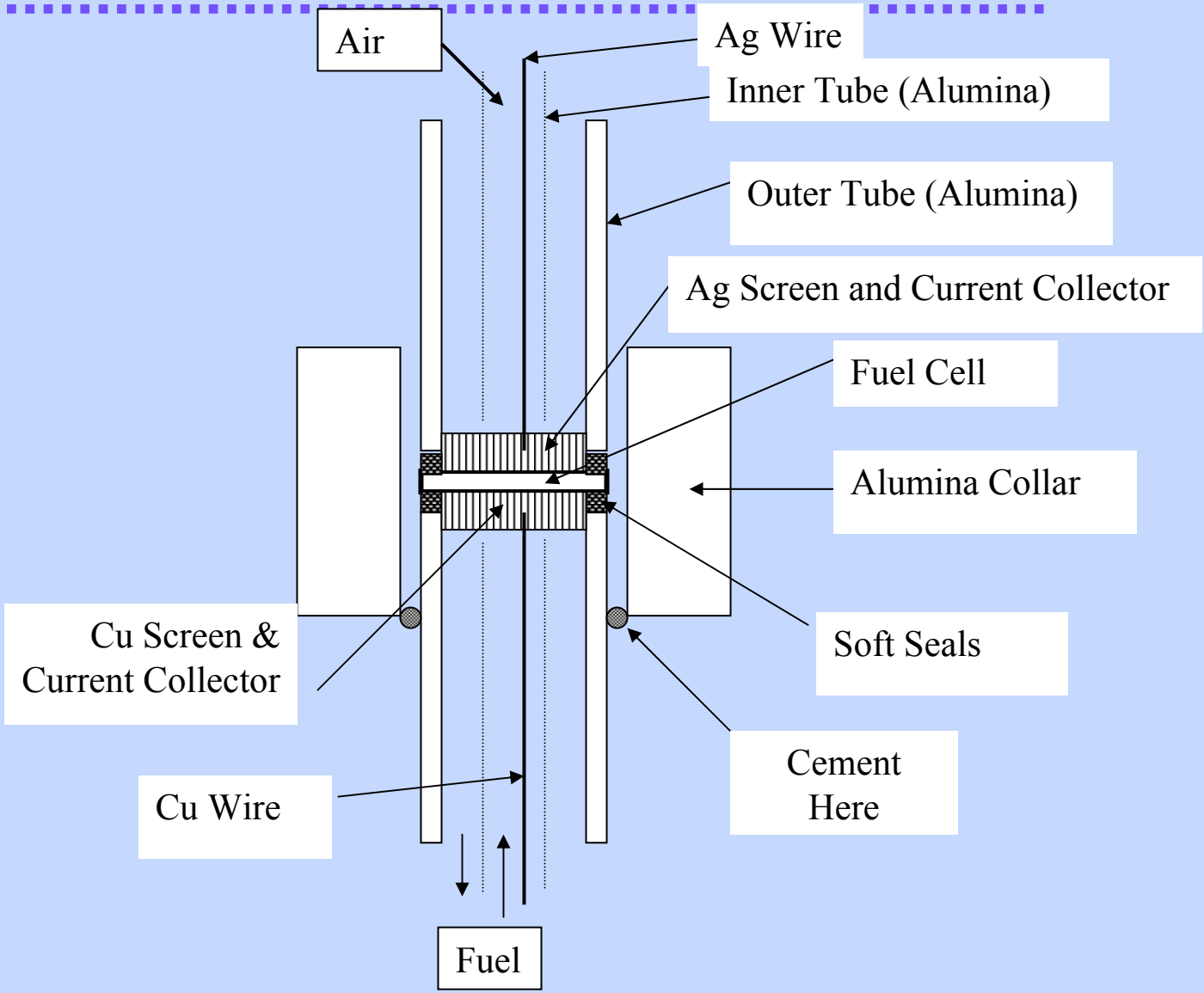
Dry CH_4 Performance at 800°C and 0.5V (~600µ Anode, 13µ Electrolyte, ~100µ Cathode)



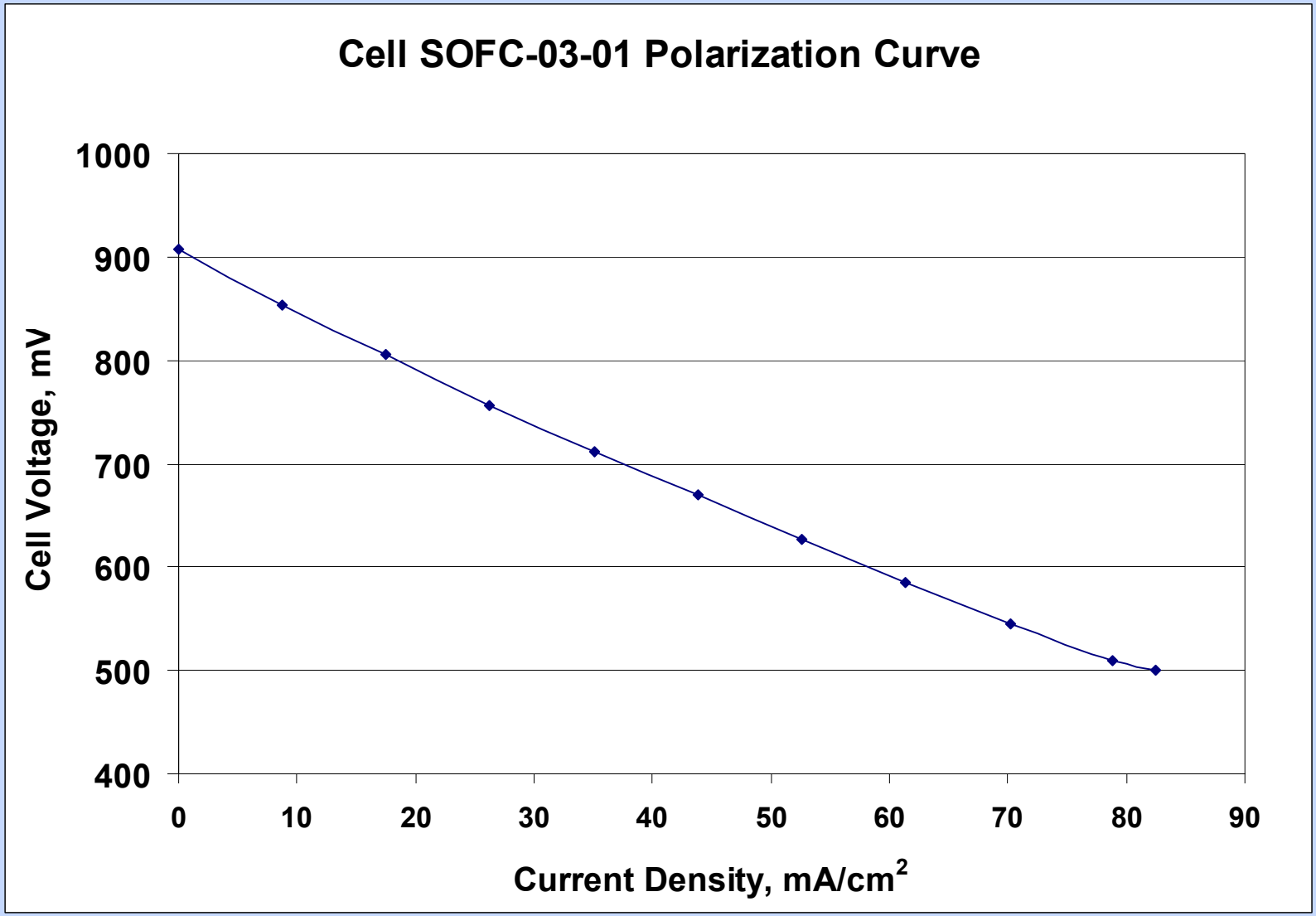
Differences Between GTI and Literature for Previous Dry CH_4 Results at 800°C*

	GTI Results	Literature Results (U. Of Pennsylvania)
OCV	OCV declines from ~0.95 to ~0.7V after 200 hrs Some C	OCV initially ~0.93 Time dependence not available
Constant Current	V decline tracks OCV decline Load accelerates C Cell life <250hrs	Not available
Constant 0.5 V	~32 mW/cm^2 to 75 mW/cm^2 in 5 hrs Then decline so that cell lasts for only 25 hrs Heavy C	Cell operates for >1000 hrs Any C does not prevent operation
* On tape-cast, wet-impregnated Cu/Ceria/YSZ/LSM Cells. GTI cells are 2.85 cm^2 with 13μ electrolyte. Literature cells are <0.5 cm^2 with 60μ electrolyte.		

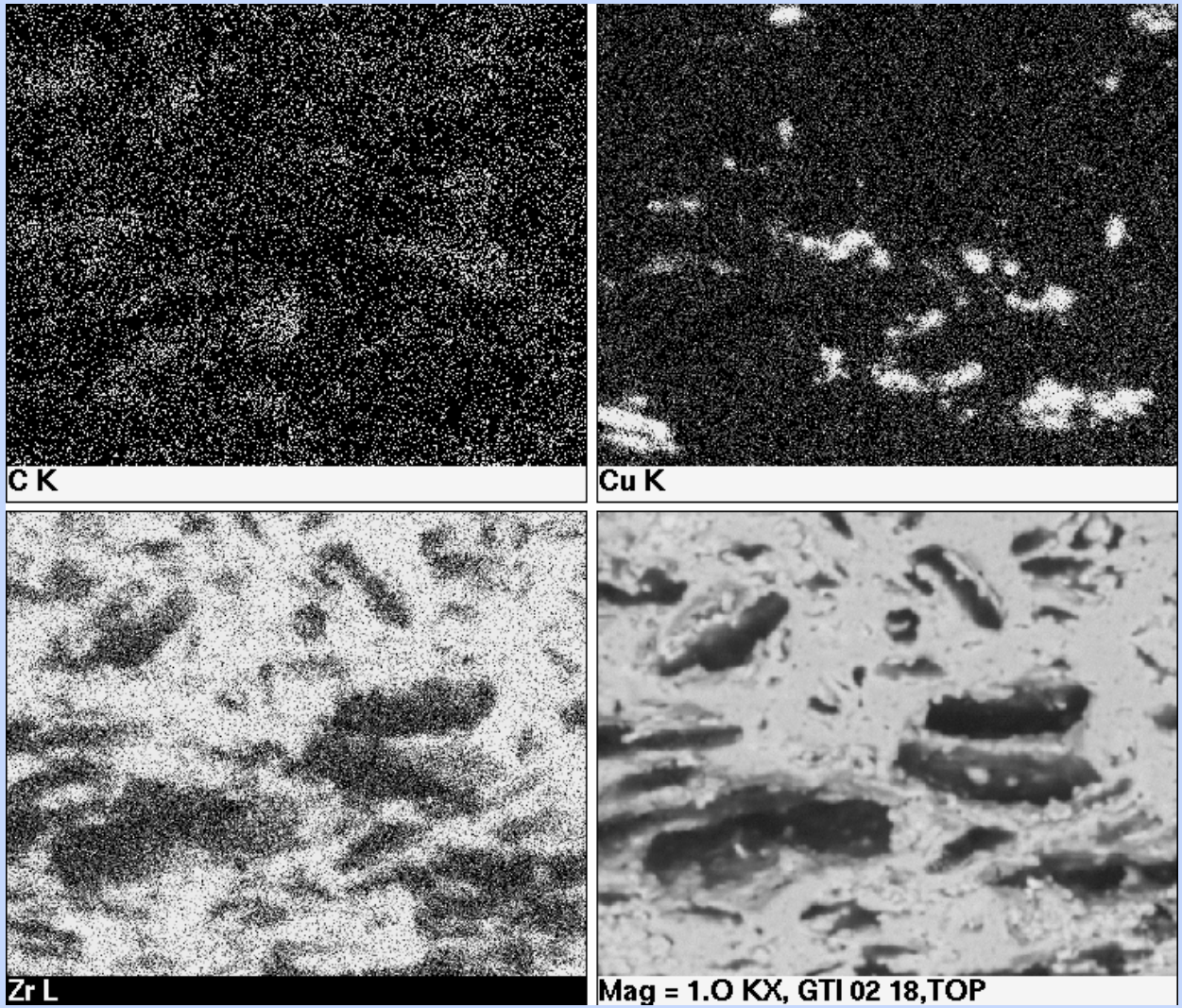
Experimental Set-Up for 3 cm^2 Cells



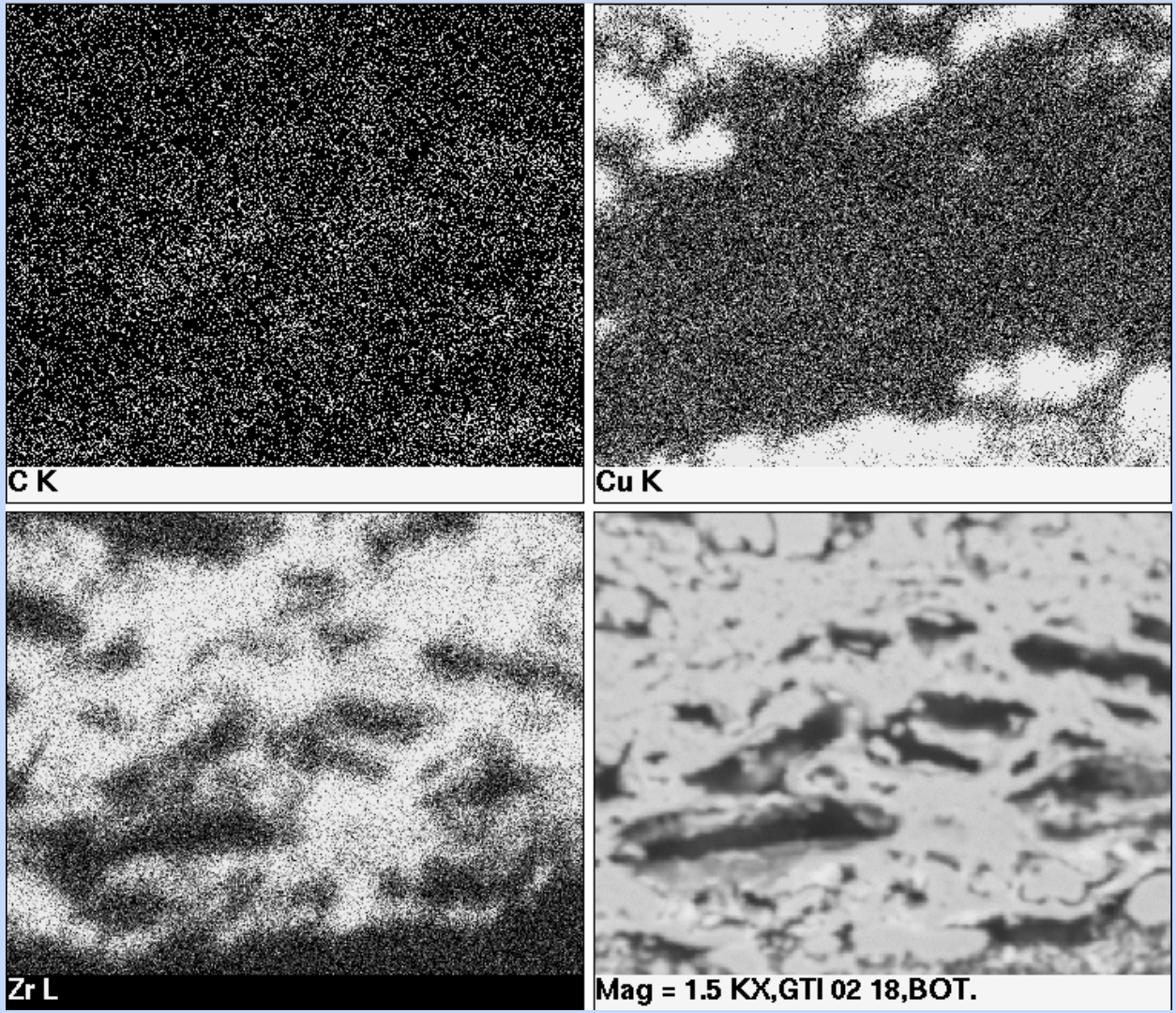
Dry CH_4 Polarization Curve
(~600µ Anode, 13µ Electrolyte, ~100µ Cathode)



SEM/EDAX of C Deposit at OCV
(Dry CH_4, 800C, 13μ Electrolyte, Top of Anode)



C Deposit at OCV (Dry CH_4, 800C, 13µ Electrolyte, Bottom of Anode)



Post-Test Cell Resistance
(Thin Electrolyte)

SOFC-03-04 Dry CH_4 (800,750,700°C)	978 Ω
SOFC-02-18 Dry CH_4 (800°C)	500 Ω
SOFC-02-07 H_2, 3%H_2O (700°C)	830,000-880,000 Ω

Candidate Reasons for OCV Decline

- **Electrical short through seal and/or electrolyte due to C deposition**
  - **Stable OCV and long life with H_2**
  - **Thin electrolyte**
  - **No edge face seal**
    - Observe C in seal area (as well as throughout the anode)
  - **More stable OCV in humidified fuel**
  - **Low cell resistance at room temperature**
- **Gas-phase C deposition due to seal and/or electrolyte leak followed by changes in gas and/or electrolyte**
- **C deposition due to other test parameters followed by changes in gas and/or electrolyte**
  - **Could include anode microstructure, flow rate, flow/temperature distribution, supply line residence time, etc.**

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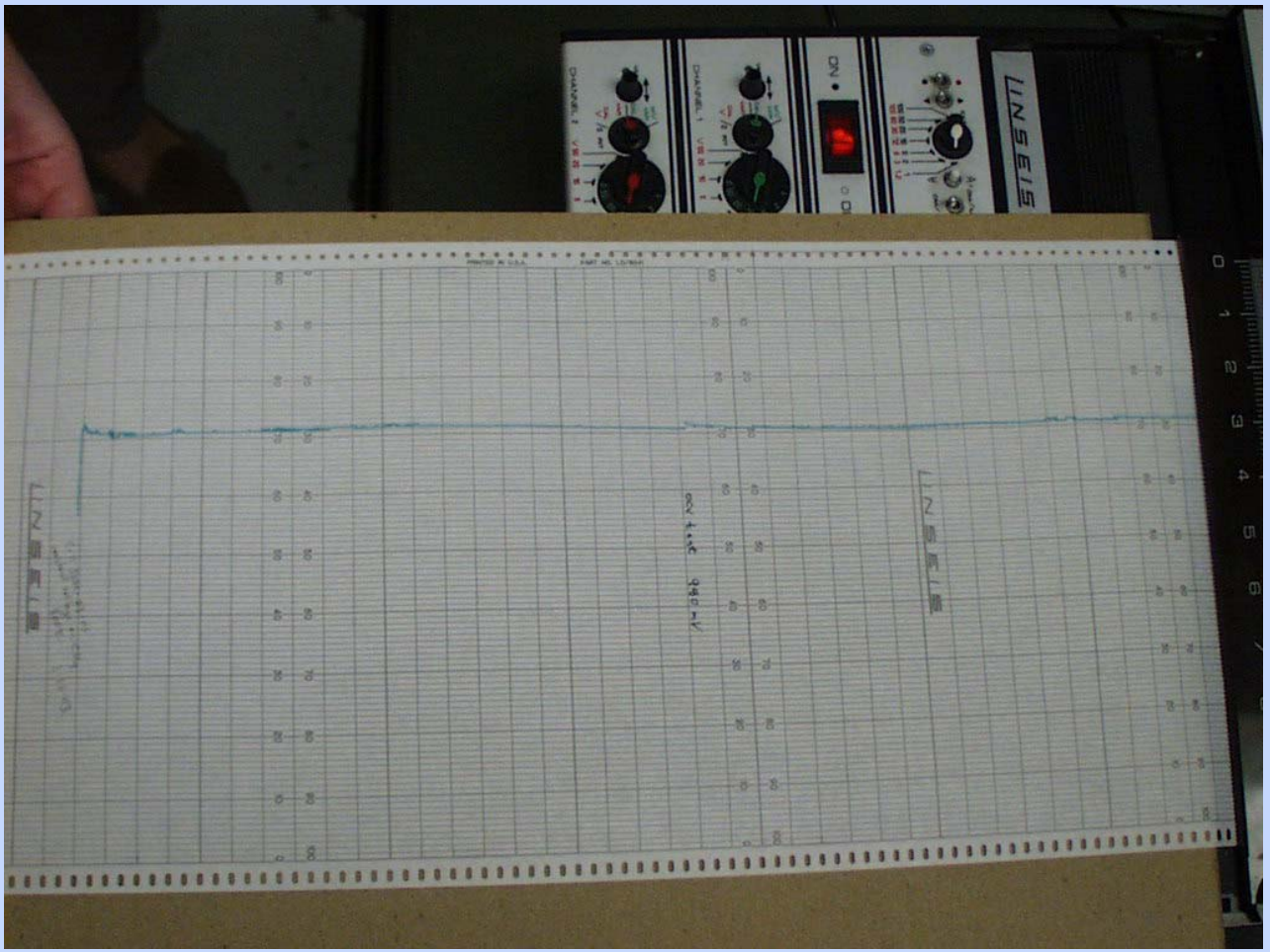
Plans For C Reduction

- Weight gain in dry HC flow
  - To rule out microstructure or fuel purity effects
- OCV stabilization
  - Thicker electrolyte
  - Thinner anode
  - Alternative sealing
  - Changing flow
  - Reduce temperature
  - Etc.
- Constant voltage experiments
  - After OCV is stabilized

Dry CH_4 Performance at 800°C and 0.5V (194µ Anode, 83µ Electrolyte, ~46µ Cathode)



OCV is 980-983 mV

Interim Objective II

- Fabricate and scale-up cells with active inter-layer and sufficient mechanical strength

Status

- Fabricated cells up to 2.5”x4”area
  - By standard dual tape-casting, wet impregnation method
  - Cells do not yet contain active interlayer
  - Mechanical strength is less than desirable

Fabrication Approach I

- Tape-cast thick, porous, μ-particle size YSZ support
  - Deposit μ-particle size active interlayer on anode support
  - Deposit thin, μ-particle size YSZ electrolyte/co-sinter at 1400-1550C
  - Apply and sinter μ-particle size cathode
  - Wet impregnation of Cu/ceria salts/calcine/reduce
- Variations planned to address issues of deposition on porous substrate, thin-layer integrity, mechanical strength, Cu agglomeration

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Fabrication Approach II

- Dry powder press porous, nm-particle size, Cu/ceria/YSZ anode
  Deposit nm-particle size, active interlayer on anode support
  Deposit nm-particle size, YSZ electrolyte
  Apply nm-particle size cathode
  Sinter structure below Cu oxide melting point

- Fabricated cermet anode support
- Variations planned to address issues of deposition on porous substrate, thin-layer integrity, mechanical strength, Cu agglomeration

Other Approaches Under Evaluation

- Tape-cast μ-particle size cermet powder
  Follow steps in method 1 except for impregnation
- Tape-cast μ-particle size Cu/ceria/YSZ cermet
  Deposition of nm-particle size interlayer and electrolyte
- Metallic-supported structures

Interim Objective III

- Develop a quantitative model for electrochemical performance in systems that are thermodynamically capable of depositing C

Status

- Thermodynamic modeling performed to compare mechanisms below for two fuel composition cases:

  1. Direct oxidation of methane

  $CH_4 + 4O^{=} \rightarrow CO_2 + 2H_2O + 8e$ (anode)

  $2O_2 + 8e \rightarrow 4O^{=}$ (cathode)

  $CH_4 + 2\,O_2 = CO_2 + 2H_2O$

  2. Methane reforming with water-shift reaction followed by oxidation of hydrogen

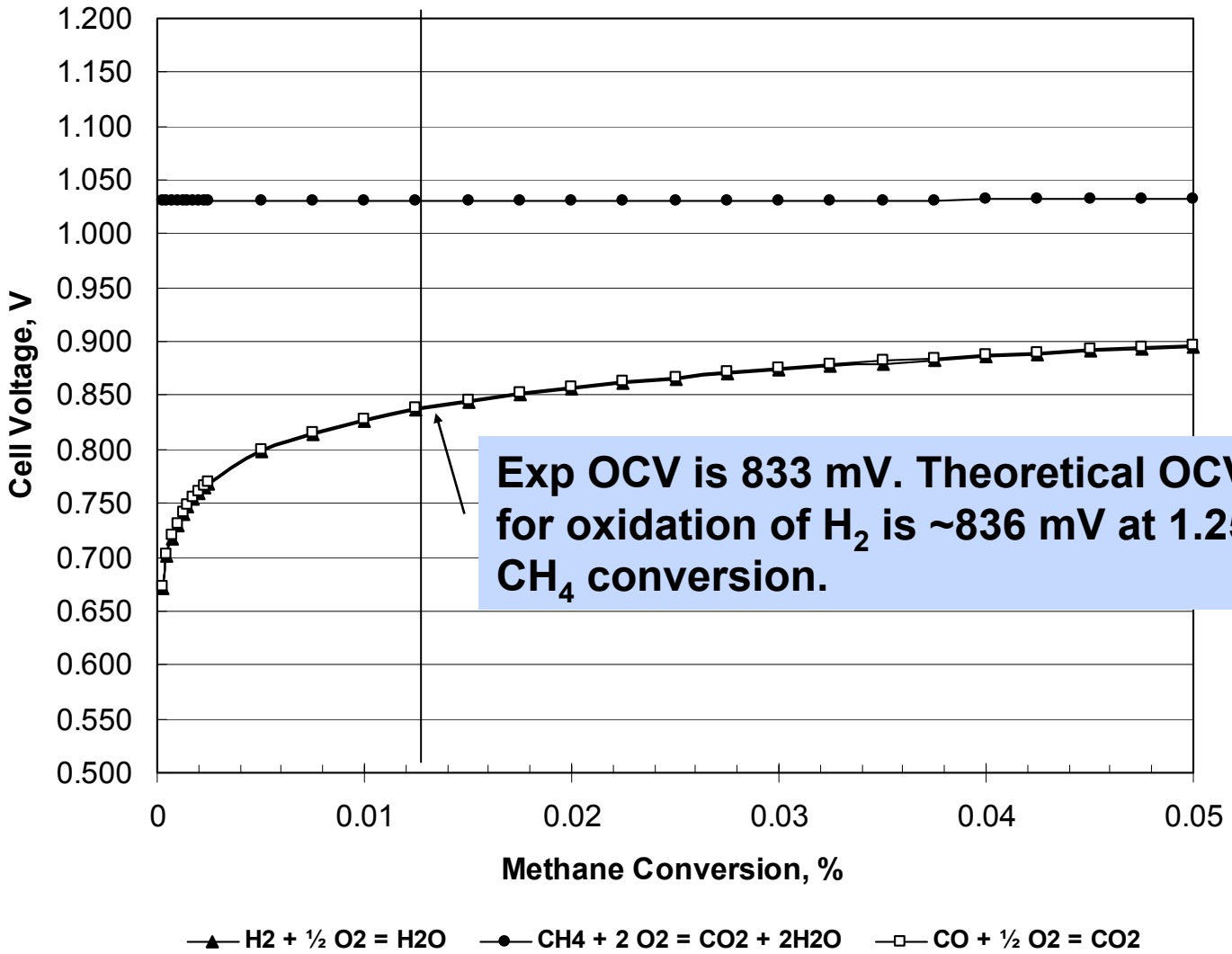
  $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$ (anode)

  $4H_2 + 4O^{=} \rightarrow 4\,H_2O + 8e$ (anode)

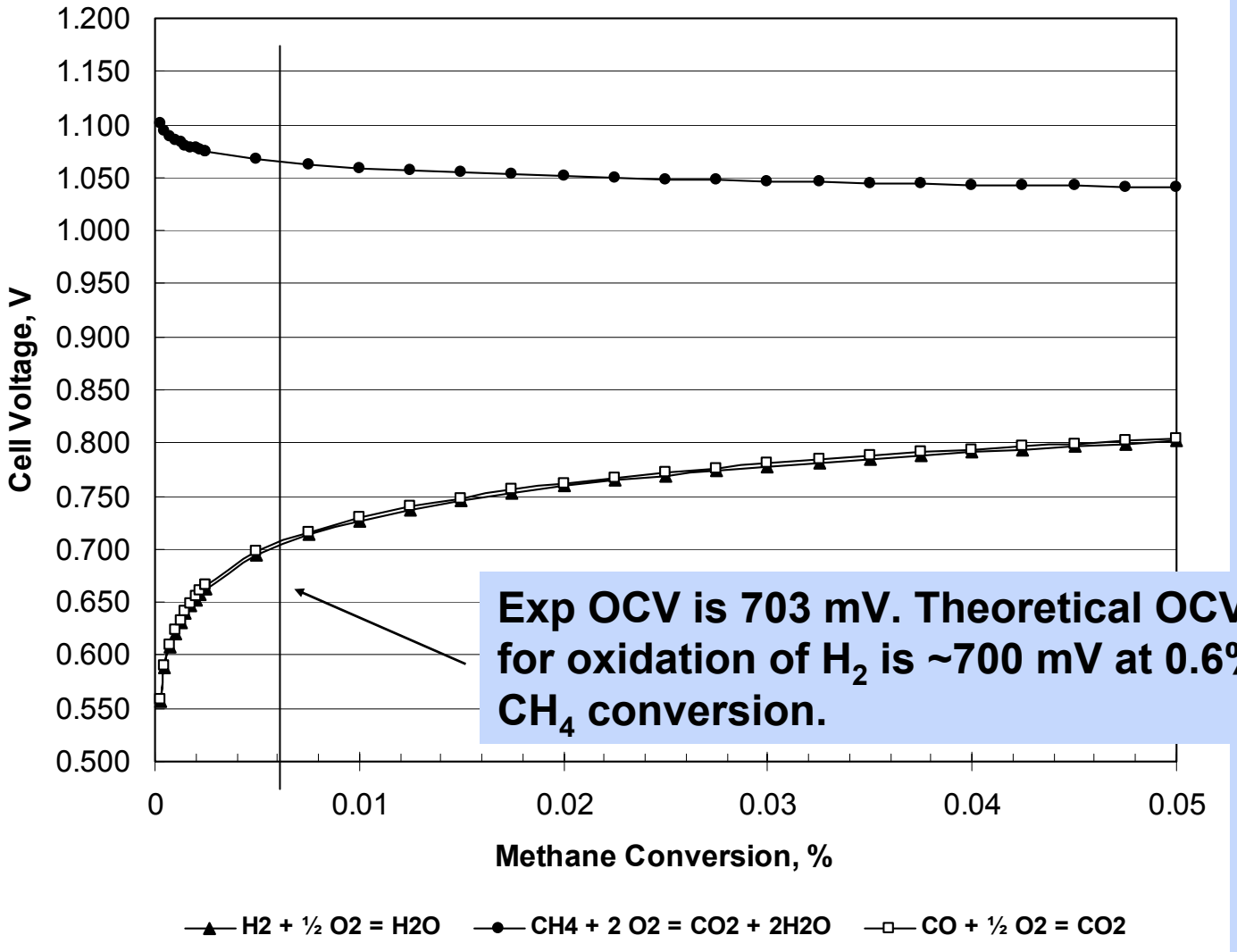
  $2O_2 + 8e \rightarrow 4O^{=}$ (cathode)

  $CH_4 + 2\,O_2 = CO_2 + 2H_2O$

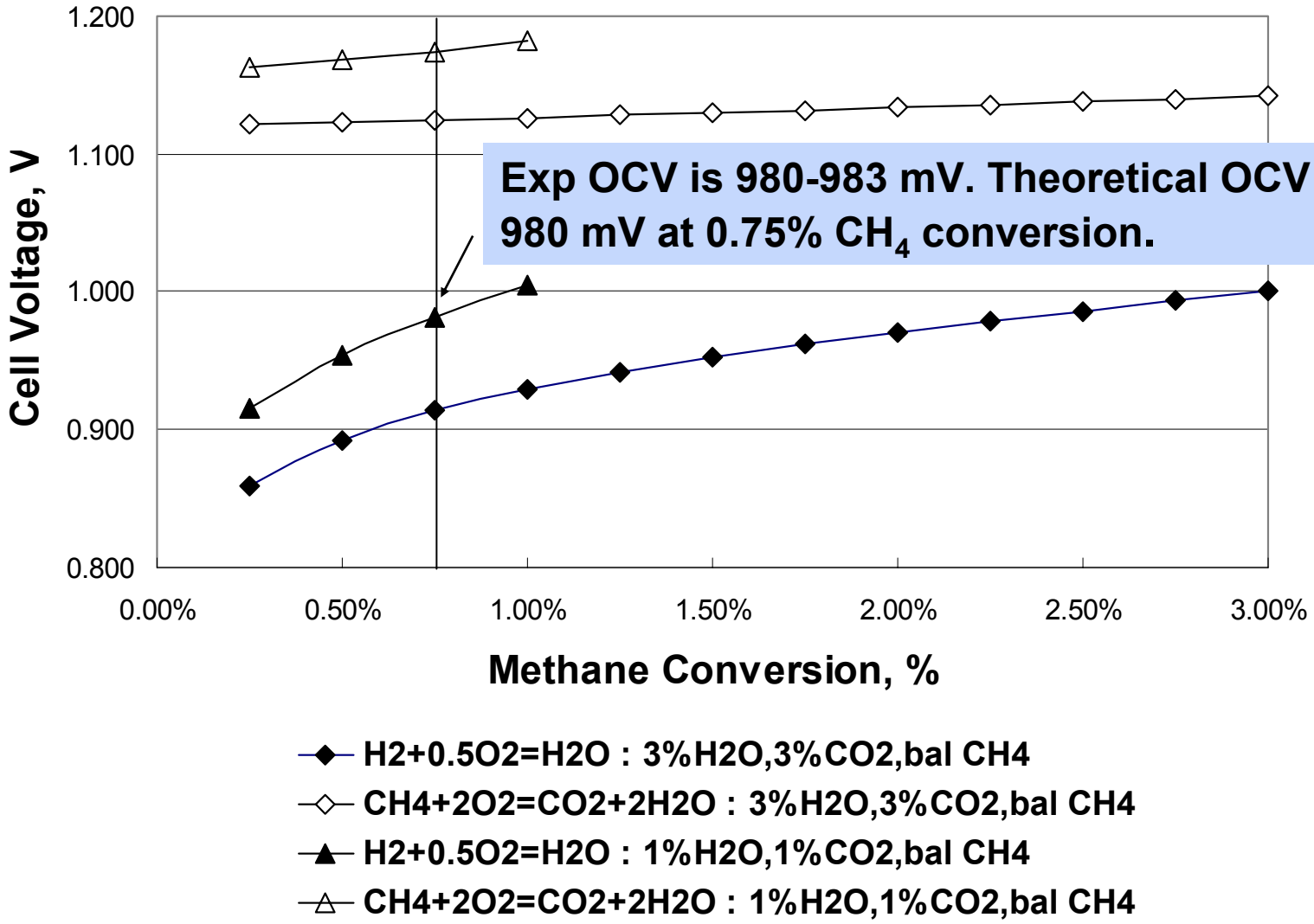
Theoretical OCV for 40%CH_4/40%H_2O/20% CO_2 at 700C and Low CH_4 Conversion



Theoretical OCV for 19.61%CH_4/80.39% H_2O at 800°C and Low CH_4 Conversion



OCV at Lower H_2O/CO_2 Concentrations



Plans

- **Kinetic and thermodynamic modeling of dry and near-dry HC oxidation to develop mechanisms for:**
  - **Electrochemical performance**
    - Changes in long-term, dry HC performance
    - Variations in C formation and cell performance under different operating conditions and cell geometries
  - **OCV properties**
    - OCV decline with time in thin-electrolyte cells
    - OCV variations with butane
    - Low dry CH_4 OCV on catalytic and non-catalytic anodes

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Conclusions

- Dry or near-dry HC oxidation is worth investigating
  - No fuel processing, no steam, no recycle of steam or fuel, simpler piping and manifolding, simpler heat management, faster response time, simpler controls
  - Research has shown that laboratory cells operating on certain HC fuels are not compromised by C deposition after >1000 hours
  - Relatively simple periodic “cleaning” of the anode may be possible

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Conclusions

- Cell life depends upon minimizing C formation
  - Higher electrolyte integrity or more tailored anode microstructure may be required for a dry HC cell as compared with a H_2-fueled cell
  - Recent results suggest that conditions for long-term operation can be achieved in 2.85cm^2 cells
- A range of approaches are available for fabrication of Cu-based cells containing an active interlayer
- Preliminary thermodynamic OCV modeling is consistent with a mechanism based on CH_4 reforming followed by H_2 oxidation

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