FARADAY TECHNOLOGY, INC.

Pulsed Electrodeposition of Gas Diffusion Electrocatalysts for CO₂ Reduction to Value-Added Products

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Outline

- Motivation – CO₂ & CH₄ Conversion
- Electrochemical Processing
 - Overview
 - Advantages of Pulse-Processing
- Pulsed FARADAYIC[®] ElectroCatalyzation of GDEs
 - Rationale and Electrodeposition Approach
 - Catalyst Material Selection
 - Prepared GDE Electrocatalysts
 - Electrocatalyst Performance Testing

Motivation

- **CO₂ Conversion**

- Abundant feedstock
- Highly distributed sources
- Environmental concerns

- **CH₄ Conversion**

- Abundant feedstock
- Fuel value only
- Value-add: upgrade to platform chemical feedstock

Electrochemical Processing

Conventional DC vs Pulse/Pulse-Reverse

Applied Electrochemistry

Current is net flow of
POSITIVE CHARGE

Applied Electrochemistry

Pulsed Waveforms vs DC

Know: *Linearized Concentration Profile*

Pulsed Waveforms vs DC

Know: *Linearized Concentration Profile*

Pulsed Waveforms vs DC

Know: Linearized Concentration Profile

Assume:

Prior Work: Copper Electrodeposition for PCBs

Standard DC Recipe

CuSO_4
 H_2SO_4
“Accelerator”
“Suppressor”
“Leveler”
Other Additives

Pulsed Waveform Recipe

CuSO_4
 H_2SO_4
Trace Cl^-
Trace PEG

Z-Interconnects Cu-Plated by Pulse-Reverse FARADAYIC® ElectroDeposition

Plante, et al. “Quantization and Characterization of Copper Plating Bath Additives by Liquid Chromatography with Charged Aerosol Detection.” Thermo Scientific. http://www.dionex.com/en-us/webdocs/113469-Pittcon12_1820-6_MPlante_PN70008_PlatingBaths.pdf

Prior Work: Lead-Free Tin

Rotating Disk Plating Tool

Sn Deposits on Cu Substrates — 1000× Magnification

U.S. Patent 8,603,315 Granted

FARADAY TECHNOLOGY, INC.

FARADAYIC[®] ElectroCatalyzation

Gas Diffusion Electrode (GDE) Electrocatalysts

FARADAYIC[®] GDE ElectroCatalyzation

TEM of Pt on Carbon

Performance Comparison

FARADAYIC® GDE ElectroCatalyzation

Electronic + Ionic Contact

FARADAYIC[®] GDE ElectroCatalyzation

Electrocatalyst Materials Selection

CO₂ Electrocatalyst Selection

Product distribution over single-metal electrocatalysts as determined by Hori et al.

Electrochimica Acta 39(11-12): 1833 (1994).

e									B	C	N
g									Al	Si	P
a	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
r	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
a	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl

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CH₄ Electrocatalyst Selection

- Selective methane oxidative coupling to ethylene using S₂ oxidant demonstrated by Zhu et al.

- “Soft” S₂ oxidant reduces over-oxidation vs O₂
 - Products cascade to CS₂ much less stable than that to CO₂
- ~15% CH₄ conversion
~20% C₂H₄ yield
- 800-1050 °C
- *Tractable for electrocatalysis?*

Figure reproduced from Zhu et al., Nat. Chem. 5: 104 (2013).

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CH₄ Electrocatalyst Selection

CuGaSe₂ Electro-codeposition for Photovoltaics

Plating Bath

- 20 mM H₂SeO₃
- 2.0 M NaSCN (complexant)
- Variable concentrations of CuSO₄ and Ga₂(SO₄)₃
- pH 2.75

N	O	F
P	S	C
As	Se	B
Sb	Te	I

Muthuraj et al., *J Electrochem Soc* 158(2): D54 (2011)

FARADAYIC[®] GDE ElectroCatalyzation

Prepared Electrocatalysts

GDE Catalysts – Sn

GDE Catalysts – Cu

GDE Catalysts – Metal/Metal Sulfides

FARADAYIC[®] ElectroCatalyzation

Electrocatalyst Testing

W-Cell Apparatus

Flow Cell Apparatus

Sn GDE – W-Cell Electrocatalsysis

(Half-cell potentials vs SHE)

Li and Oloman. *J Appl Electrochem* 35: 955, 2005.

Agarwal et al. *ChemSusChem* 4: 1301, 2011.

Kopljar et al. *J Appl Electrochem* 44: 1107, 2014.

Cu GDE – Flow Cell Electrocatalysis

Ma et al. *J Power Sources* 301: 219, 2016.

M⁰/MS_x GDEs – Flow Cell Electrocatalysis

M⁰/MS_x GDEs – Flow Cell Electrocatalysis

Summary

- Wide variety of active GDE catalyst materials can be deposited via pulsed FARADAYIC[®] ElectroCatalyzation
 - Readily scalable process
- High-activity CO₂ conversion catalysts
 - Demonstrated in industrially-relevant, scalable form factor
 - Performance competitive with or superior to literature
 - Total activities (mA/cm²)
 - Formate/ethylene selectivity
 - Durability appears promising; further testing is pending
- Challenges remain with CH₄ conversion
 - Poor aqueous CH₄ solubility ←**X**→ Need for protic electrolyte
 - Alternative approach: Electrodeposition of chemical catalysts?

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Thank You!