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Particle Size and Morphology of Carbon Dioxide Reduction Electrocatalysts Fabricated by Pulse/Pulse-Reverse Electrodeposition

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Motivation

- **CO₂ Conversion**

- Environmental concerns
- Abundant carbon feedstock for value-added products
 - CO, formate, hydrocarbons
- Point sources (e.g., power generation)
 - Co-location of capture & conversion
- Direct conversion of gas-phase CO₂
 - Gas-diffusion electrode (GDE) electrolyzer

Pulsed Waveforms – Enhanced Process Control

Electrochemical Machining, Polishing, Deburring, Through-Mask Etching

Anodic Pulse “Tuned” to:

- Control current distribution

→ Eliminates need for viscous, low water content electrolytes

Cathodic Pulse “Tuned” to:

- Reduce oxide/depassivate surface

→ Eliminate need for HF

Electrodeposition/Plating, Electrocatalysis

Cathodic Pulse “Tuned” to:

- Enhance mass transfer
- Control current distribution

→ Simplify chemistry

Anodic Pulse “Tuned” to:

- Remove H_2 effects

→ Acidify interface

E.J. Taylor “Adventures in Pulse/Pulse Reverse Electrolytic Processes: Explorations and Applications in Surface Finishing” J. Appl. Sur. Fin. 3(4) 178-89 (2008).

Prior Work: Lead-Free Tin

Rotating Disk Plating Tool

Sn Deposits on Cu Substrates — 1000× Magnification

U.S. Patent 8,603,315 Granted

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

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FARADAYIC[®] ElectroCatalyzation

Gas Diffusion Electrode (GDE) Electrocatalysts

FARADAYIC® GDE ElectroCatalyzation

TEM of Pt on Carbon

Performance Comparison

FARADAYIC® GDE ElectroCatalyzation

Electronic + Ionic Contact

ElectroCatalyzation Pretreatment

***“Floating” on
Ionomer Dispersion***

***Low-Power
Air Plasma Treatment***

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	F
g											Al	Si	P
a	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
r	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
a	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

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GDE Catalysts – Sn

GDE SEM – Sn

Ionomer Pretreat
Microparticulate

Ionomer Pretreat
Micro/Nanoparticulate

Plasma Pretreat
Nanoparticulate

*No Observed
Nanoparticles*

Trends with ElectroCatalyzation Parameters – Sn

Deposit Observed?

Duration ↑ Deposits ↑

$R^2 = 0.22$ $p = 0.002$

Deposit Size?

Peak Current ↑ Size ↓

$R^2 = 0.11$ $p = 0.21$

GDE Catalysts – Cu

GDE SEM – Cu

No Deposit

Microstructured Deposit

Nanostructured Deposit

Trends with ElectroCatalyzation Parameters – Cu

Multiple Linear Regression

Parameter Down-Selection by Minimization of Akaike Information Criterion

		Deposit Observed? <i>1 = Yes; 0 = No</i>		Nanostructured Deposit? <i>1 = Yes; 0 = No</i>	
No Deposit	<i>n = 2</i>	<i>R</i> ²	<i>0.988</i>	<i>0.979</i>	
Microstructured Deposits	<i>n = 2</i>				
Nanostructured Deposits	<i>n = 4</i>				
		<i>Effect</i>	<i>p-Value</i>	<i>Effect</i>	<i>p-Value</i>
		<i>I</i> _{peak,f}	↑ 0.011	— 0.011	— 0.105
		<i>I</i> _{peak,r}	↑ 0.011	↑ 0.011	0.105
		<i>t</i> _{on,f}	↑ 0.011	↑ 0.011	0.017
		<i>t</i> _{off,f}	↓ 0.018	↓ 0.018	0.008
		<i>t</i> _{on,r}	↓ 0.012	↓ 0.012	0.033
		<i>Duration</i>	—	↓ 0.006	0.006

All samples ionomer-pretreated

$$0 \leq \frac{I_{p,r} t_{on,r}}{I_{p,f} t_{on,f}} = \frac{Q_r}{Q_f} \leq 0.55$$

Summary

- Wide variety of active GDE catalyst materials can be deposited via pulsed FARADAYIC[®] ElectroCatalyzation
 - Readily scalable process
- Influence/control over particle size/structure demonstrated
- Significant variability in Sn properties for samples studied
 - Plasma pre-treatment appears favorable
 - Suggests exploration of wider current range potentially valuable
- Expected trends of Cu properties vs ElectroCatalyzation parameters

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Thank You!