



ELECTROLYTIC ORGANIC DESTRUCTION

OZONO ELETTRONICA INTERNAZIONALE S.r.l.



Reasons for Organic Destruction

- Increasing regulatory restrictions
- Lower level on Toxic Release Inventory List
- Avoid high cost deep well injection
- Avoid future liability
- Reuse valuable resources
- Avoid organic contaminant accumulation
- Avoid the use/storage of toxic chemicals



Choices

- Chemical addition
- Thermal processes
- Biological
- UV
- Membrane processes
- Adsorption
- Electrolytic



Electrons Less Expensive

Reagent	Cents/mole
Electrons @ 6 cents/KWH, 3.5 V	0.6
Hydrogen Peroxide	3.8
Sodium	7.5
Magnesium	7.9
Zinc	8.6
Hydrazine	14
Sodium Hydrosulfite	25
Sodium Dichromate	39
Potassium Permanganate	45
Sodium Borohydride	170
Stannous Chloride	280



Technical Advantages

- Eliminate waste for zero discharge
- Regenerate spent process solutions
- Recover valuable resources
- Generate chemicals on site
- Adjust pH without acid or base
- No corrosive, hazardous, toxic chemicals



Tech Advantages Continued

- Controlled by electricity added
- Ambient pressure and temperature
- “Mineralization” to H_2O and CO_2
- Anodes selective to desired reaction
- Sludge often avoided



Indirect vs Direct Electrooxidation

- Indirect Electrooxidation

 - Hypochlorite

 - Ce(IV)

 - Co(III)

 - Ag(II)

 - Fe(III)

- Direct Electrooxidation

 - Oxygen evolution preferred

 - Typically requires high oxygen overpotential
anode

 - Adsorption at the electrode surface

 - Generation of reactive species, hydroxyl radicals

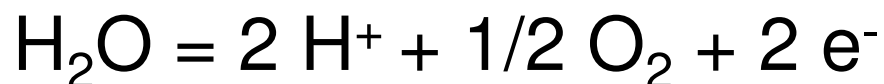


Electrode Reactions

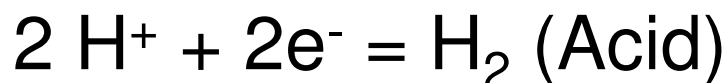
- Desired Anode Reaction



- Competing Anode Reaction



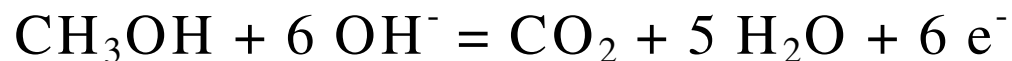
- Typical Cathode Reactions



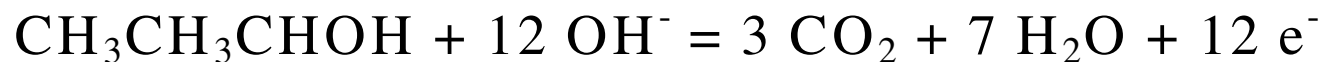


More Complex Molecules

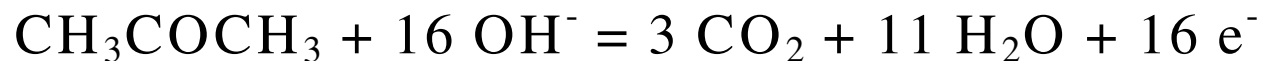
Methanol



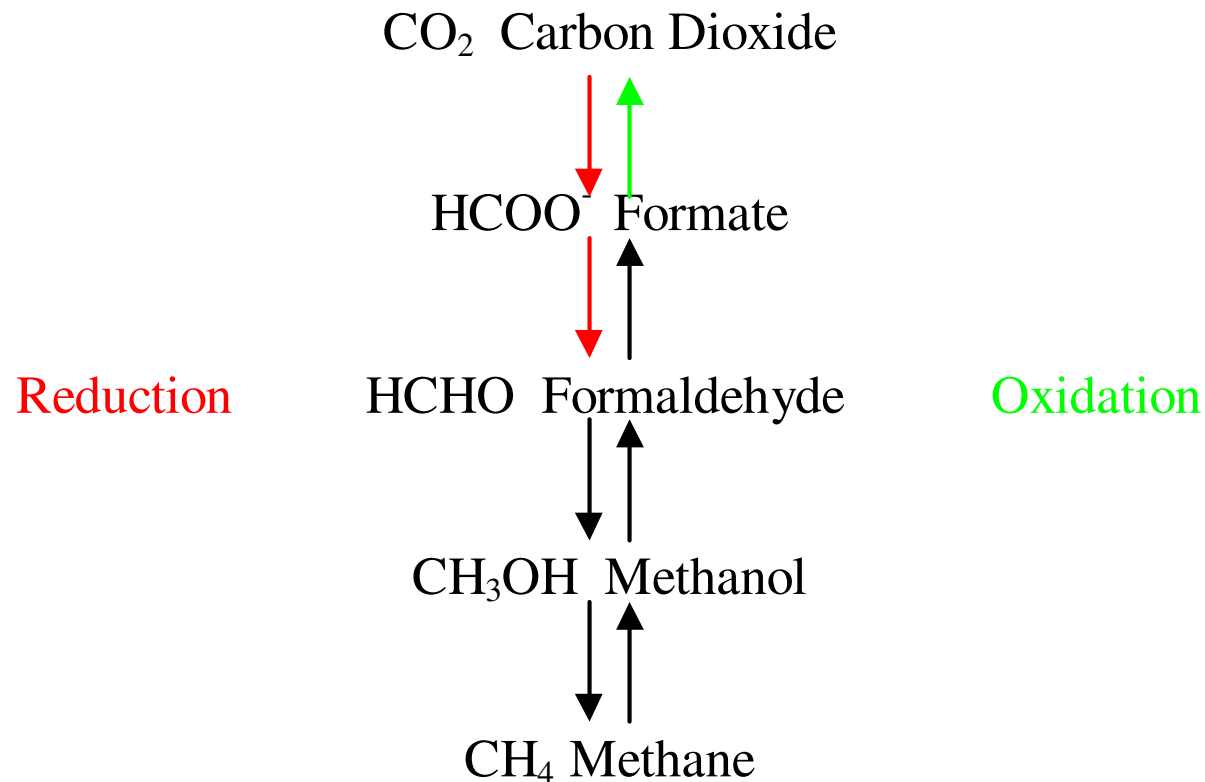
Isopropanol



Acetone



Formate Oxidation/Reduction Products





Electrode Potentials in 1.5 M H_2SO_4 at Room Temperature

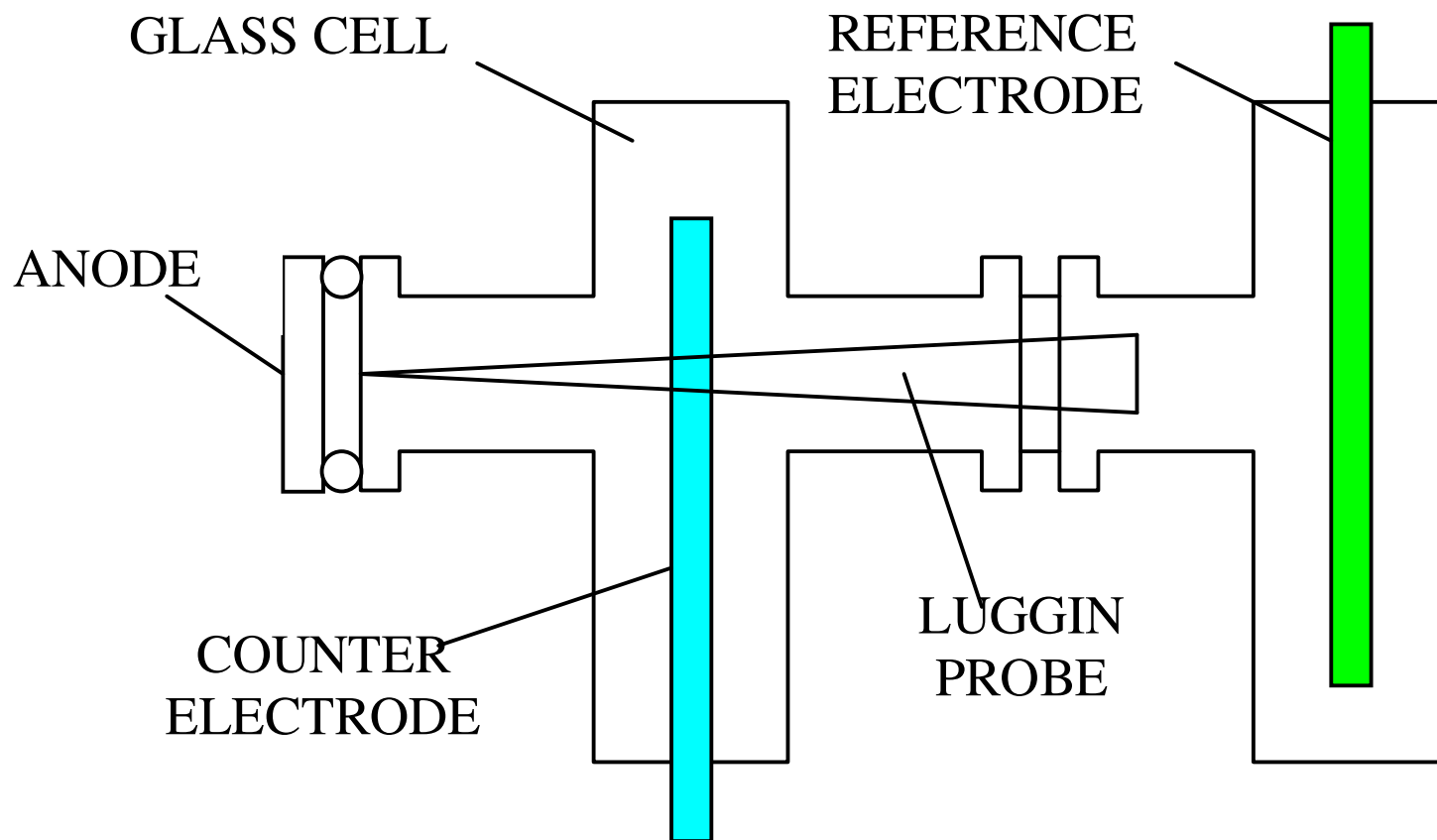
	Potential V Vs NHE	
	10mA/sq cm	100 mA/sq cm
Iridium Oxide/ Ti	1.59	1.67
Platinum or Pt/Ti	2.01	2.11
Lead Dioxide	2.21	2.34
Tin Oxide	2.05	2.23



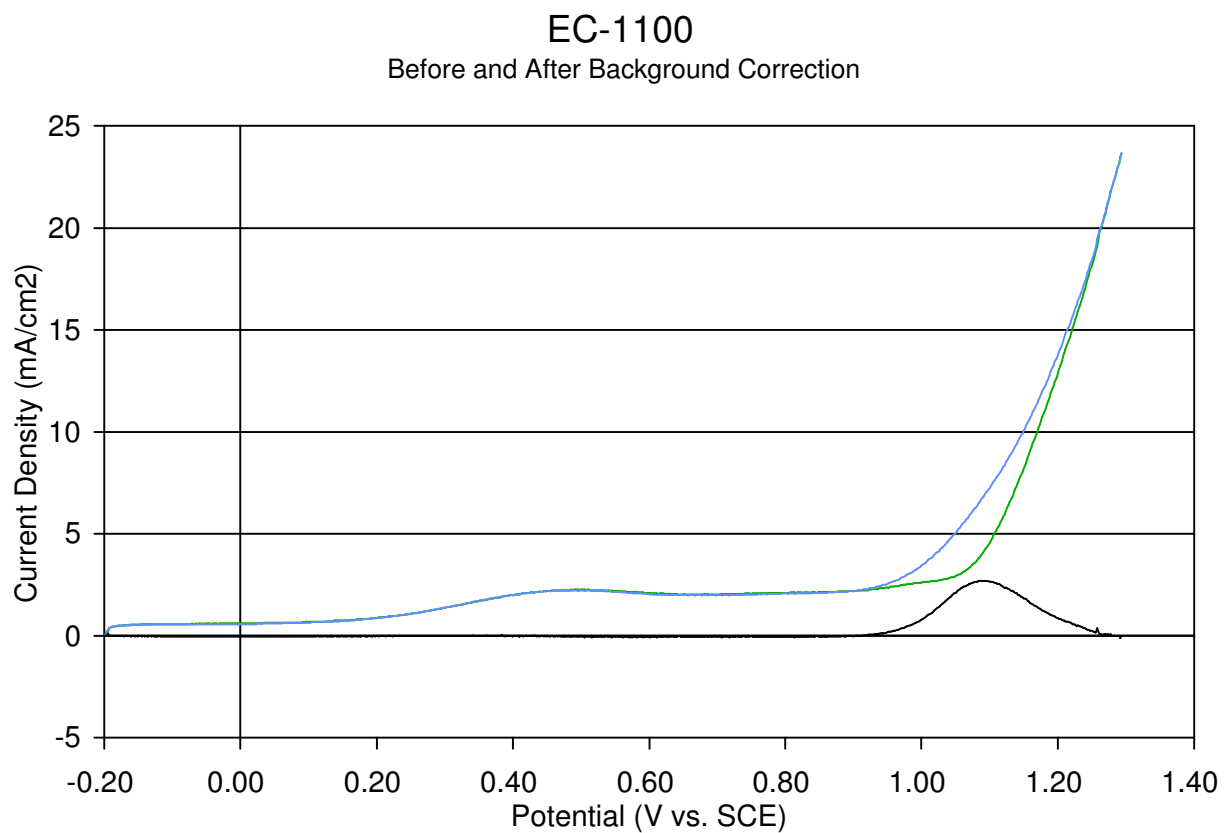
Electrochemical Oxidation Index

Initial Electrochemical Oxidation Index		
Organic Compound	SnO₂	Pt
Ethanol	0.49	0.02
Acetone	0.21	0.02
Tartaric Acid	0.34	0.27
Malonic Acid	0.21	0.01
Benzoic Acid	0.79	0.1
Naphthalene 2 Sulfonic Acid	0.51	0.04
Phenol	0.6	0.15
Anilene	0.43	-
Benzen-Sulfonic Acid	0.29	-
Nitrobenzene	0.8	-
4 Chlorophenol	0.35	-

Background Corrected Cyclic Voltammetry

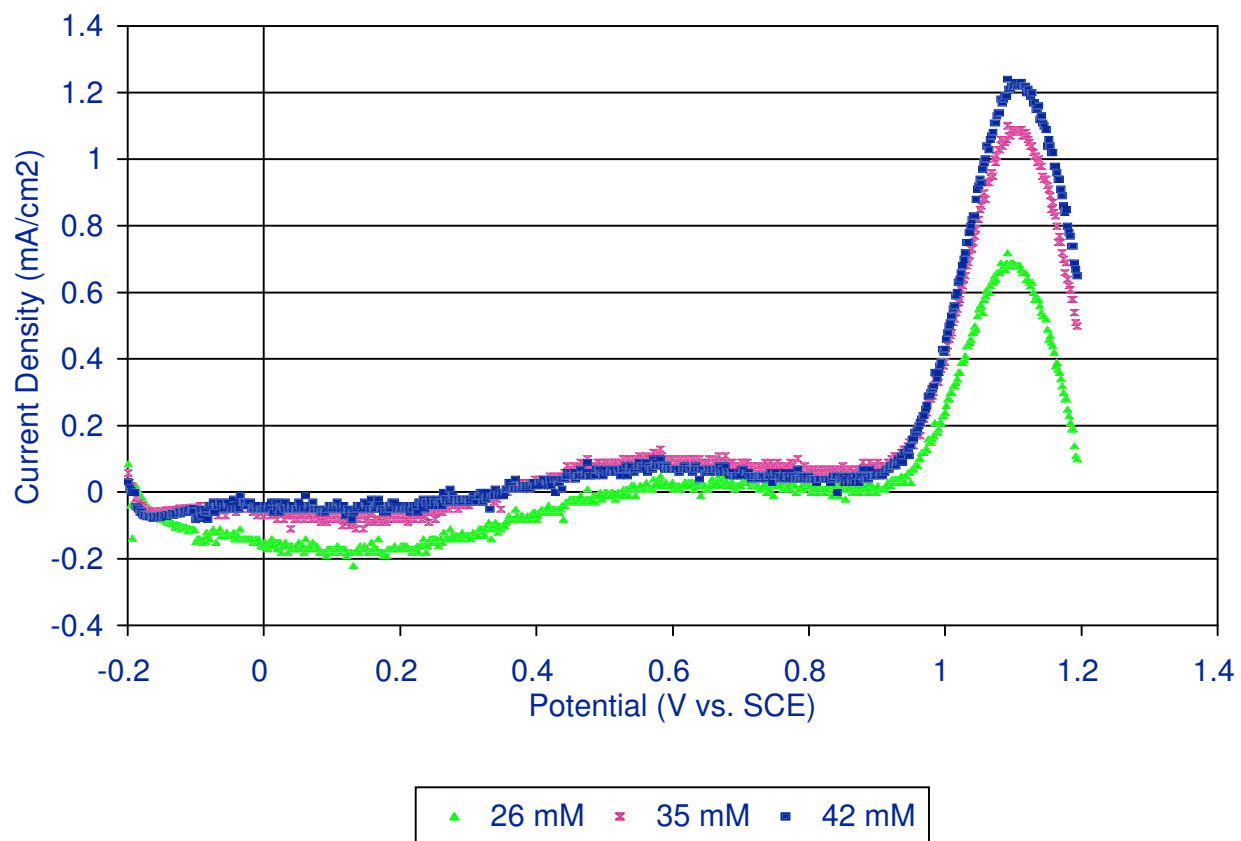


BCCV Example

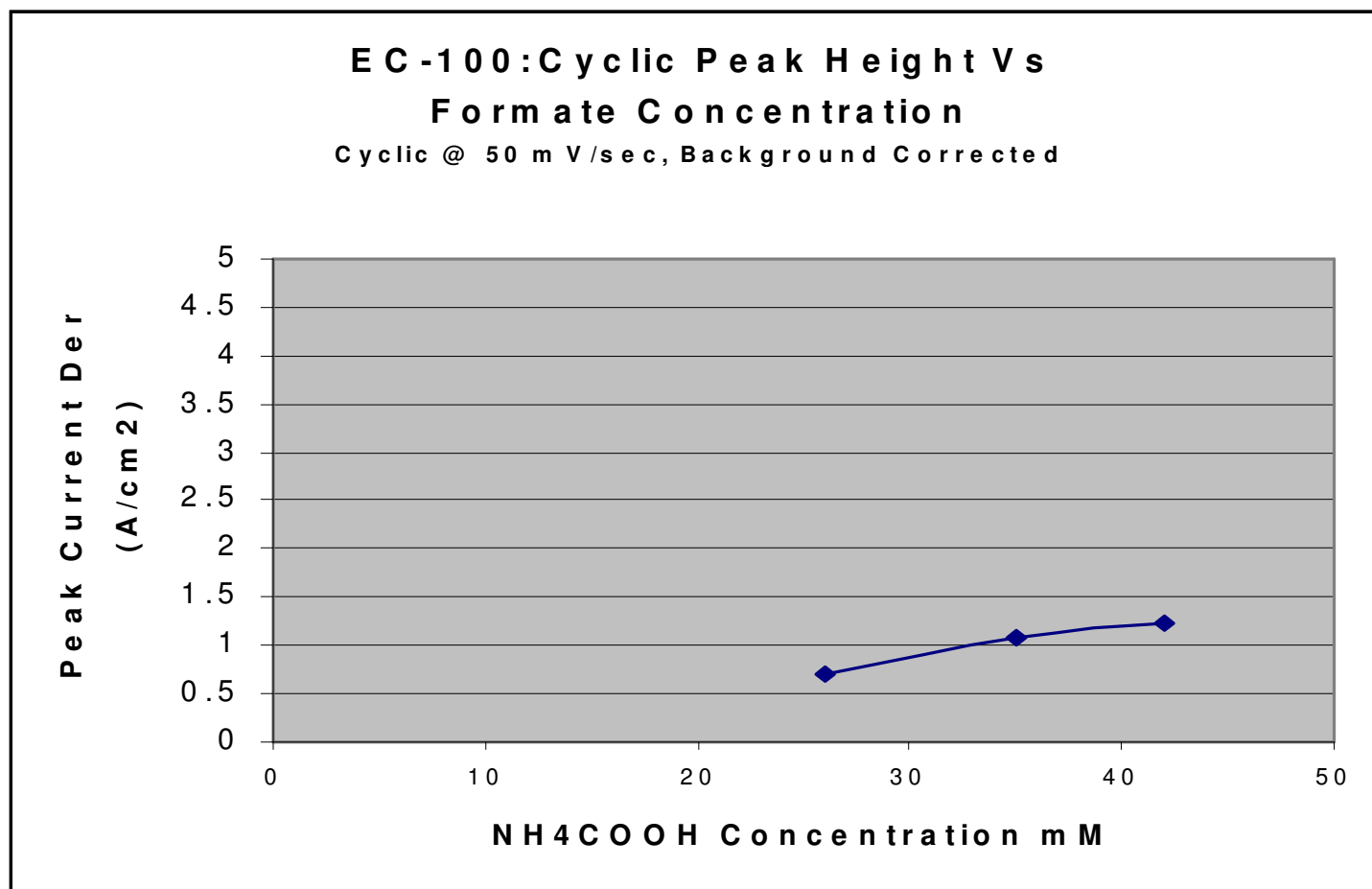


BCCV on EC-100

EC-100 in $(\text{NH}_4)_2\text{H}_2\text{PO}_4/\text{NH}_4\text{COOH}$
50 mv/sec, Background Corrected

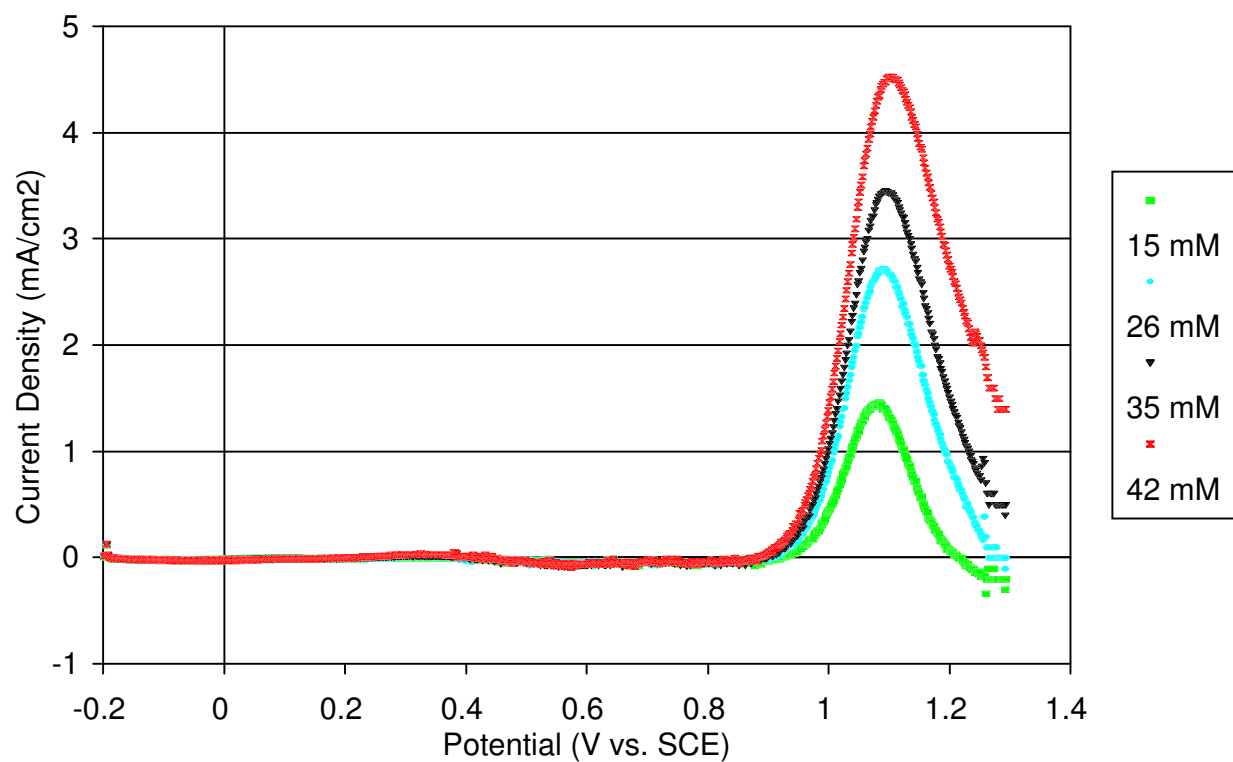


Peak Heights on EC-100

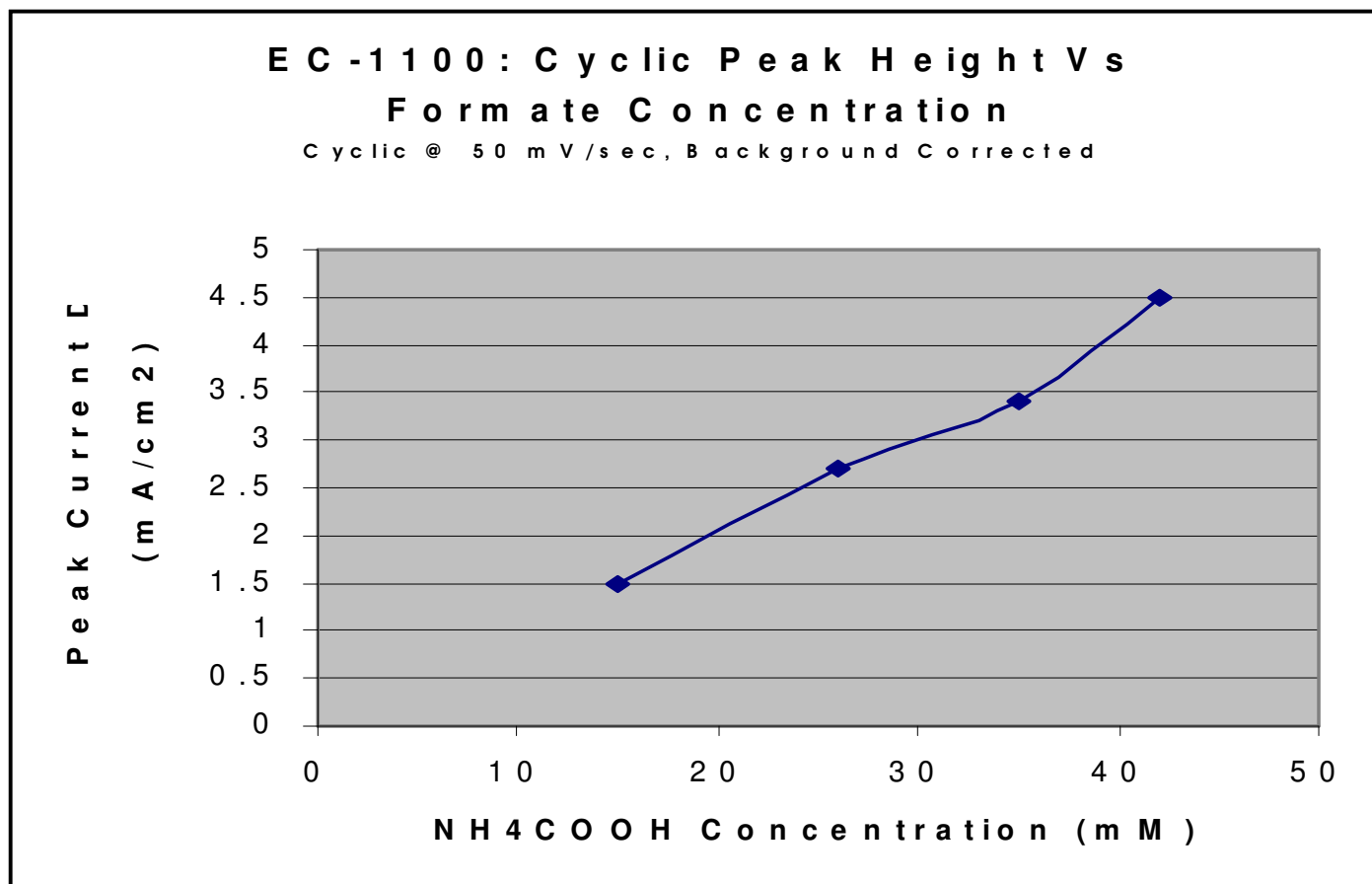


BCCV on EC-1100

EC-1100LT: (NH₄)H₂PO₄/NH₄COOH
50 mV/sec, Background Corrected



Peak Heights on EC-1100





Limiting Current Density

$$I_{\text{limiting}} = zFDA C_b / d$$

Where:

z = number of electrons per equivalent, 1

F = Faradays constant, 9.65×10^4 amp sec

D = Diffusion coefficient, $\sim 2 \times 10^{-6}$ cm²/sec Fe⁺³

A = Electrode area, basis 1 sq cm

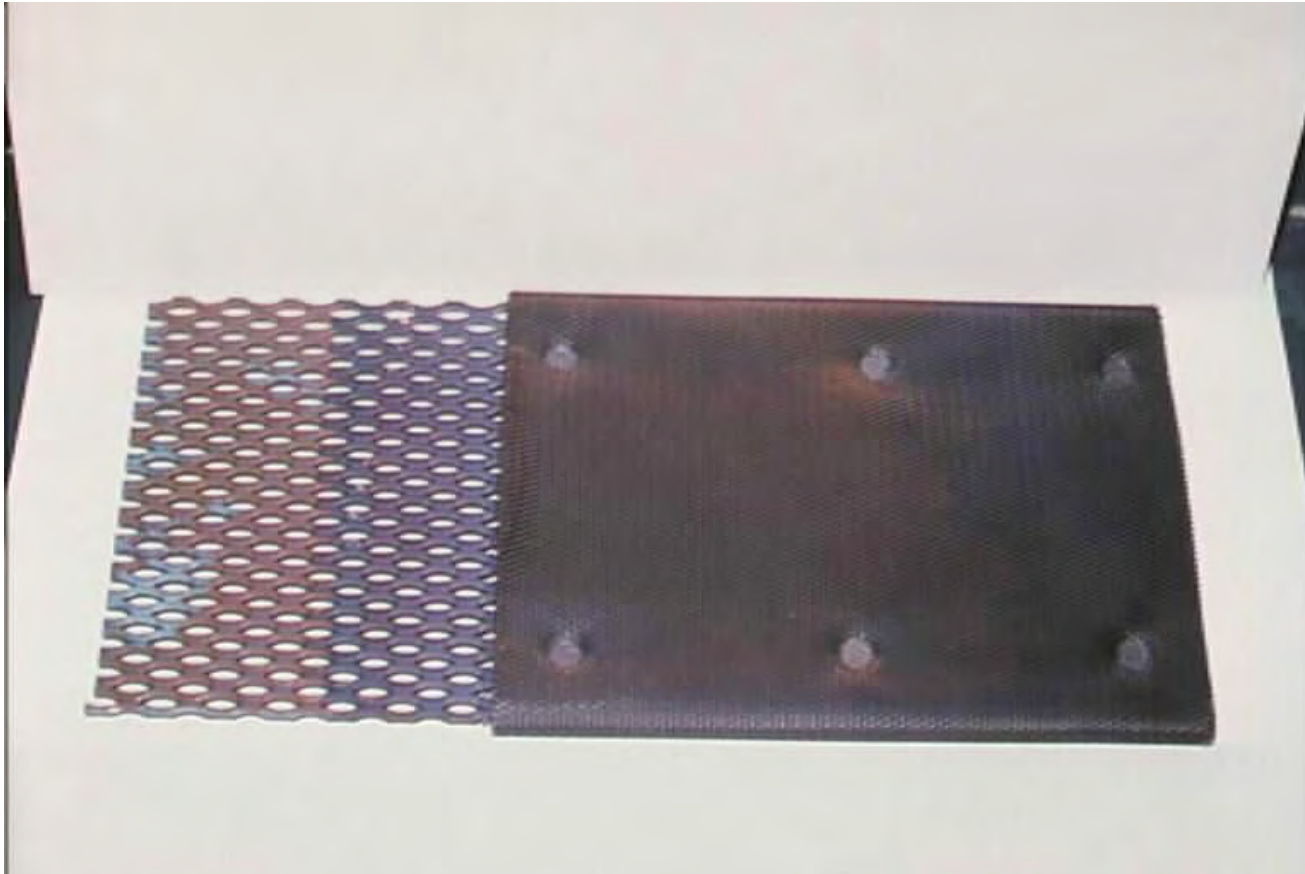
C_b = Fe⁺³ concentration, moles/cc

d = diffusion layer thickness $\sim 1 \times 10^{-3}$ cm

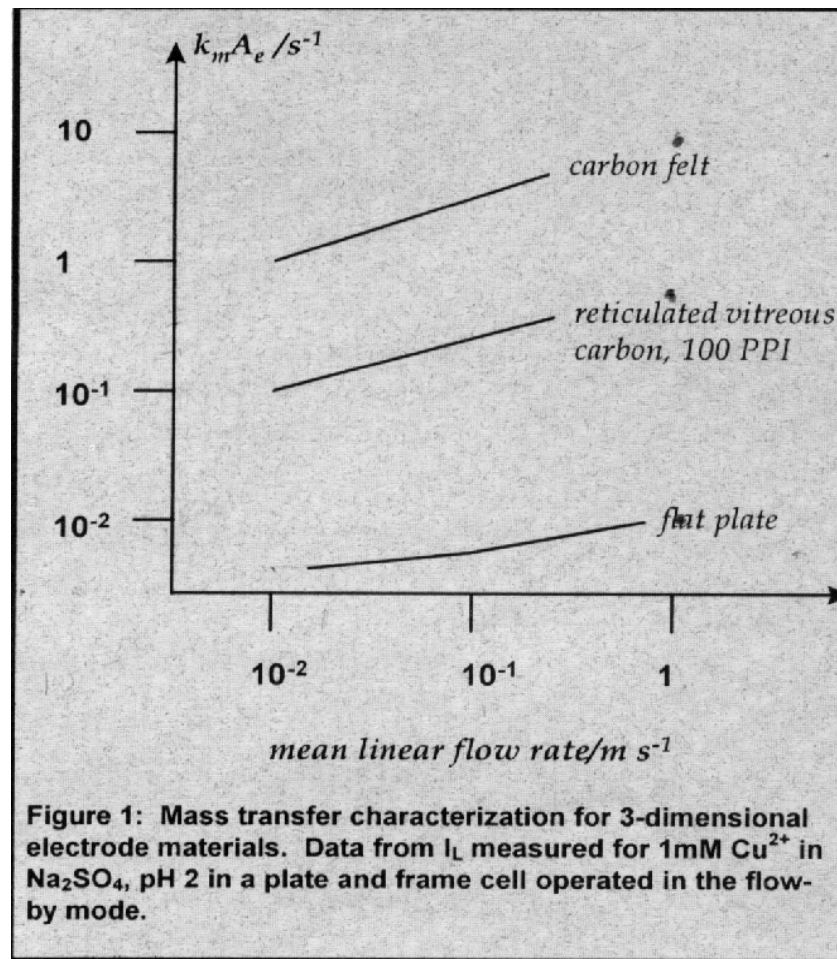
ETC 48 Multilayer Mesh Anode




Bench Scale MLM Anode



Mass Transfer Rate vs Velocity and Electrode Type





Electrodes, Electrolyzers, and Operating Conditions

1. Chemical resistance
2. Current density
3. Lifetime
4. Current efficiency
5. Mass transfer (Fluid velocity)
6. Footprint
7. Need for a separator (Reduction byproducts)
8. Operating conditions
9. Fit with “partner” processes
10. Ease of operation and maintenance
11. Capital and operating cost

ETC 48 Electrolyzer

