Electrochemical Treatment of Waste Water Using Boron Doped Diamond Electrode (BDD)

Subramanian Tamilmani

Srini Raghavan

Wayne Huang

Materials Science and Engineering Department

University of Arizona

James Farrell

Chemical and Environmental Engineering

University of Arizona

Outline

✓ ***CMP Waste water treatment – ESH impacts.***
✓ ***Background of BDD electrodes.***
✓ ***Oxidation of organics using BDD – A review.***
✓ ***Treatment of Copper CMP waste water.***
✓ ***Summary.***

Copper CMP Waste Water

- Waste from an integrated polisher and cleaning tool is mostly water
    - 5000 gallons of waste per day per tool
    - 5 – 20 ppm of dissolved copper
    - 500 – 1000 ppm of total suspended solids (TSS)
    - 100 – 400 ppm of total dissolved solids (TDS)
    - Organic complexants (e.g., Citric acid)
    - Organic inhibitors (e.g., Benzotriazole)

ESH Impacts

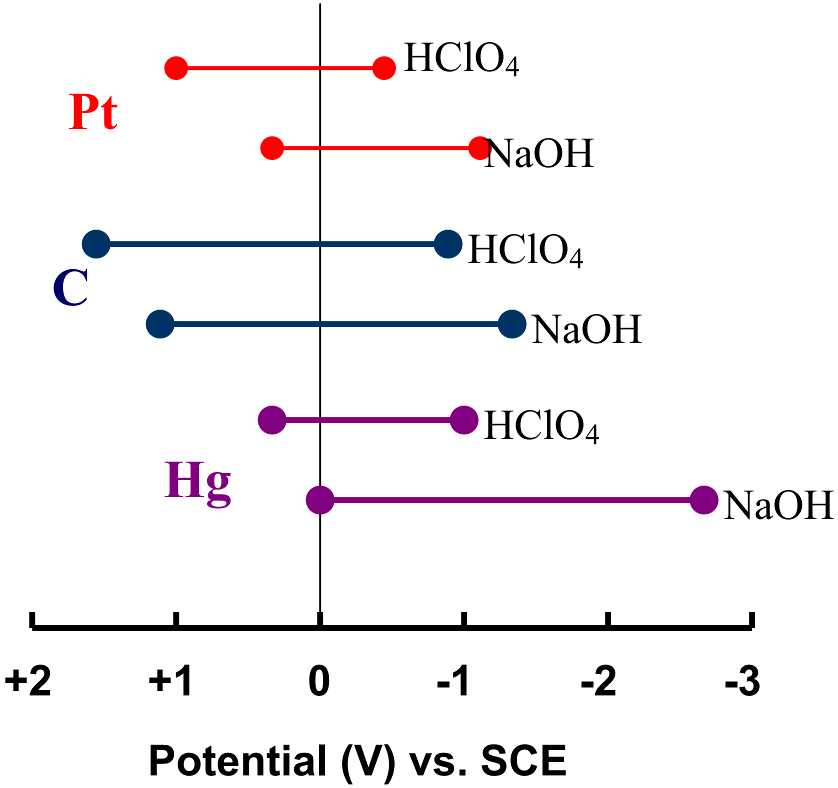
- CMP & CMP rinse are projected to use 30% of facility water
- Recycling of process water is necessary to meet SIA projections for reduced water consumption
- Effluent must be reduced to less than 5 ppm TSS
- Copper levels must be <1 ppm* prior to discharge

* Depends on the local regulations

Electrochemical Treatment of Wastewater

- Treatment by oxidation , reduction or a combination of those process.
  - Oxidation of organics to simpler non-toxic waste or carbon dioxide.(Citric acid to CO_2)
  - Reduction of reducible species like metallic ions. (Cu^{2+} to Cu)
- Avoids the use of chemicals
- Electrode materials:
  - Dimensionally stable (active and non-active electrodes)
  - Very high oxygen overpotential

Comparison of Electrode Materials



- The extent of water stability region is a primary concern in choosing the electrode material.
- Platinum has a very small water stability region.
- Mercury electrodes have a very high hydrogen over voltage but are unsuitable for any application at the anodic side.
- Carbon based electrodes have a reasonably wide operating voltage range.

Conventional Carbon Based Electrodes

- Carbon fibers, glassy carbon and graphite.
- Layers of condensed, six member rings with **sp^2**-hybridized carbon atoms trigonally bonded to one another.
- The variation in crystallite size and extent of microstructural order has important implications for electron-transfer kinetics for a given redox reaction.
- Used in various electrochemical processes (electroanalysis, energy storage and electrosynthesis)

Diamond Thin Films (Chemistry)

- Wide bandgap semiconductor, E_g=5.5 eV
- Extreme hardness, high electrical resistance, chemical inertness, high thermal conductivity and high electron hole mobility.
- Each carbon atom is tetrahedrally bonded to four other carbons using **sp**^{3}-hybridization.
- Microstructurally, the atoms are stacked as six member rings.
- Can be grown on a variety of substrates.

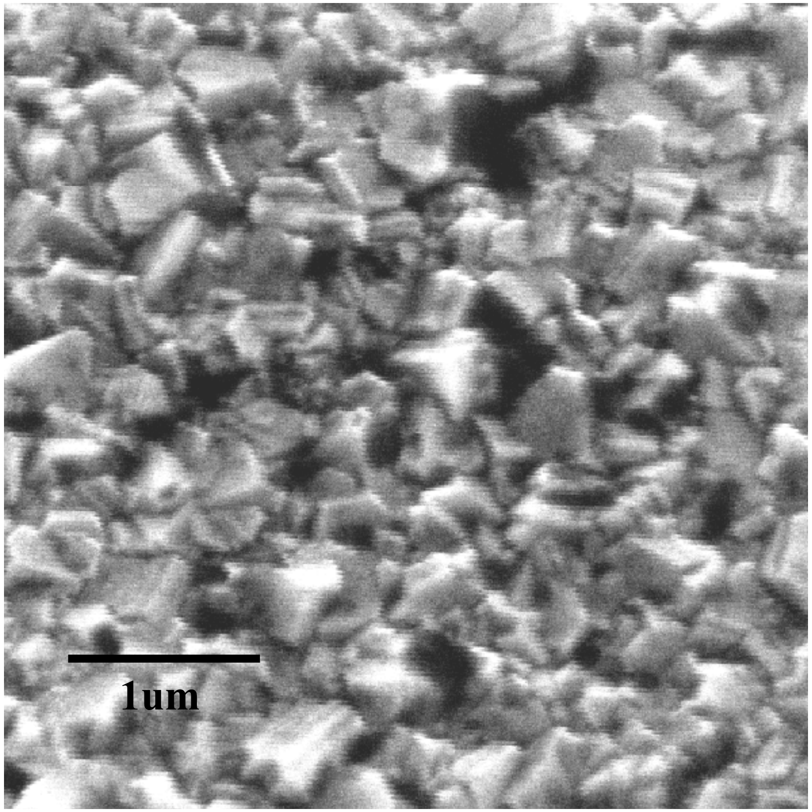
Boron Doped Diamond Thin Films (BDD)

- Carbon atoms can be substituted with Boron impurities during film growth.
- Depending on doping level the diamond film can behave as an insulator, semiconductor or a semimetal.
- Doping levels of 10,000 ppm B/C yields films with resistivities $<0.1\ \Omega$-cm.
- The rough polycrystalline morphology and the presence of non-diamond carbon impurity has made it difficult for electronic application.
- BDD films are recently being used in electrochemical applications.

Growth of BDD Films

- Diamond films are grown by *Hot Filament CVD* (filament temp ~ 2100°C) or *Microwave Plasma assisted CVD* (microwave power: 1-1.3 kW).
- Substrates - silicon, silicon carbide, graphite, niobium, titanium and tantalum. (Temp: 800-1000°C)
- Substrate pretreatment – Mechanically roughened and cleaned and seeded with fine diamond powder.
- Gas source – 0.5-4% methane in hydrogen.
- Boron source – B_2H_6, $B(CH_3)_3$ gas or B_2O_3 solid target.

SEM Micrograph of BDD Film

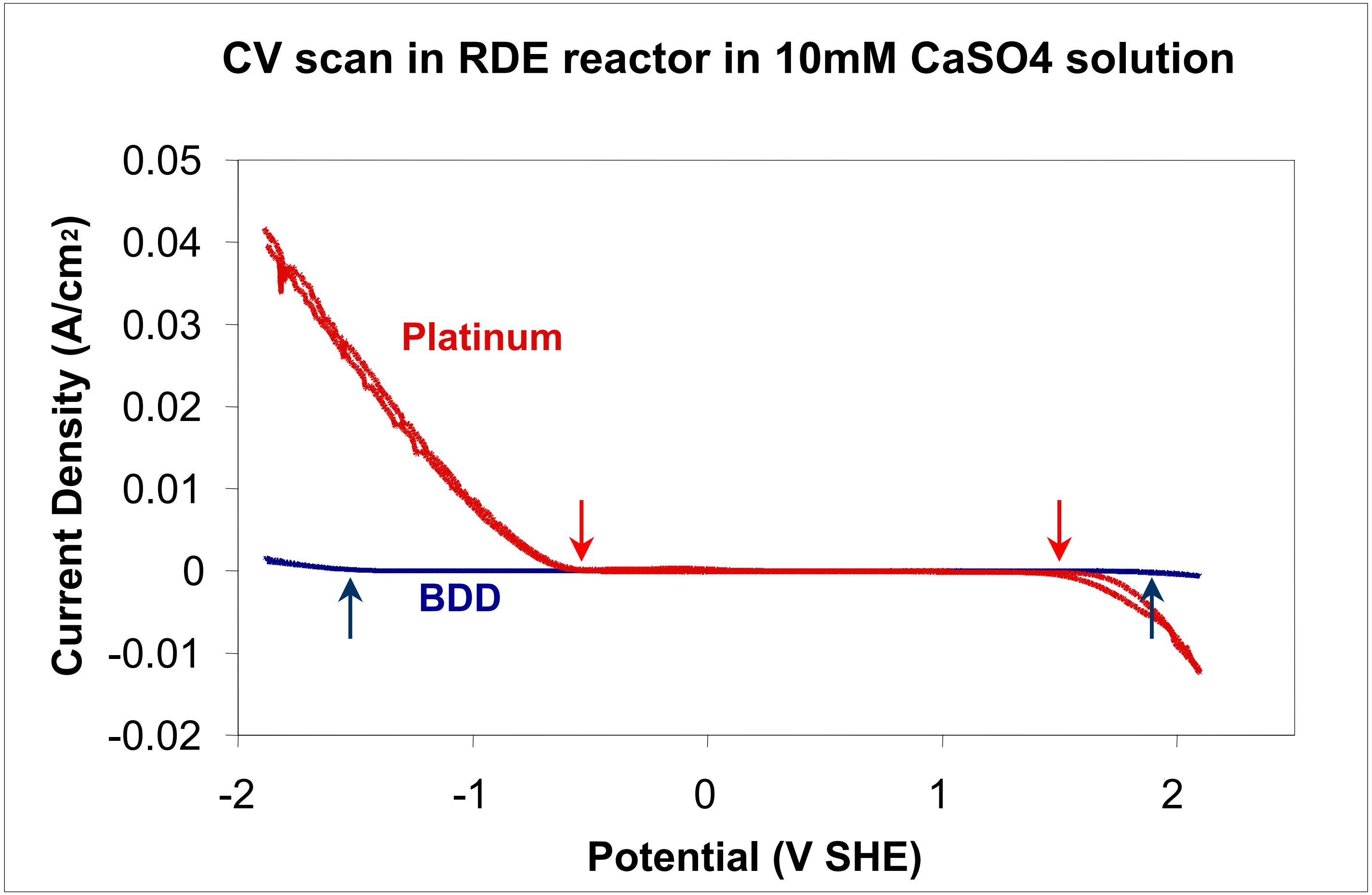


- BDD films grown on p-Si substrate via HF CVD
- Columnar
- Random textured
- Polycrystalline

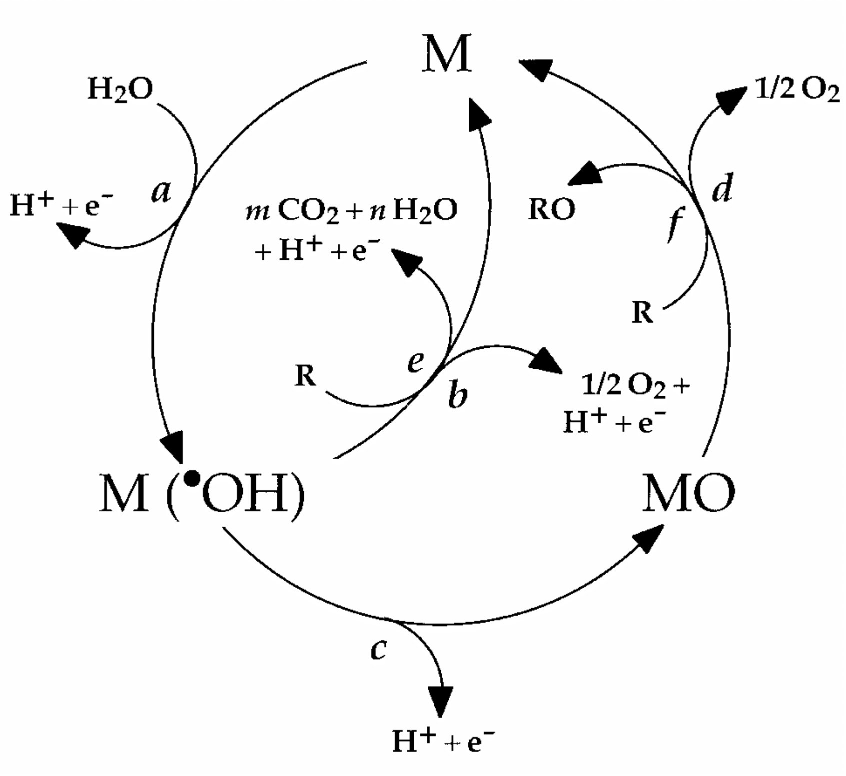
Electrochemical Activity of BDD

- ➢ Nonactive electrode.
- ➢ Wide electrochemical potential window.
- ➢ High overpotential for oxygen evolution.
- ➢ Generates hydroxyl radicals at the anode.
- ➢ Very low voltammetric background currents and double layer capacitances.
  - ✓Absence of electroactive carbon oxygen functionalities
  - ✓Lower charge carrier density at the surface.
  - ✓Electrode surface may be an array of microelectrodes.

Wide Potential Window of BDD Electrodes



Oxidation Mechanism in Active and Non-active anodes.



M – Active side on the anode.

R – Organic compound.

a) Discharge of water molecules to form adsorbed hydroxyl radicals (*OH).

b) Electrochemical oxidation of physisorbed hydroxyl radicals. (H_2O/H_2O_2 redox couple)

c) Electrochemical oxidation of the surface. (M/MO redox couple)

d) Release of oxygen in a chemical decomposition.

e) Electrochemical oxidation mediated by physisorbed (*OH) radicals.

f) Heterogeneous catalytic oxidation at electro-oxidized active sites.

Oxidation of Organics

- Oxidation of phenol using BDD electrodes at E=2.5V vs SHE anodic potential, converts 20% of the phenol to CO_2 , and oxidation at E=3.1V vs SHE converts 80% of phenol to CO_2.

  J. Iniesta et al./ Electrochemica Acta 46 (2001) 3573-3578.

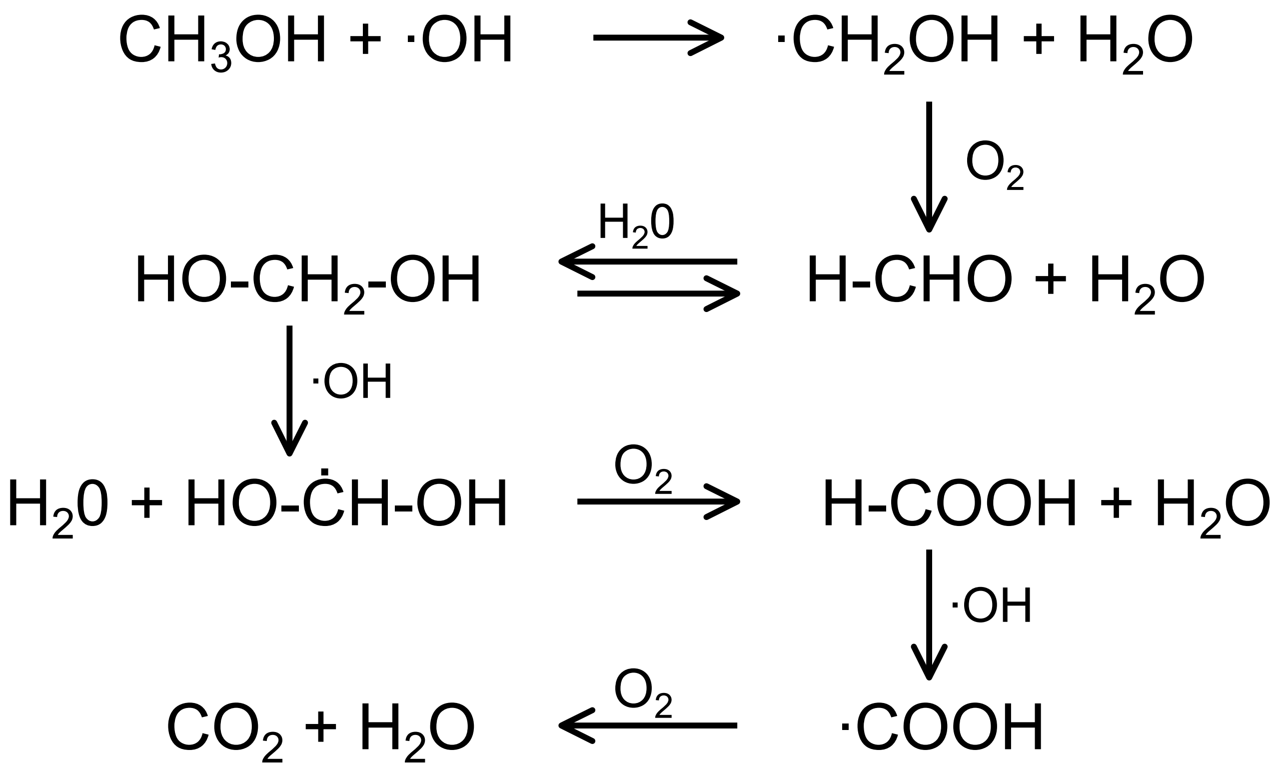
- BDD electrodes have been used to oxidize simple carboxylic acids like acetic acid, formic acid and oxalic acid with an average current efficiency of 90%.

  D. Gandini et al. Journal of Applied Electrochemistry 30, 1345-1350 (2000).

- Oxidation of 2-napthol at BDD electrodes leads to complete incineration of 2-napthol at very high anodic potentials. Assuming a diffusion controlled process, a good agreement of the experimental data with the theoretical model is obtained.

  M. Panizza et al. Journal of Electroanalytical chemistry 507 (2001) 206-214.

Reaction Mechanism



$CH_3OH + \cdot OH \longrightarrow \cdot CH_2OH + H_2O$

$\cdot CH_2OH \xrightarrow{O_2} H\text{-}CHO + H_2O$

$HO\text{-}CH_2\text{-}OH \overset{H_20}{\rightleftarrows} H\text{-}CHO + H_2O$

$HO\text{-}CH_2\text{-}OH \xrightarrow{\cdot OH} H_20 + HO\text{-}\dot{C}H\text{-}OH$

$H_20 + HO\text{-}\dot{C}H\text{-}OH \xrightarrow{O_2} H\text{-}COOH + H_2O$

$H\text{-}COOH + H_2O \xrightarrow{\cdot OH} \cdot COOH$

$CO_2 + H_2O \xleftarrow{O_2} \cdot COOH$

Organic pollutant

↓

Aldehydes

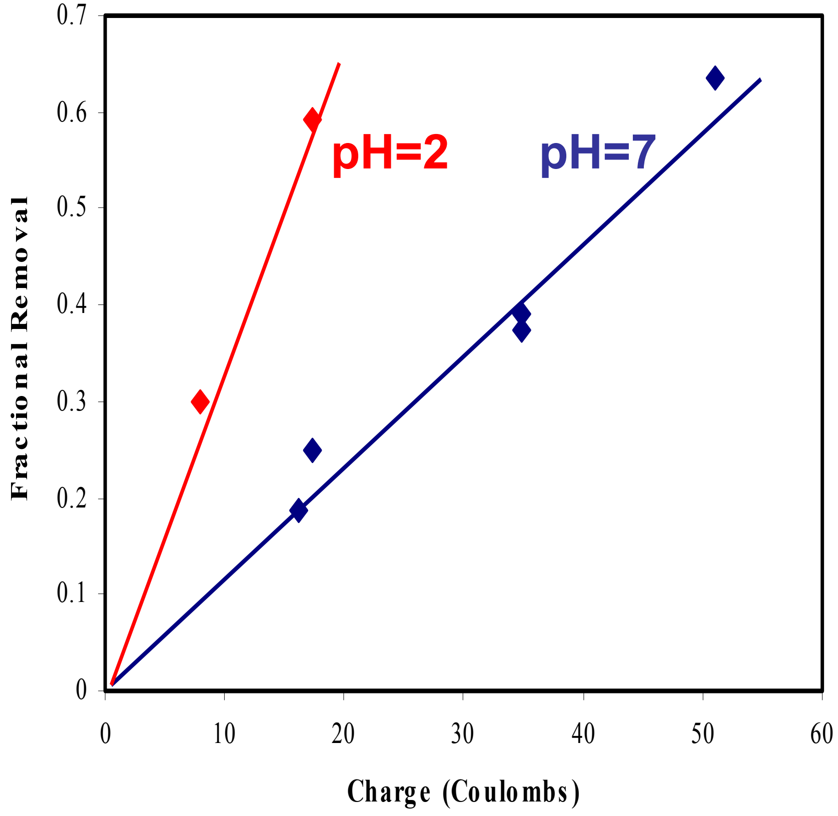
↓

Carboxylic acids

↓

Carbon dioxide

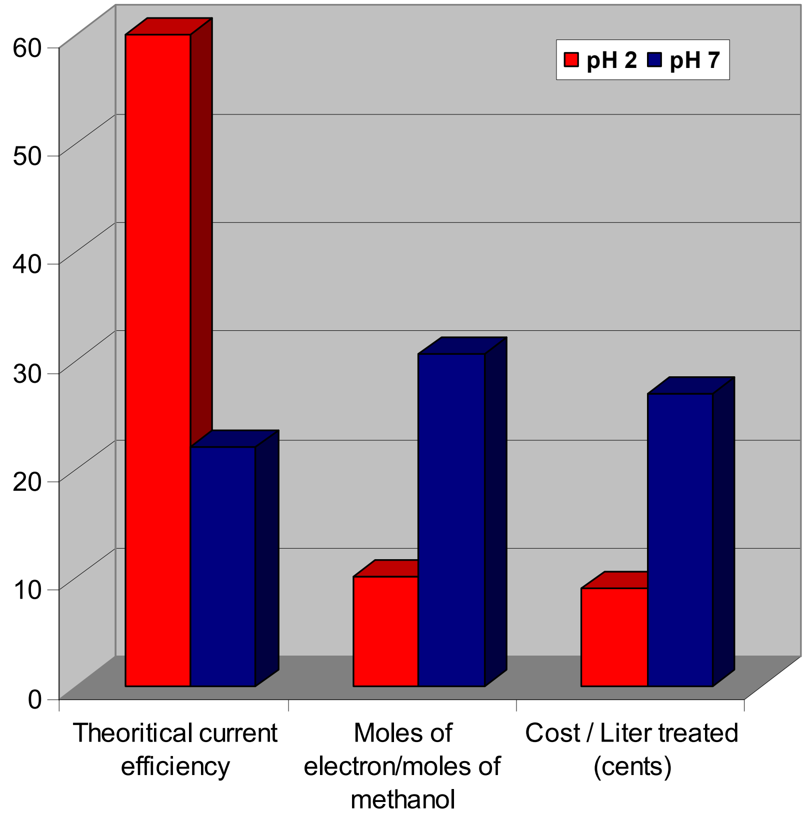
Methanol Oxidation



- Continuous Flow through reactor
- Galvanostatic mode.
- Initial methanol conc.=100ppm
- Flow rate = 5 ml/min.
- Residence time = 116 sec
- Methanol analyzed by GC.

* Research done by Prof. Farrell’s group, Chemical and Environmental Engineering Department, University of Arizona.

Methanol Oxidation



- Theoretical current efficiency calculated assuming one electron transfer.
- Cost calculated on a basis of 30 cents/mole of electron.
- Much cheaper than other treatment processes.

Objectives of the Research at U of A

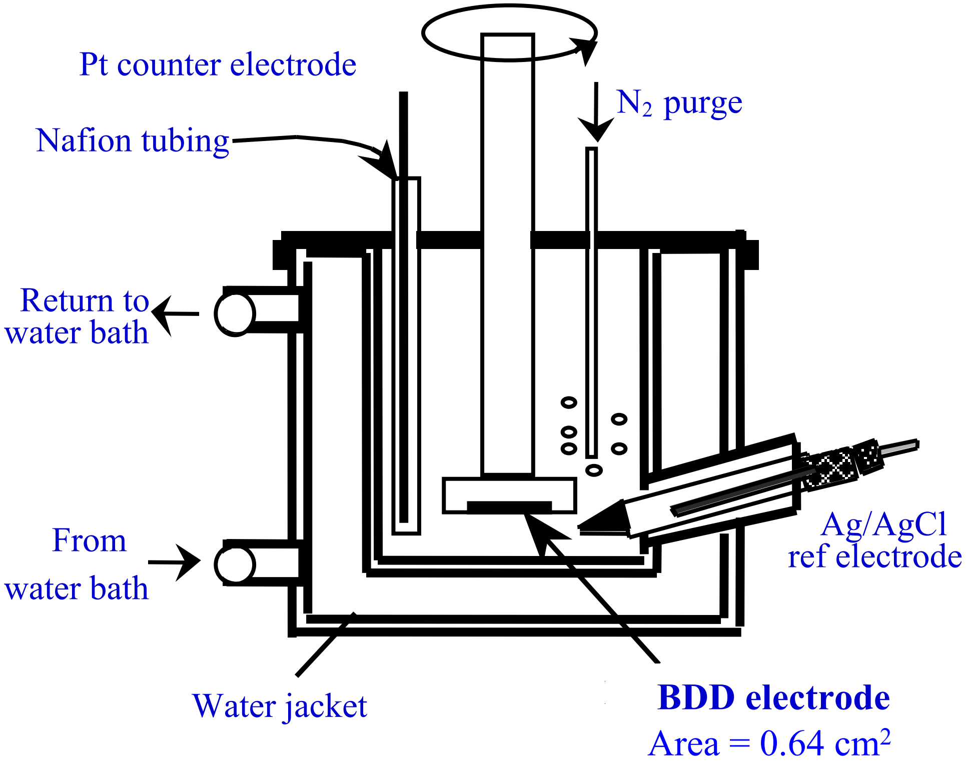
- Investigate the feasibility of removal of uncomplexed and complexed copper ions from dilute streams by direct electrodeposition on Boron Doped Diamond (BDD) material

- Simultaneous removal of organic complexants and copper from CMP waste water

Currently Practiced Technology:

Micro- or ultrafiltration followed by ion exchange and electrowinning

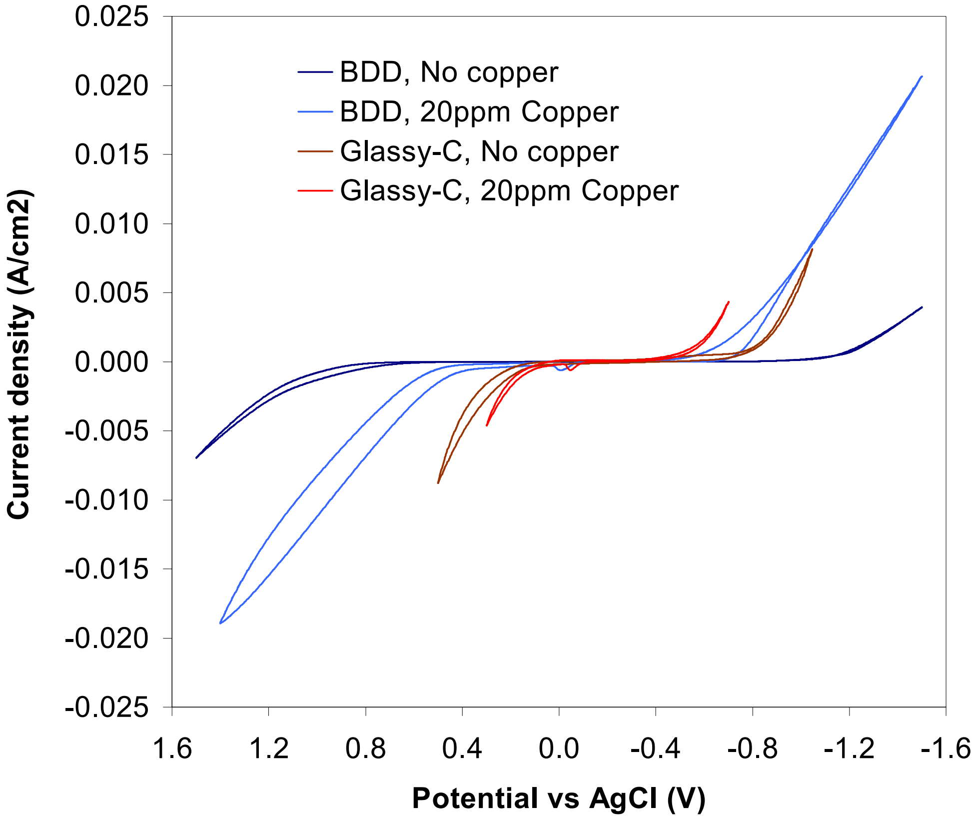
Methods



Rotating Disk Electrode Reactor

- Electrode rotated at 100 rpm
- Reactor volume – 30ml
- EG&G model 273 A potentiostat
- Copper ions determined by AAS
- Citrate ions determined by CE

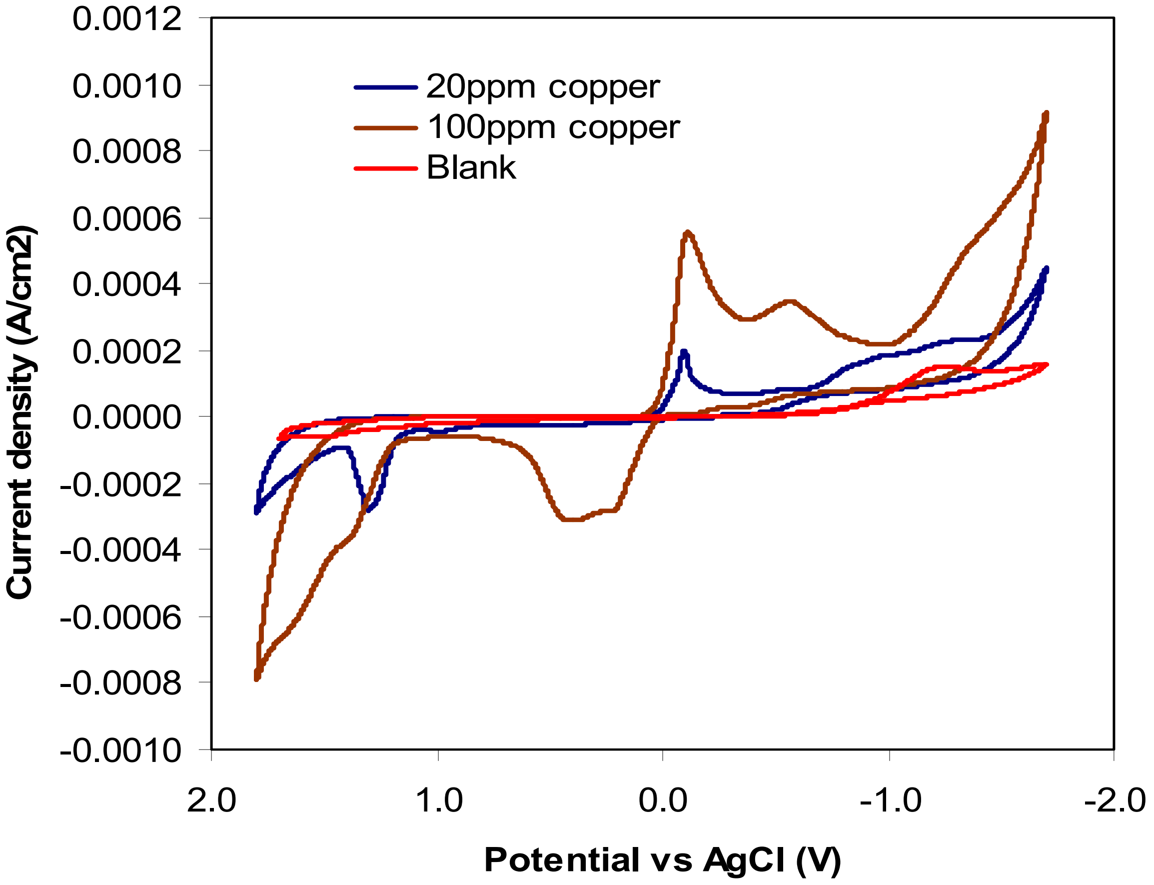
Cyclic Voltammetry : BDD & Glassy Carbon



CV scans obtained on BDD & Glassy carbon in 0.5M hydroxylamine solution at pH 5.8.

- ➢ Wide EC window for BDD in the presence and absence of copper.
- ➢ Presence of copper causes rapid increase in current, even at lower potentials.
- ➢ No clear peak for copper reduction due to complexation at the given pH.
- ➢ Distinct copper oxidation peak.

Cyclic Voltammetry on BDD

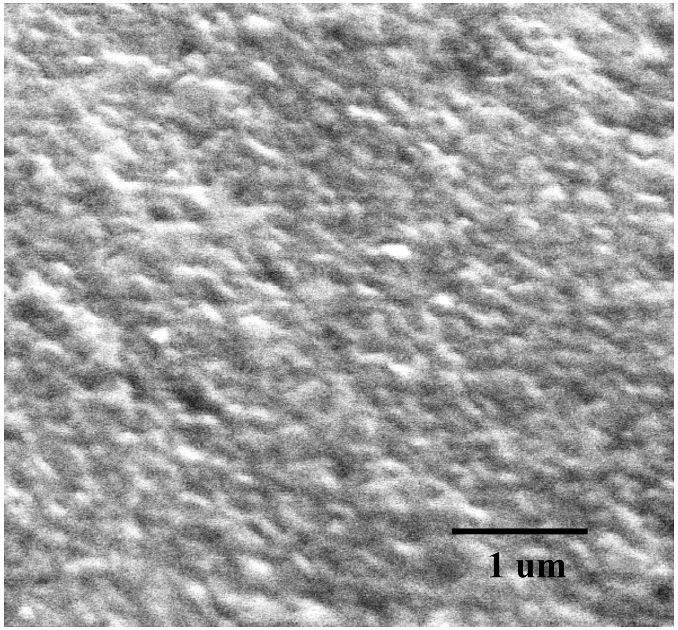


CV scans of 0.05M potassium sulfate solution with varying levels of copper on BDD electrode at pH 5.8.

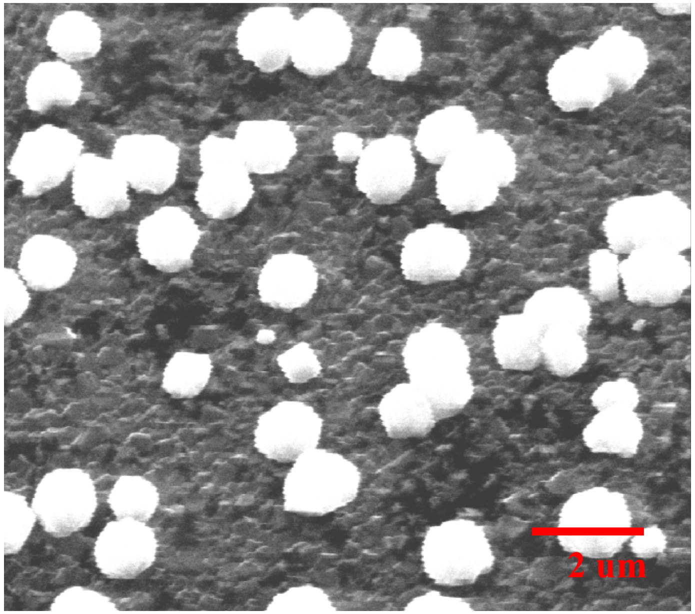
- ➢ Distinct copper reduction peak.
- ➢Peak size is dependent on the copper concentration.

SEM Micrographs of Copper Deposits

Copper on Copper electrode

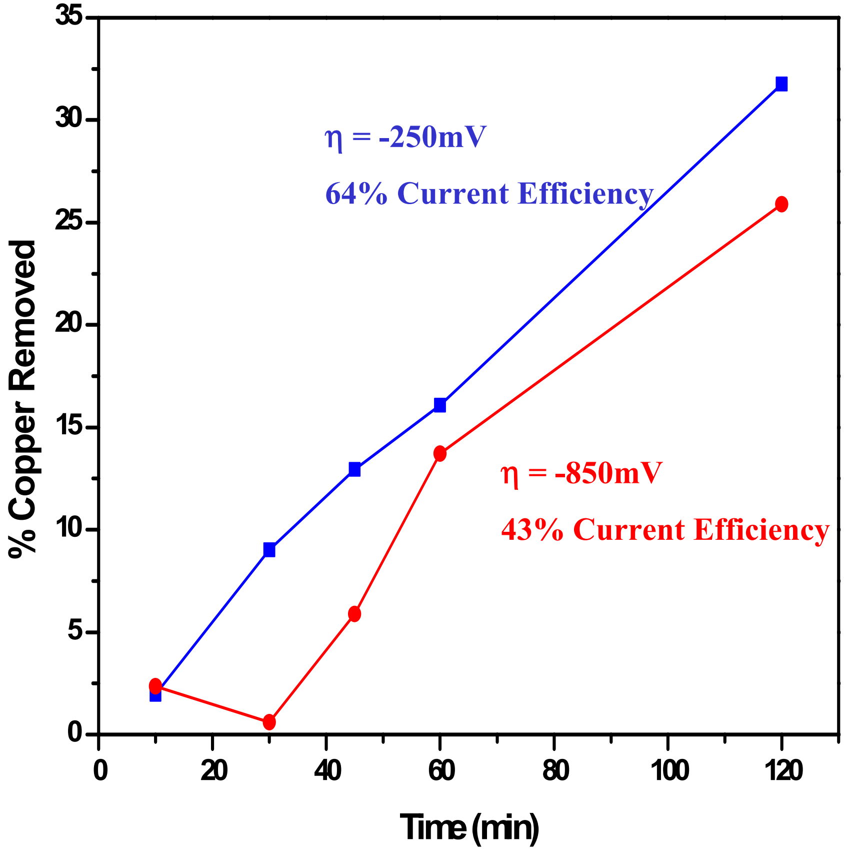


Copper on BDD electrode



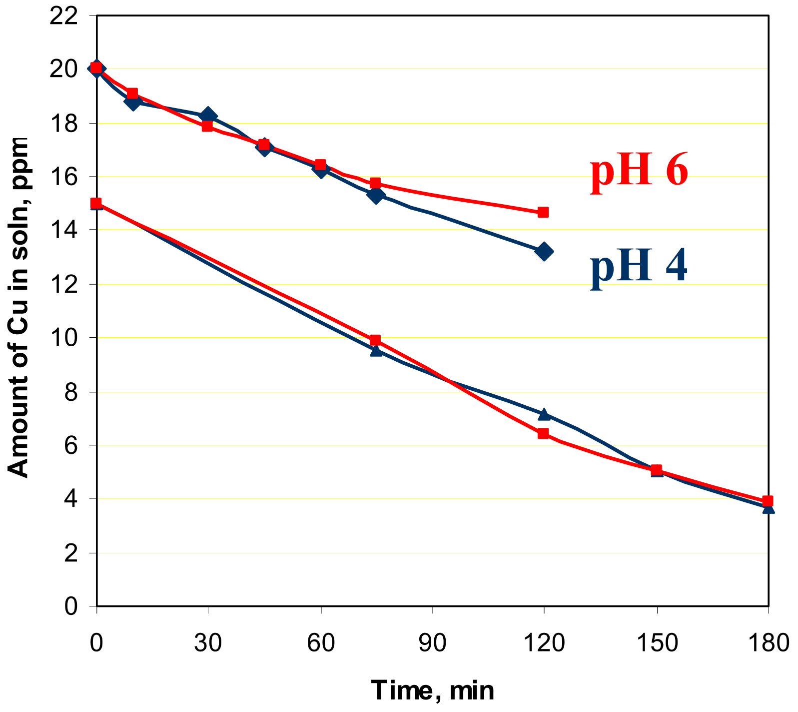
Copper deposits obtained after 90 minutes of polarization at -200mV vs Ag/AgCl in a 50 mM K_2SO_4 solution containing 20 ppm copper.

Copper Removal as a Function of Time

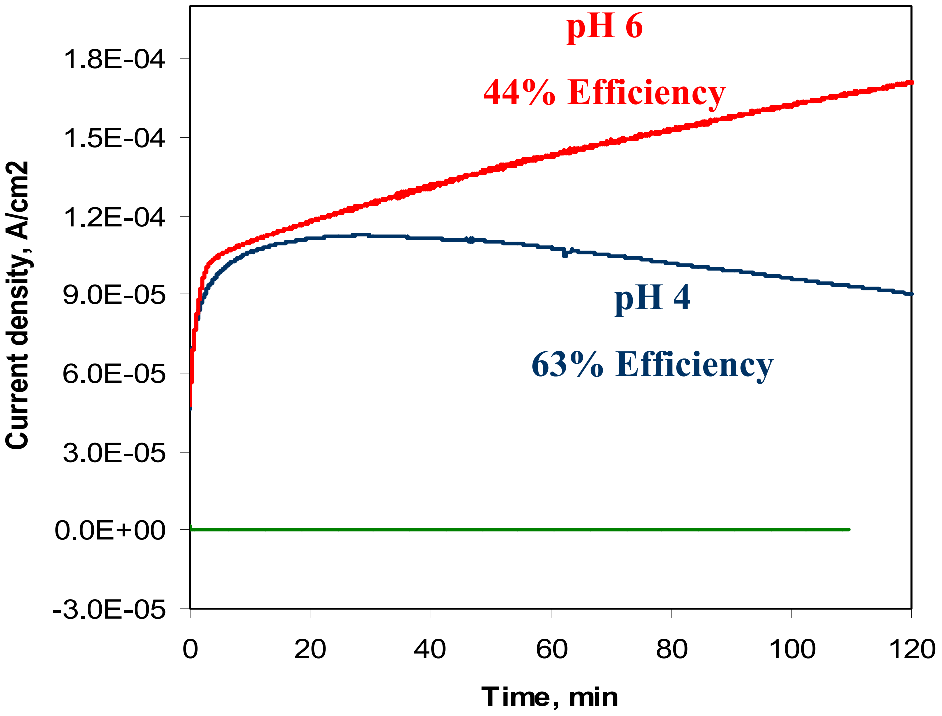


- Copper deposition on BDD electrode at two different overpotentials.
- Solution: 20ppm Cu in 50mM K_2SO_4 at pH 6.
- Copper concentration determined by AAS.
- Current efficiency calculated with $1e^-$ transfer.

Effect of pH



Copper electrodeposition on a BDD electrode from 50mM K_2SO_4 solution containing 15 and 20ppm copper at different pH values



Chronoamperometric curves for copper deposition at -200 mV vs Ag/AgCl in 50mM K_2SO_4 solution containing 20ppm copper at different pH.

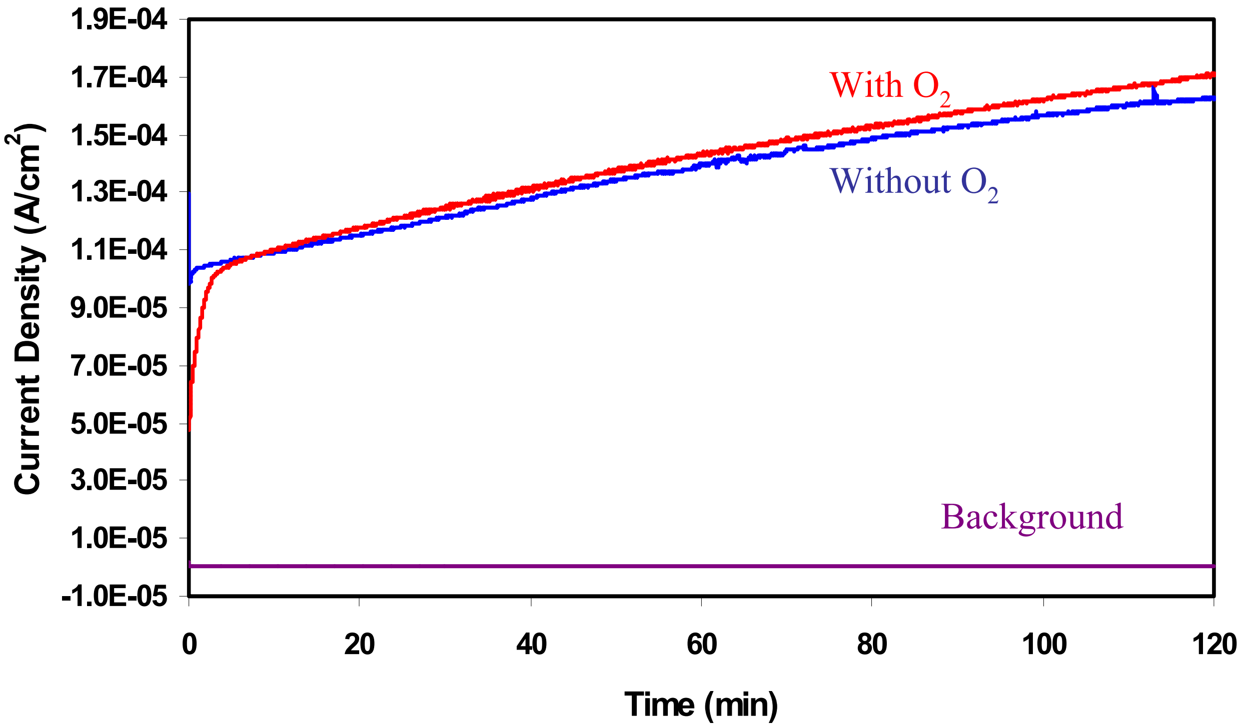
Kinetics of Copper Removal

- At a fixed electrode potential the copper removal kinetics could be described by a kinetic expression of the form:

$$\frac{d[Cu^{2+}]}{dt} = -k_o \qquad k_o \text{ is Zero}^{th} \text{ order rate constant}$$

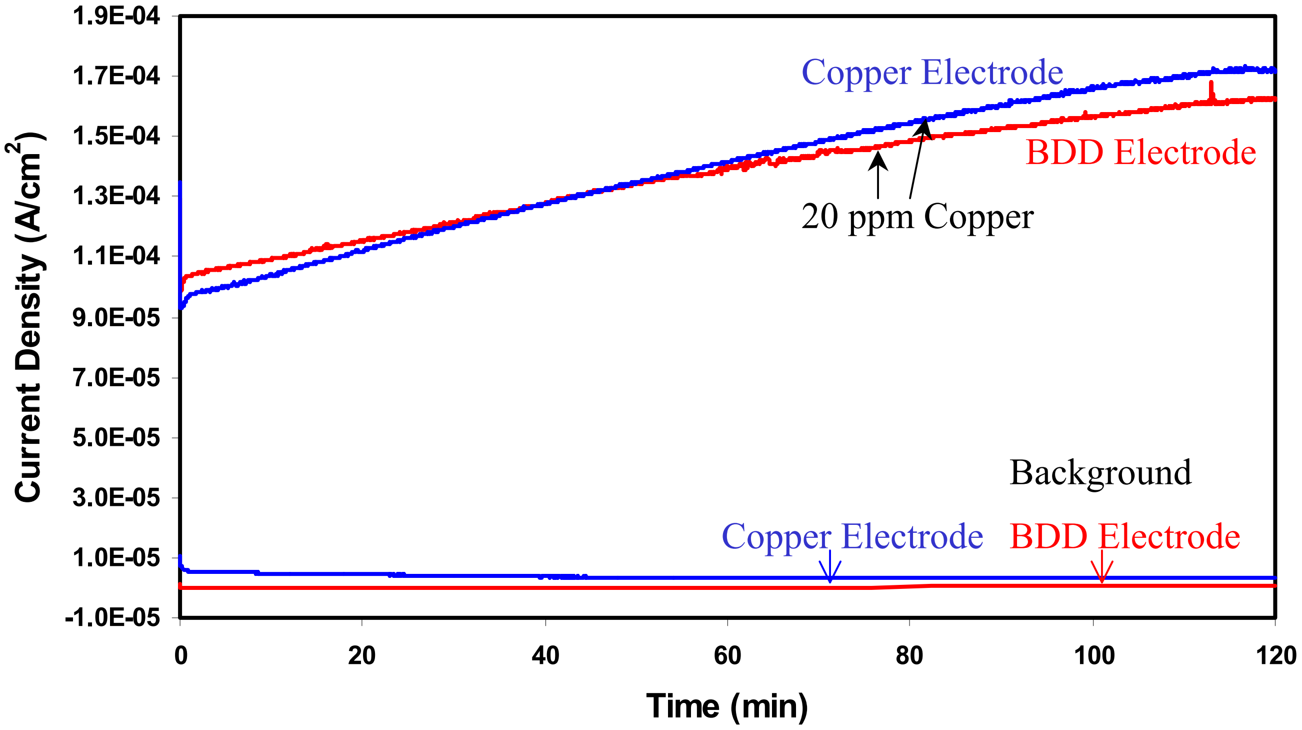
- Model fits the data shown
- k_o is independent of pH

Effect of Dissolved Oxygen on Cu deposition



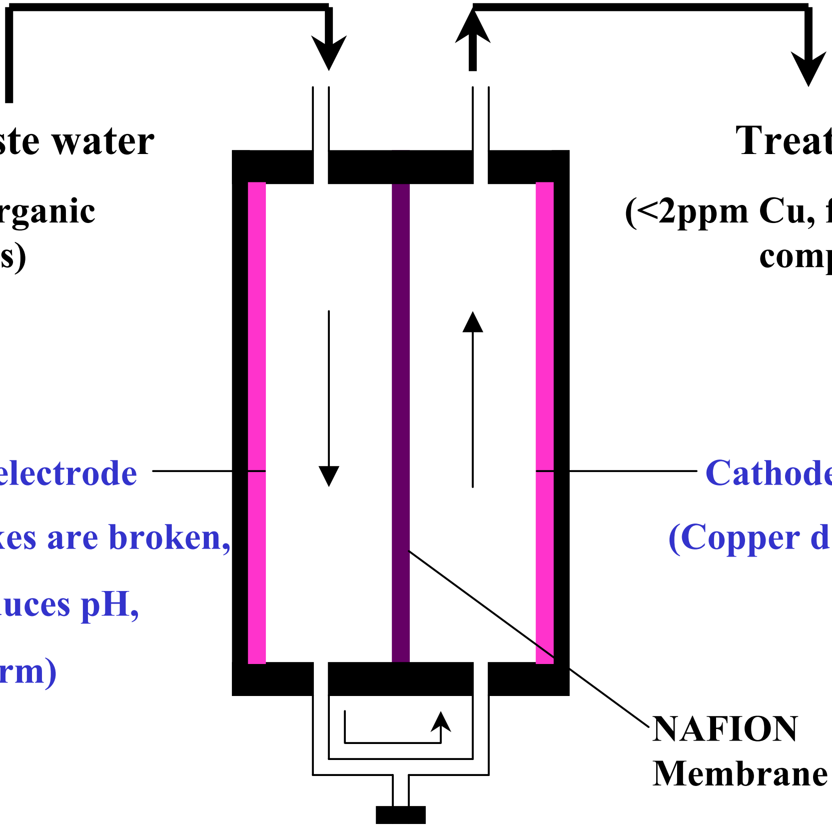
- ➢Chronoamperometric curves obtained on a BDD at a cathodic overpotential of 250mV
- ➢50mM K_2SO_4 solution with 20ppm copper at pH 6
- ➢**Presence of oxygen does not affect the copper removal**

Comparison of Copper and BDD Electrodes



Chronoamperometric curves of Cu and BDD electrodes at a cathodic overpotential of 250 mV in 50mM K_2SO_4 solution with 20ppm copper.

Prototype Copper Removal Module



Inlet of CMP waste water

(15 ppm Cu+ Organic complexants)

Treated water

(<2ppm Cu, free from organic complexants)

Anode - BDD electrode

(Cu-Organic complexes are broken,

Water oxidation reduces pH,

Copper is in Cu^{2+} form)

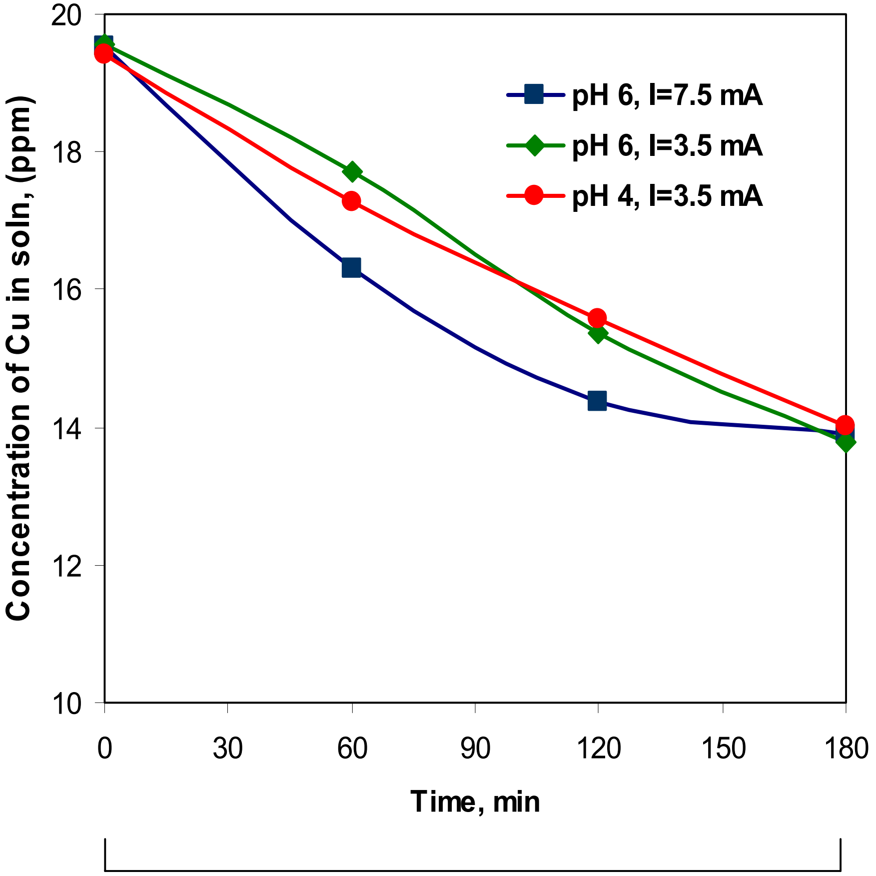
Cathode - BDD electrode

(Copper deposits on cathode)

NAFION Membrane

Sampling point to measure the organic complexants

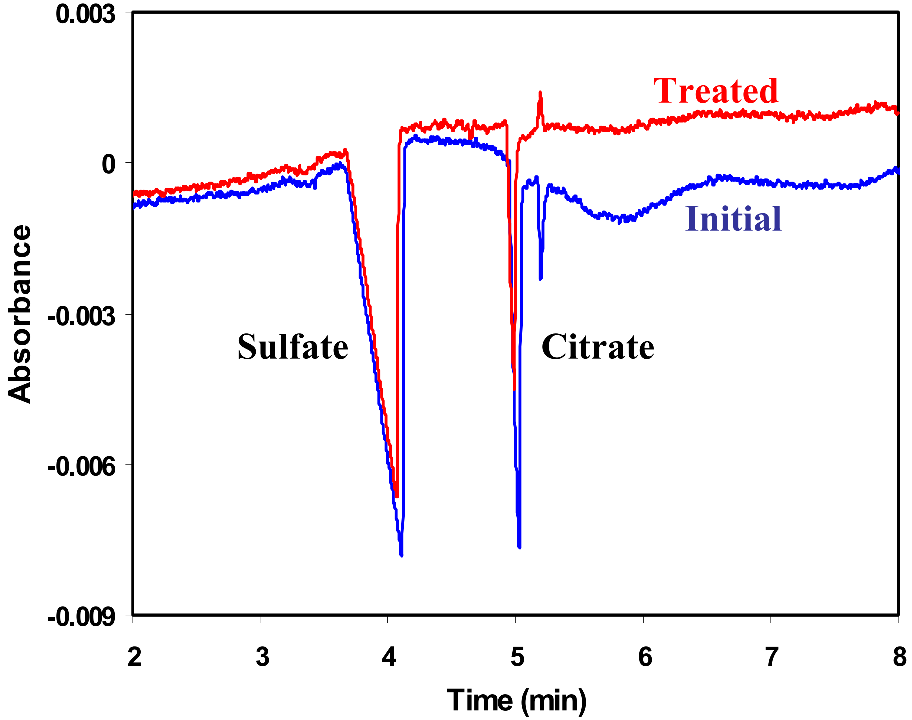
Copper Removal in a Recirculated Batch Reactor



Time in cathode chamber (18 min)

- Galvanostatic mode
- Inlet solution: 50mM K_2SO_4 with 20ppm copper
- Flow rate = 8 ml/min
- Residence time per pass 3min
- Mass transfer limited.

Citrate Removal by Oxidation



- Citric acid oxidation in a flow cell
- Inlet solution: 50mM K2SO4 with 100ppm Citric acid at pH 6
- Anode Potential: 2.5V
- Residence time: 50 minutes
- TOC of outlet is reduced by 20%

Capillary Electrophoresis curves showing sulfate and citrate peaks. The decrease in height of citrate peak indicates the removal of citrate.

Proposed Reactions for Copper-Citrate

Anode reactions

Water oxidation produces hydroxyl radicals:

$$H_2O \rightarrow H^+ + OH^\bullet + e^-$$

Indirect citrate oxidation through free radical chain reaction:

$$OH^\bullet + Cu - C_6H_8O_7 \rightarrow CO_2 + H_2O$$

Direct citrate oxidation at anode surface:

$$Cu - C_6H_8O_7 + 5\,OH^- \rightarrow Cu^{2+} + 6\,CO_2 + 13\,H^+ + 20\,e^-$$

Cathode reaction

Direct copper reduction at cathode surface:

$$Cu^{2+} + 2\,e^- \rightarrow Cu^0$$

Summary

- BDD electrodes can be used as cathodes for copper reduction and as anodes to oxidize organic complexants
- Copper deposits as particles on BDD film
- Copper deposition from dilute solutions (15ppm Cu) is mass transfer limited

Future Work

- Evaluate the efficiency of BDD electrodes in oxidizing organic complexants in CMP waste water
- Optimize operating parameters of the flow reactor to improve current efficiency

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