Electrochemical Treatment of Wastewaters Containing Organic Compounds

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Treatment Technologies

1. Adsorption - activated carbon, zeolites
2. Air stripping
3. Membranes - reverse osmosis

Disposal issues

4. Chemical Oxidation - UV/H_2O_2 or O_3
5. Biological treatment - activated sludge; anaerobic
6. Electrochemical reduction
7. Electrochemical oxidation

Compounds of Interest

- chlorinated solvents - carbon tetrachloride (CT); trichloroethylene (TCE)
- water miscible solvents - methanol
- metal chelating agents - citrate

Reduction vs. Oxidation

oxidation

$CCl_4 + 2H_2O \rightarrow CO_2 + 4H^+ + 4Cl^-$

reduction

$CCl_4 + 4H_2O \rightarrow CH_4 + 2O_2 + 4H^+ + 4Cl^-$

$$E = E^o + \frac{RT}{nF} \ln \frac{\{ox\}}{\{red\}}$$

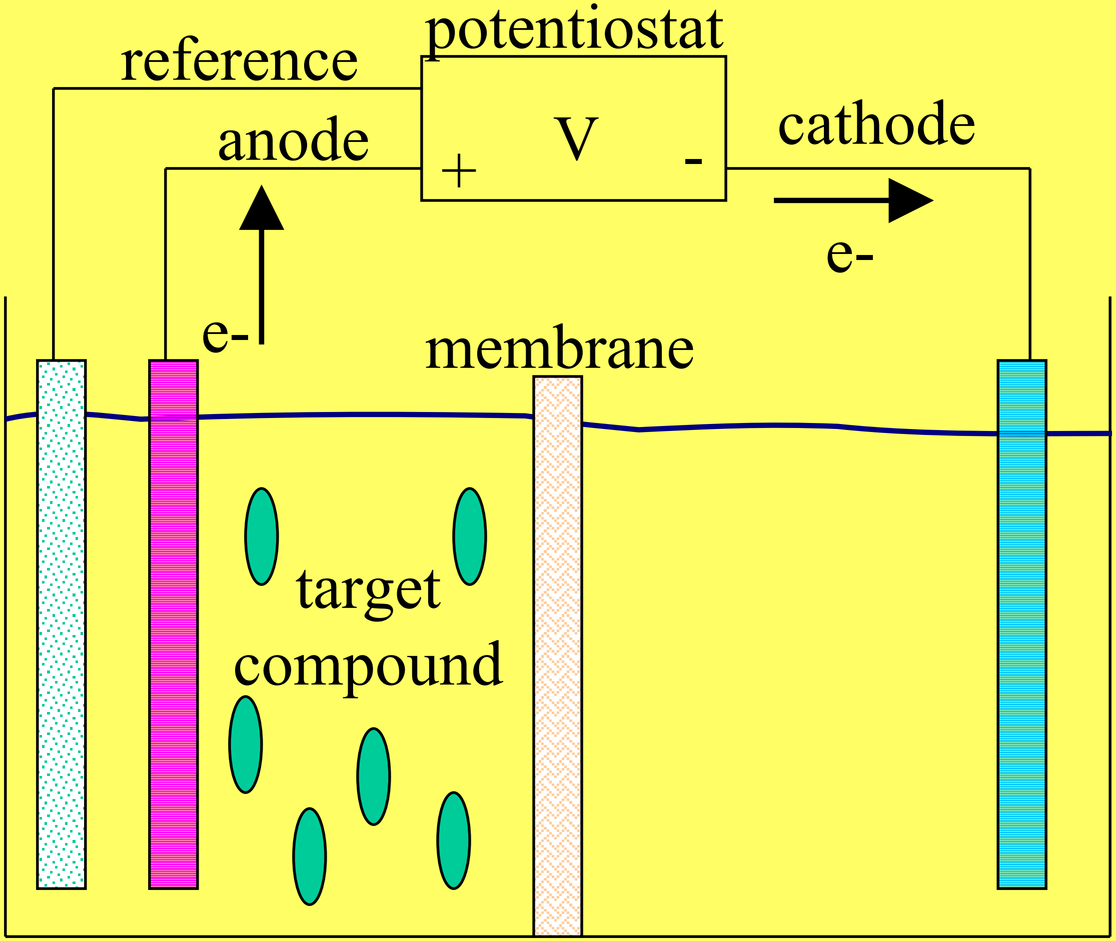
$$\{CCl_4\} = \{CO_2\} = \{CH_4\}; \;\; \left\{Cl^-\right\} = 10^{-3}; \;\; \left\{H^+\right\} = 10^{-7}; \;\; \{O_2\} = 0.21$$

E = 2.09 V

$$\Delta G = -nFE$$

E = -0.39 V

Three Electrode Cell



$H_2O \rightarrow 0.5\ O_2 + 2H^+ + 2\ e^-$ $H_2O + e^- \rightarrow 0.5\ H_2 + OH^-$

Competing reactions

Water Reduction

$M + H^{+} + e^{-} \rightarrow M - H^{\bullet}$ Volmer Discharge

M = metal cathode
H$^{\bullet}$ = atomic hydrogen radicals

- Adsorbed H$^{\bullet}$ available to react with organic species.
- High concentrations of H$^{\bullet}$ result in H_2 evolution.

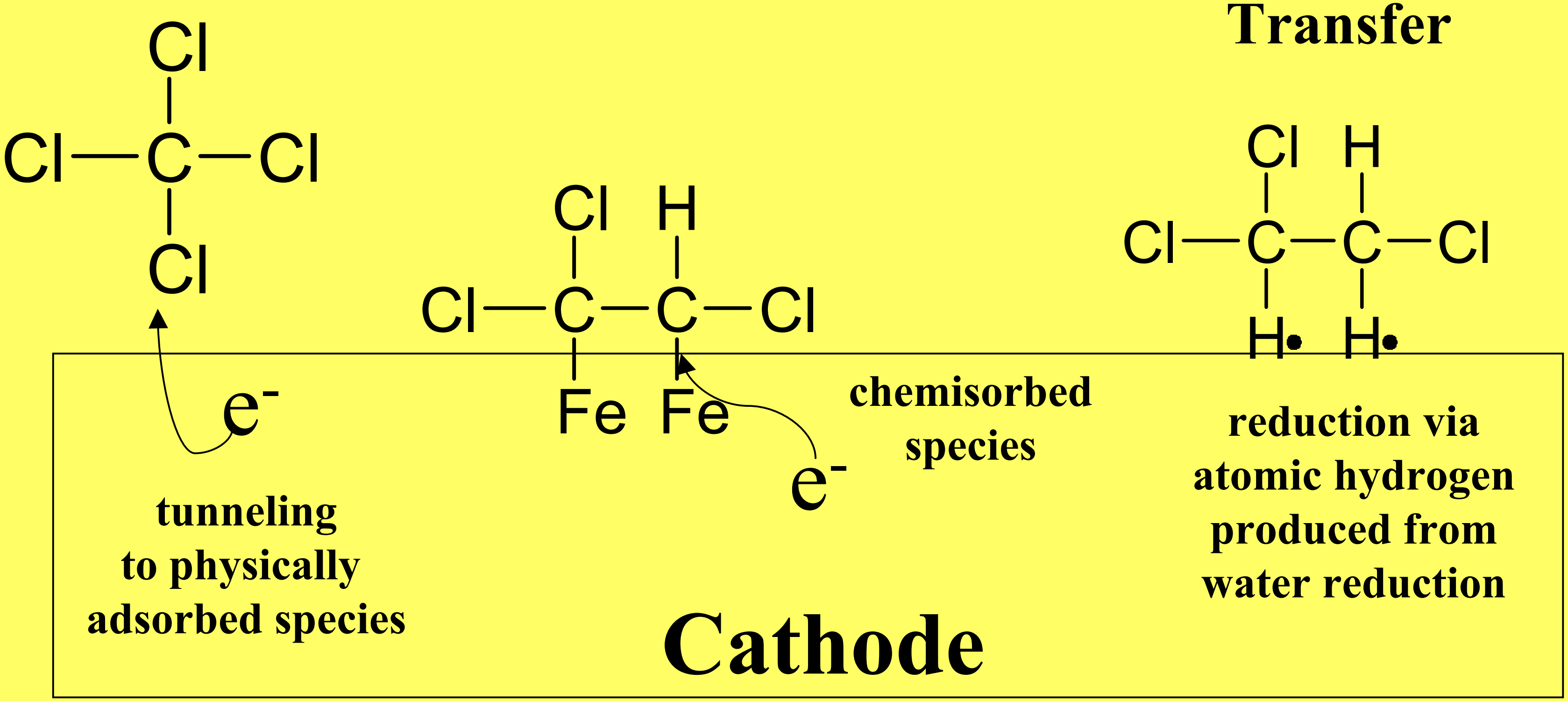
$2\,M - H^{\bullet} \rightarrow 2\,M + H_2$ Tafel Recombination

$M - H^{\bullet} + H^{+} + e^{-} \rightarrow M + H_2$ Electrochemical Desorption

Reduction - Electron Transfer Mechanisms

Direct Electron Transfer

Indirect Electron Transfer



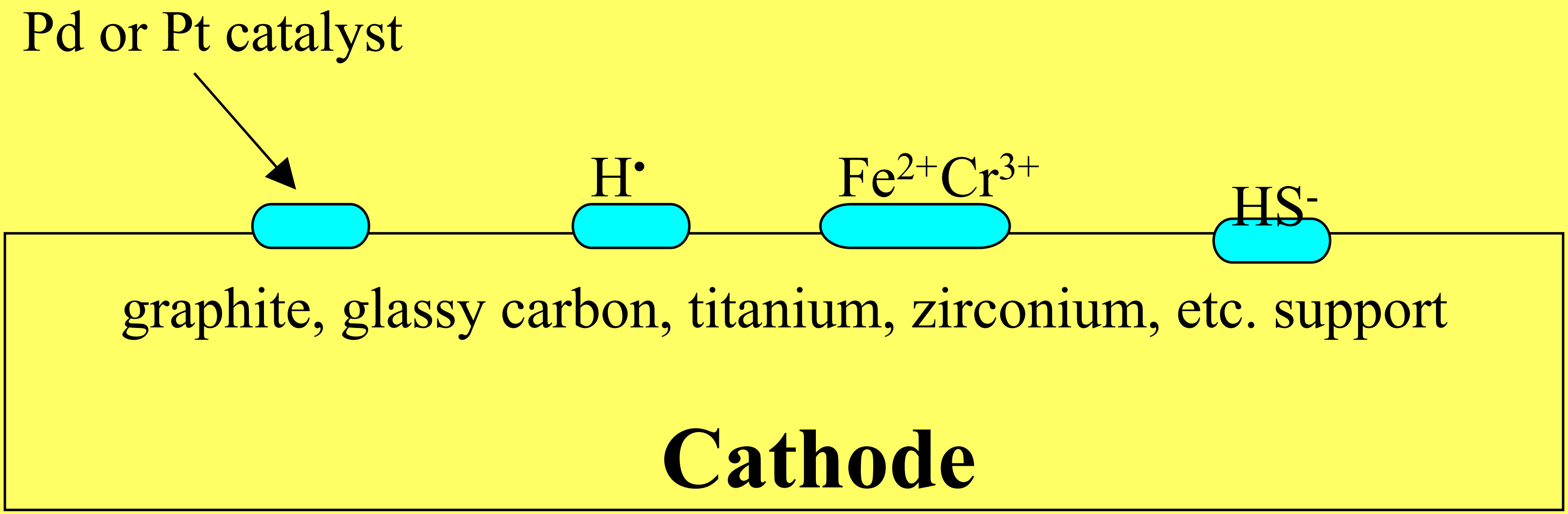
tunneling
to physically
adsorbed species

chemisorbed
species

reduction via
atomic hydrogen
produced from
water reduction

Cathode

Reduction Catalysts



Pd or Pt catalyst

$H^{\bullet}$

$Fe^{2+}Cr^{3+}$

HS^{-}

graphite, glassy carbon, titanium, zirconium, etc. support

Cathode

- Pd & Pt adsorb high concentrations of highly reactive $H^{\bullet}$.
- Catalyst may be fouled by deposition of redox active metals or sulfur compounds.
- Catalyst adhesion to support material is not perfect and loss of catalyst occurs over time.

Water Oxidation

$$MO_x + H_2O \rightarrow MO_x(OH^\bullet) + H^+ + e^-$$

$$MO_x(OH^\bullet) \rightarrow MO_{x+1} + H^+ + e^-$$ Active Electrodes

- MO_x is a metal oxide site on the anode surface.
- Water oxidation produces adsorbed $OH^\bullet$ radicals.
- Active oxygen species may oxidize organic compounds.
- High concentrations of active oxygen species lead to O_2 evolution.

$$MO_x(OH^\bullet) \rightarrow 0.5\ O_2 + H^+ + e^- + MO_x$$

Non-active Electrodes
PbO_2; SnO_2

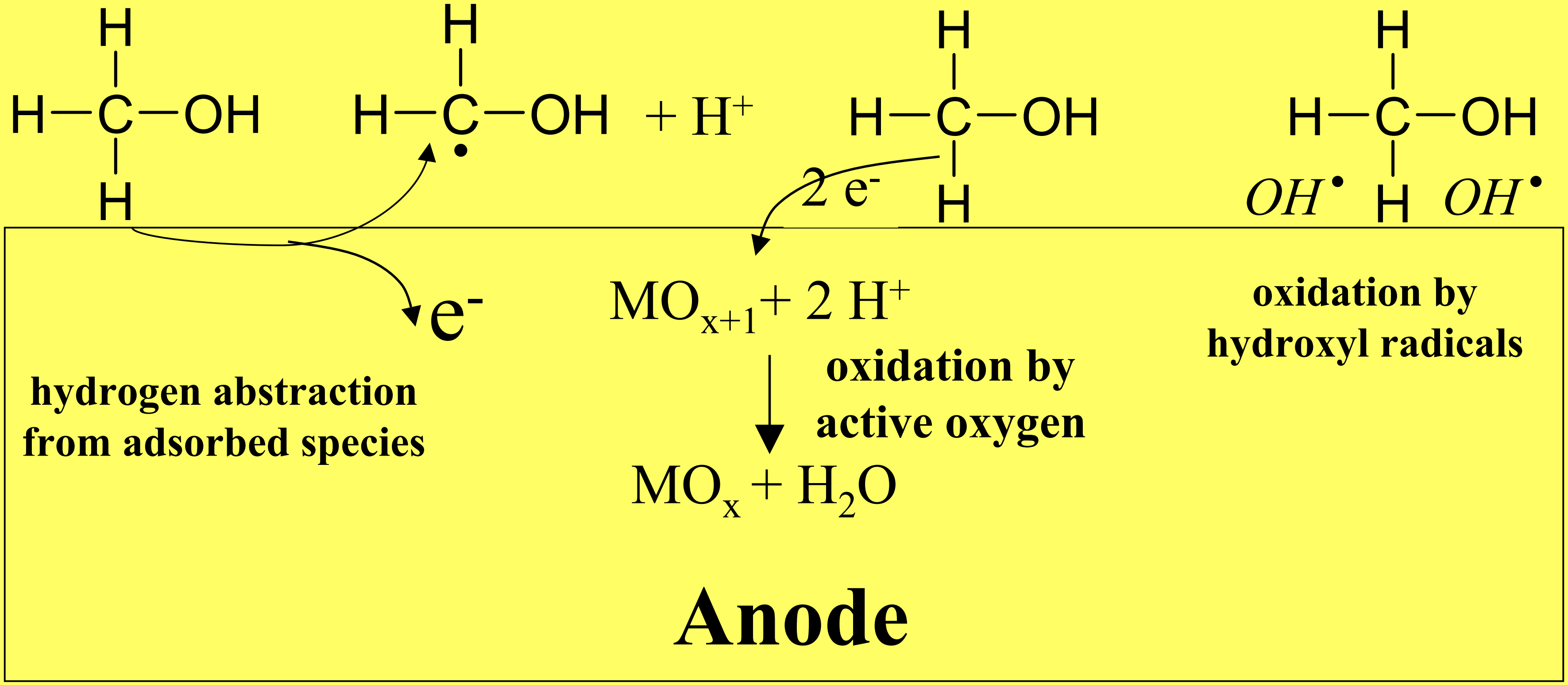
$$MO_{x+1} \rightarrow 0.5\ O_2 + MO_x$$

Active Electrodes
IrO_2; RuO_2

Oxidation - Electron Transfer Mechanisms

Direct Oxidation

Indirect Oxidation



$+ H^+$

$2\ e^-$

e^-

$MO_{x+1} + 2\ H^+$

$MO_x + H_2O$

$OH^\bullet$ $OH^\bullet$

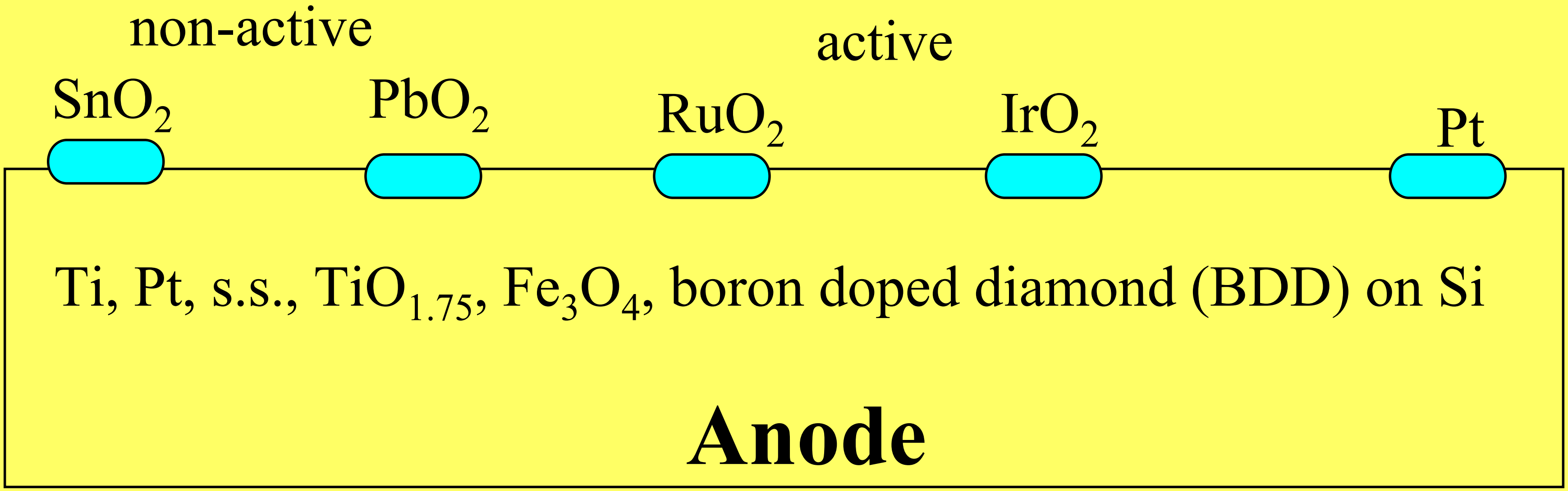
hydrogen abstraction from adsorbed species

oxidation by active oxygen

oxidation by hydroxyl radicals

Anode

Oxidation Catalysts



non-active

active

SnO_2 PbO_2 RuO_2 IrO_2 Pt

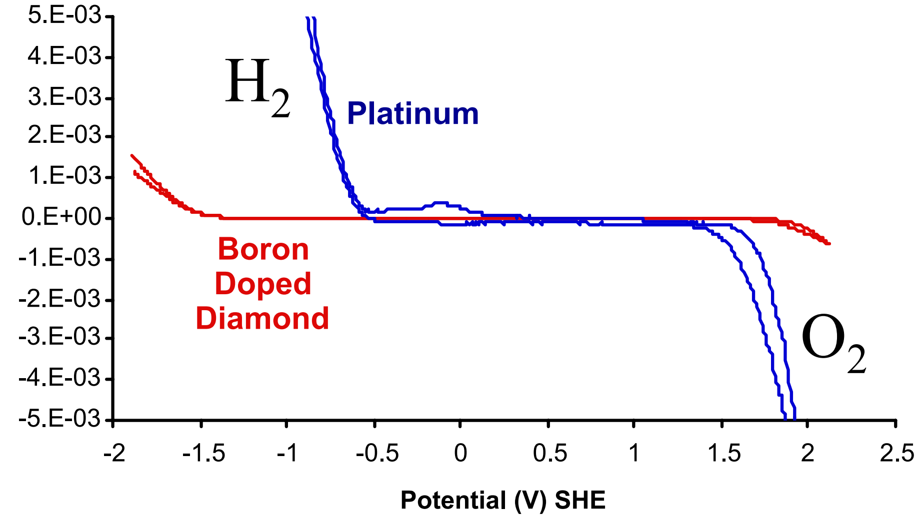
Ti, Pt, s.s., $TiO_{1.75}$, Fe_3O_4, boron doped diamond (BDD) on Si

Anode

- Titanium substrate is dimensionally stable (DSA®) due to a thin protective oxide film.
- Other oxides are resistant to further oxidation.
- All anodes will wear and lose electrical conductivity and their catalyst coatings.

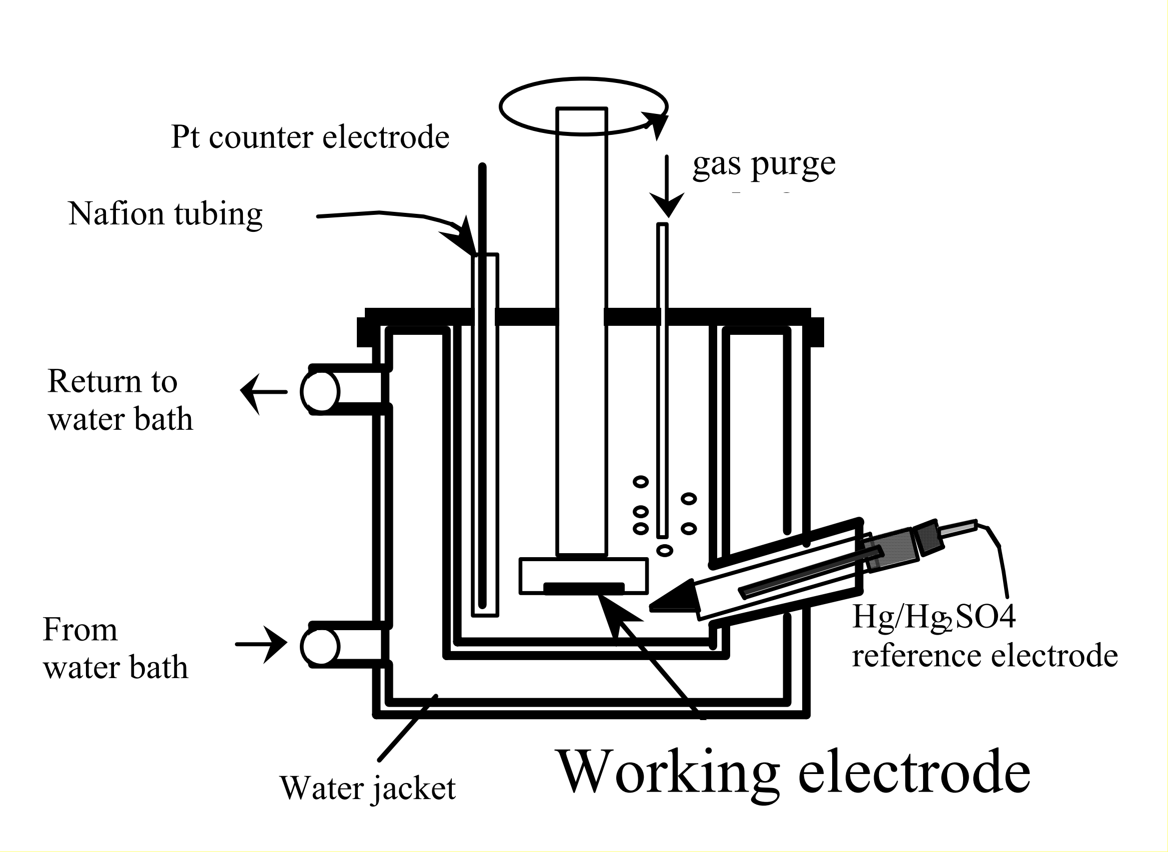
Effect of Electrode Material on Background Currents

Cyclic Voltammetry Scans with Platinum and Boron Doped Diamond Film Electrodes in Blank Electrolyte Solutions

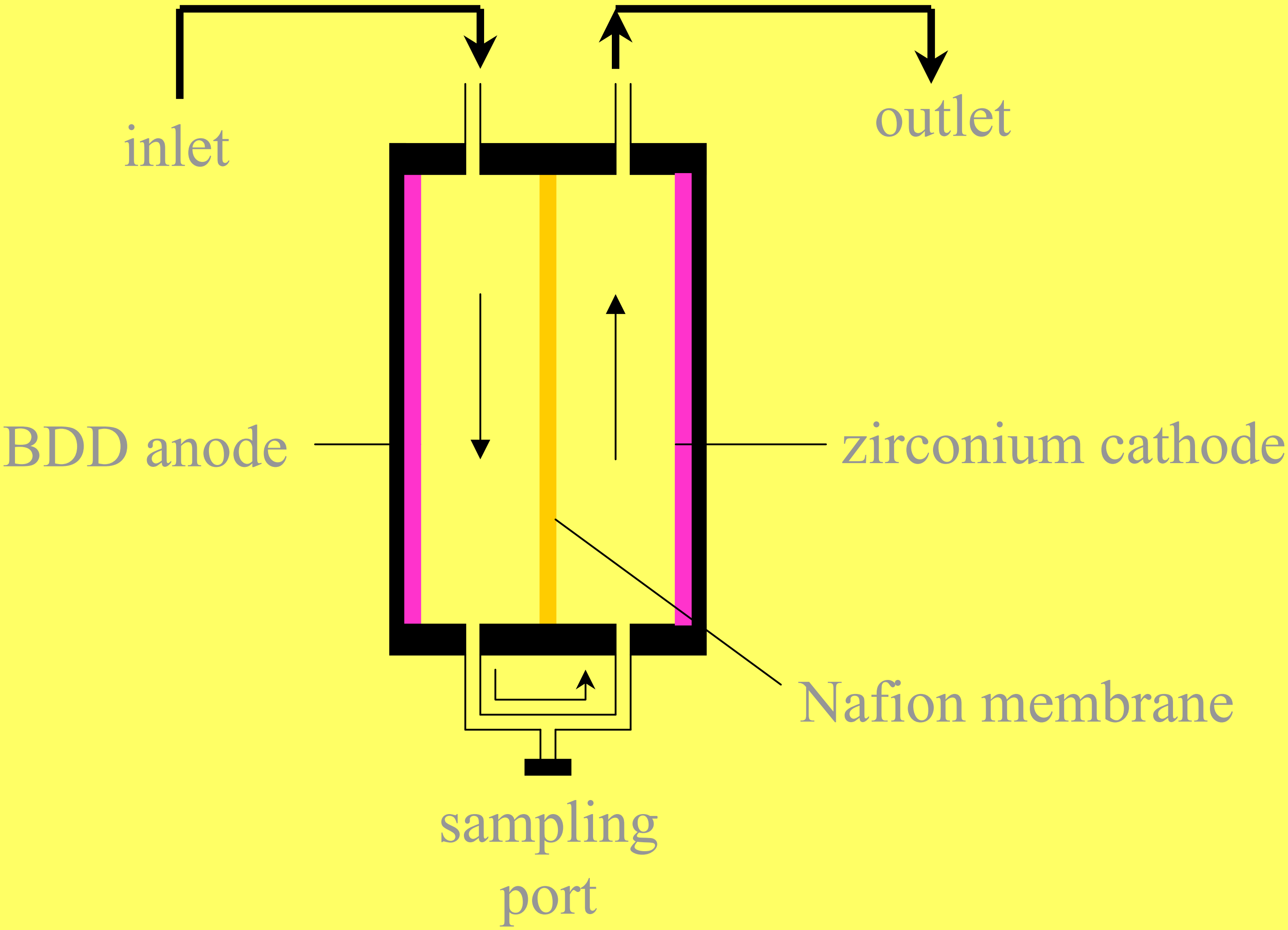


- Wider potential window for BDD due to absence of chemisorbed intermediates.
- Decreased reactions with solvent result in greater current efficiencies for reaction of the target compound.

Methods: Rotating Disk Electrode Reactor

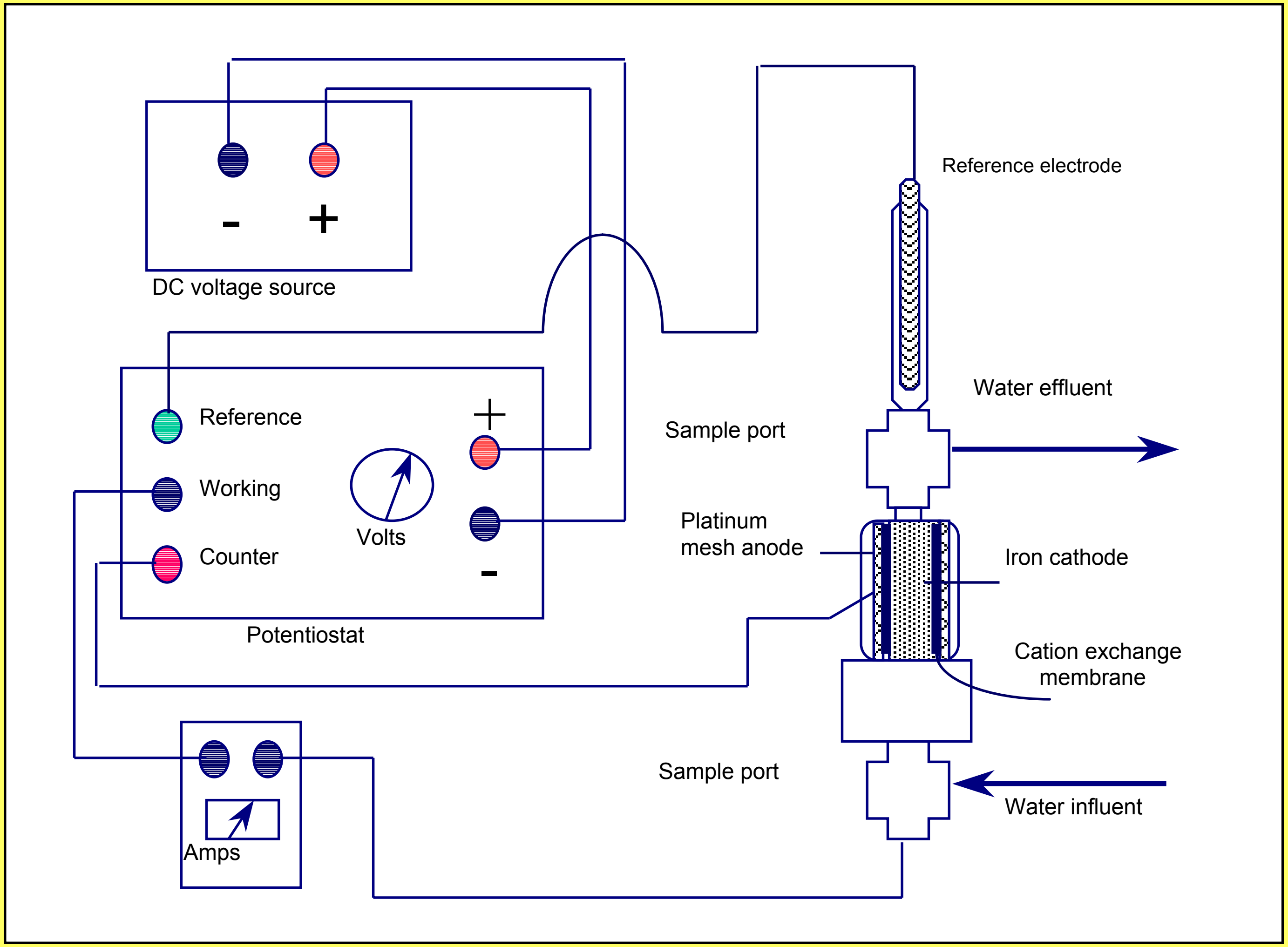


Methods: Flow-through Reactor



- Diacell® 102 from CSEM (Centre Suisse d'Electronique et de Microtechnique).

Methods:High Surface Area Flow-through Reactor



Background - Kinetics

Electron Transfer Kinetics: Butler-Volmer Equation

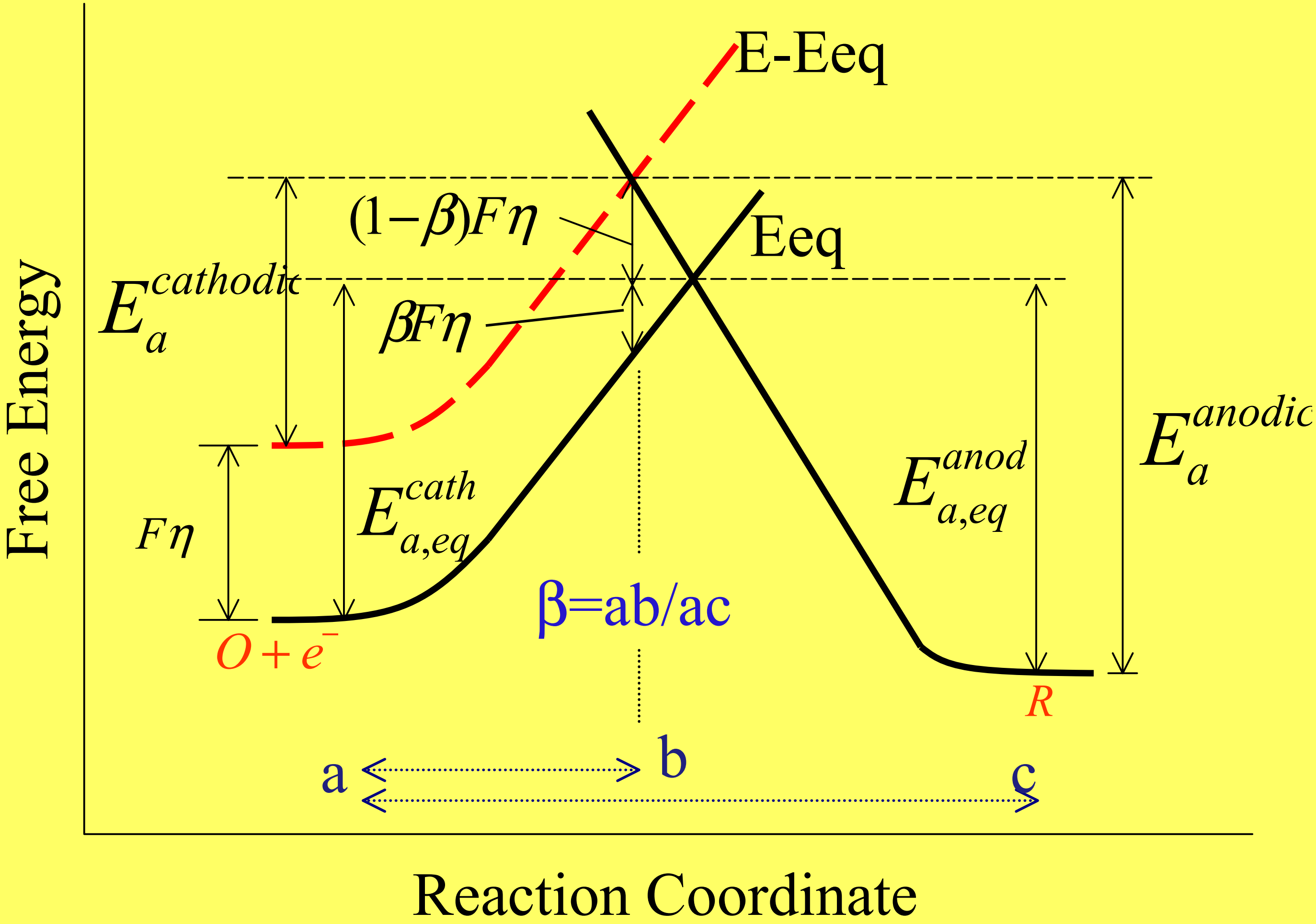
$$i = i_0[e^{-\alpha F(E-E_{eq})/RT} - e^{\omega F(E-E_{eq})/RT}]$$

forward reverse

i = current
i_o = exchange current
α = e^- transfer coefficient
ω = e^- transfer coefficient
F = Faraday constant
E = potential
E_{eq} = equilibrium potential
R = gas constant
T = temperature

$\alpha =$ transfer coefficient
$\alpha = \gamma + r\beta$
$\gamma = \# e^-$ before RLS
$r = 1$ RLS involves e^-
$r = 0$ RLS without e^-
$\beta =$ symmetry factor

Overpotential (η) Provides the E_a



Reductive Dechlorination

1. Rate-limiting step determination.
2. Reaction mechanism determination.
3. Current efficiencies.

Rate Limiting Step Determination

1. Determine the effect of temperature on the α for CT and TCE.

For an electron transfer RLS, α should be independent of T.

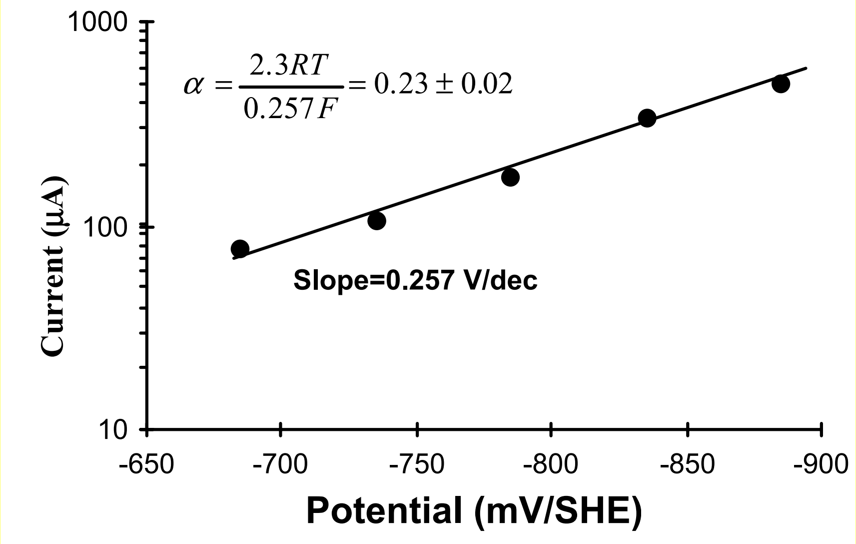
$$i = i_0[e^{-\alpha F(E-E_{eq})/RT} - e^{\omega F(E-E_{eq})/RT}]$$

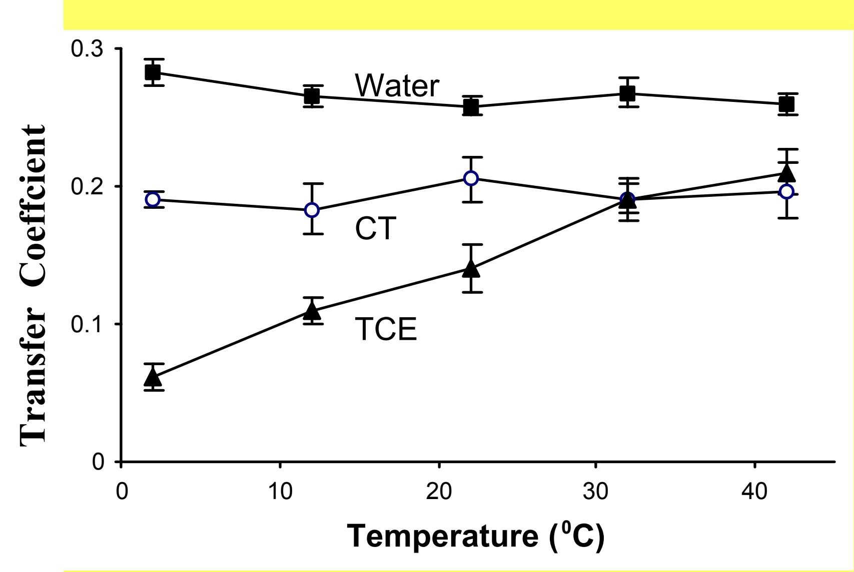
2. Determine the effect of potential (E) on the E_a for CT and TCE.

For an electron transfer RLS, E_a should decrease with decreasing E.

$$E_a = E_a^{eq} + \alpha F(E - E_{eq})$$

Transfer Coefficient Analysis

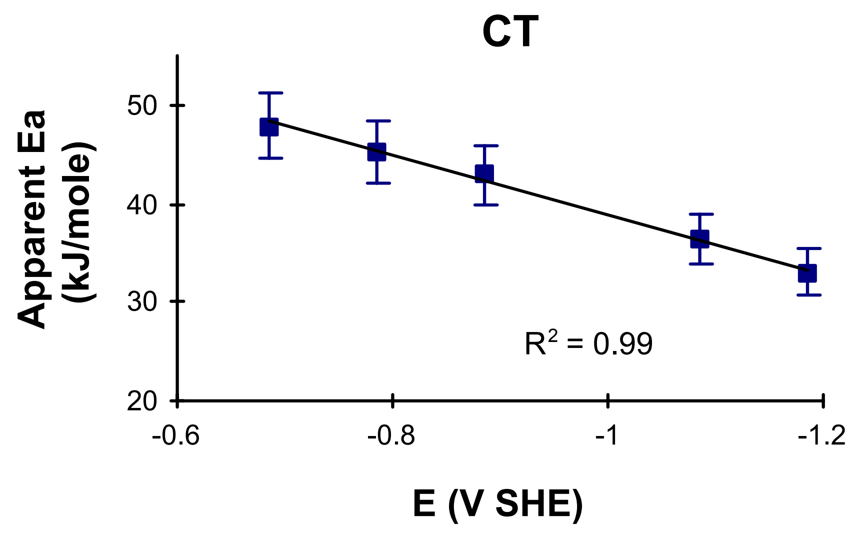


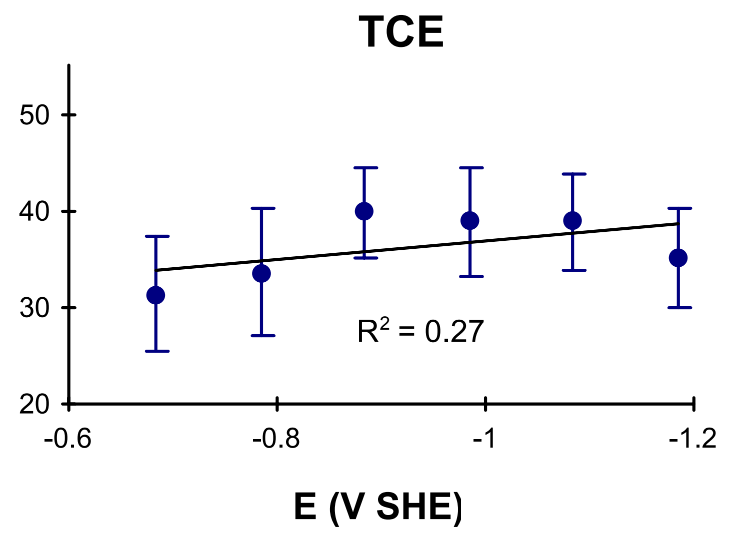


Electron transfer coefficients were determined from the potential dependence of the reaction rates.

- α_{CT}: independent of T → electron transfer RLS.
- α_{TCE}: T dependent → chemical dependent RLS.
- α_{water}: independent of T → electron transfer RLS.

Activation Energy Analysis





$$E_a = E_a^{eq} + \alpha F(E - E_{eq})$$

- **CT: Decrease in E_a → electron transfer RLS.**
- **TCE: No decrease in E_a → chemical dependent RLS.**

Reaction Products

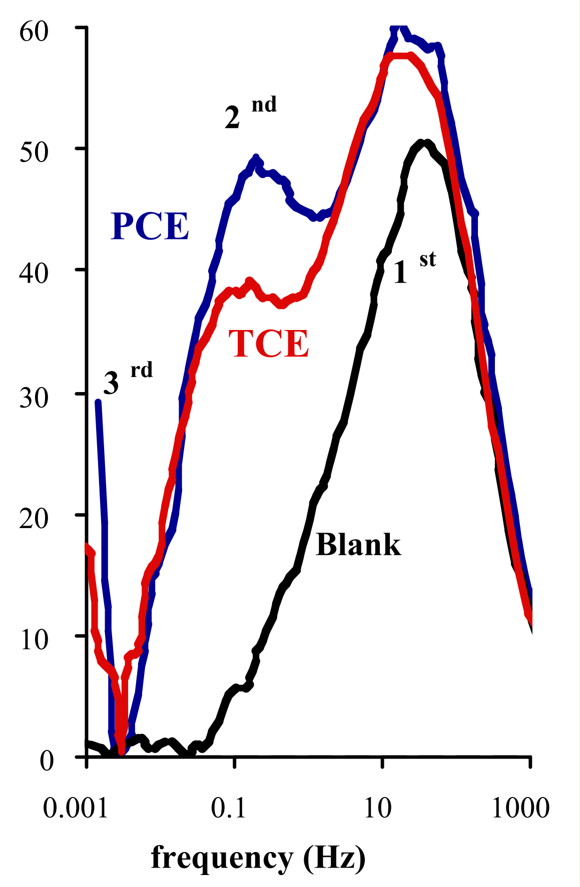
$$CCl_4 \rightarrow CHCl_3 \rightarrow CH_2Cl_2 \rightarrow CH_3Cl \rightarrow CH_4$$

Intermediate chlorinated products consistent with physical adsorption (short surface interaction).

$$C_2HCl_3 \xrightarrow[RLS]{2e^-} (C_2HCl) \xrightarrow[fast]{4e^-} C_2H_4$$

Complete dechlorination consistent with a chemical adsorption mechanism (long surface interaction).

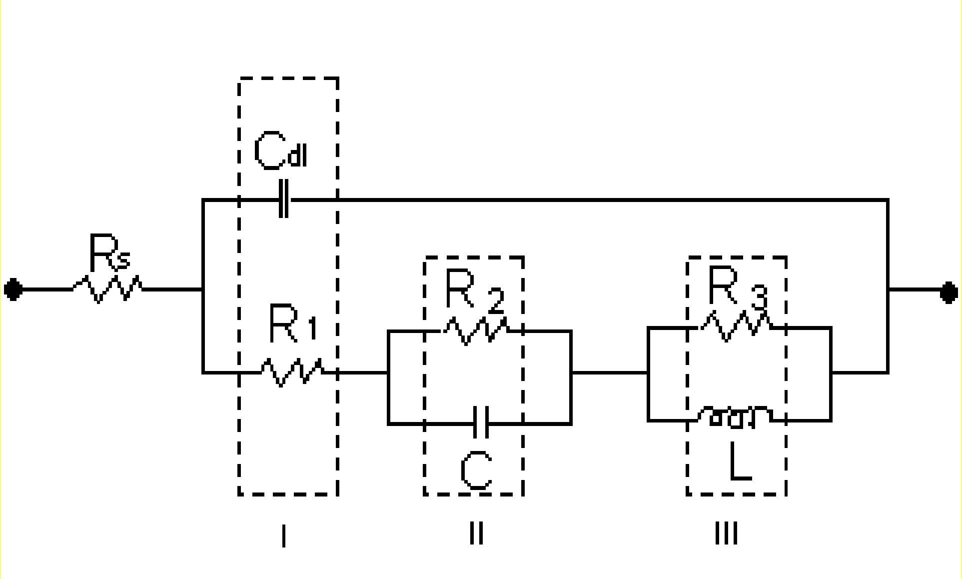
Impedance Spectroscopy Analysis

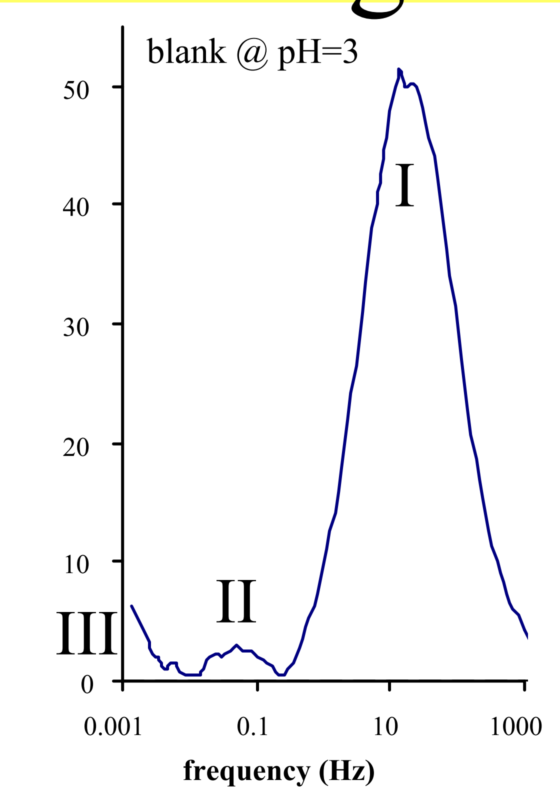


- Each peak indicates a unique electron transfer reaction.
- Peak 1 is for water reduction.
- Peaks 2 & 3 are for TCE reduction.
- Two peaks for TCE reduction indicate two electrons transferred during rate limited steps.

Bode phase plot for an iron wire immersed in blank electrolyte and TCE solutions.

Equivalent Circuit Modeling





R_s=solution resistance.

C_{DL}=double layer capacitance.

R_1=charge transfer resistance associated with reaction 1.

C_2= capacitance associated with reaction 2.

R_2=resistance associated with reaction 2.

R_3=charge transfer resistance associated with reaction 3.

L_3=inductance associated with reaction 3.

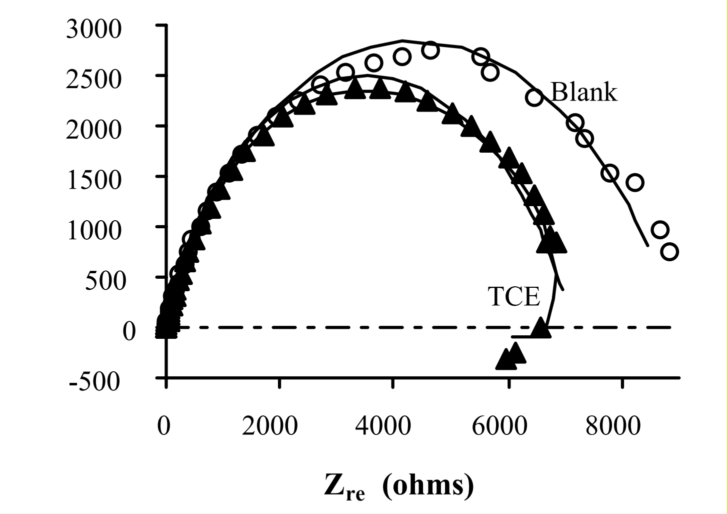
H_2 Evolution Reactions

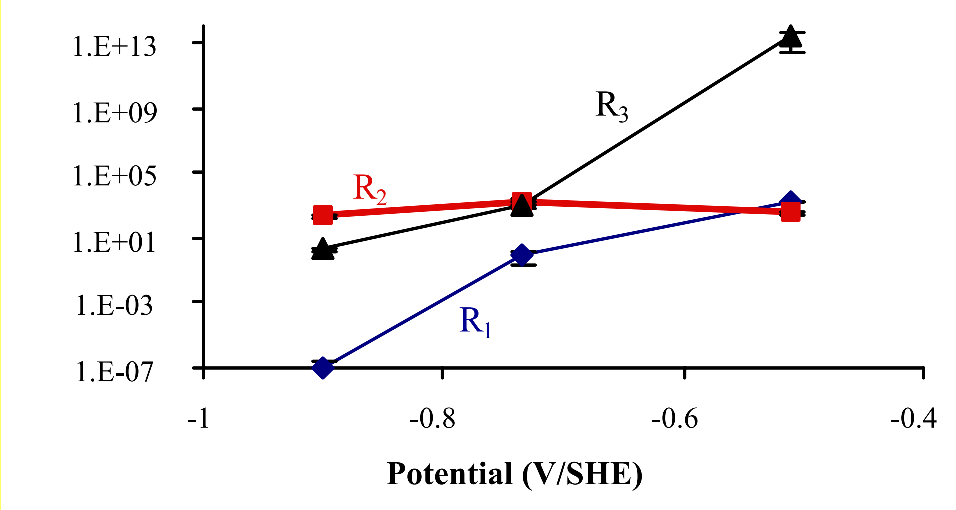
1 $Fe + H^+ + e^- \rightarrow FeH^\bullet$

2 $FeH^\bullet + FeH^\bullet \rightarrow 2Fe + H_2$

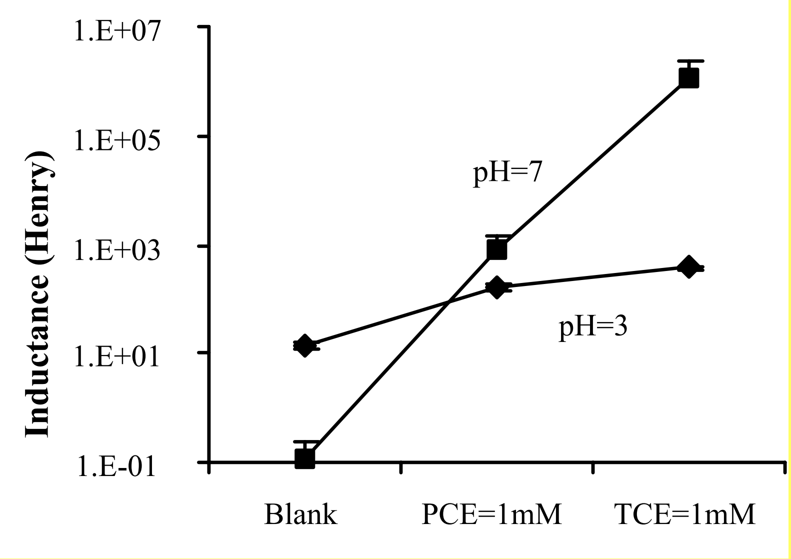
3 $FeH^\bullet + H^+ + e^- \rightarrow Fe + H_2$

Circuit Modeling for TCE



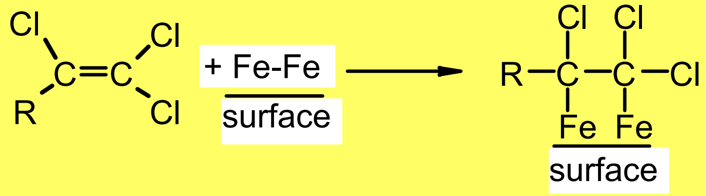


- Weak potential dependence for R_2 suggests a reaction with $H^{\bullet}$.
- Inductance at low frequencies suggests a slow chemical reaction proceeding an electron transfer step.



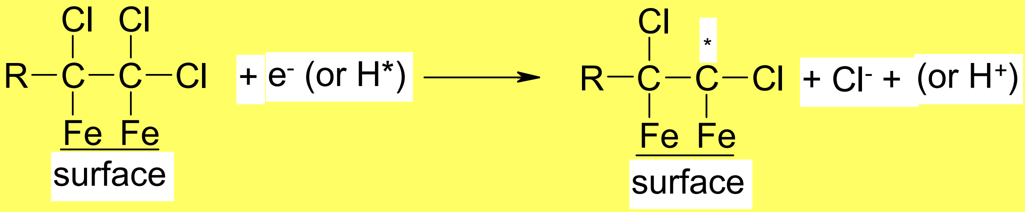
Proposed TCE Mechanism

1.



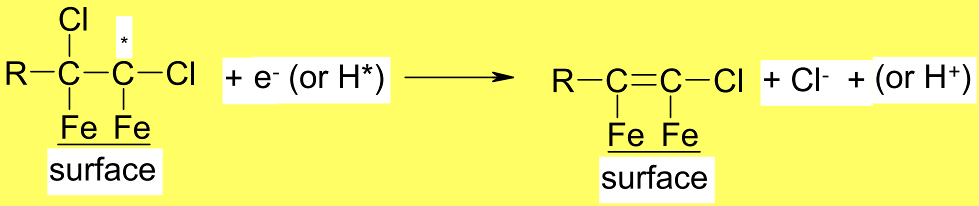
Chemisorption - fast

2.



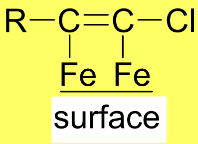
Slow direct reduction

3.



Slow direct reduction

4.

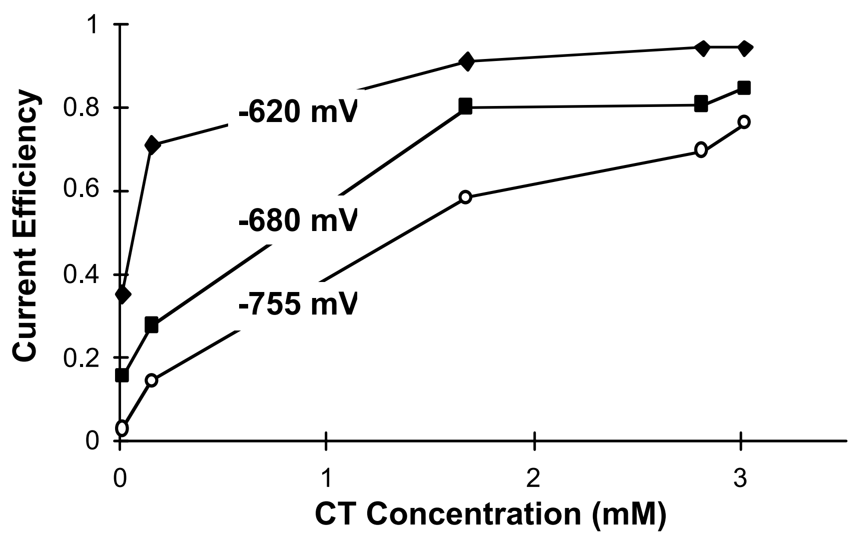


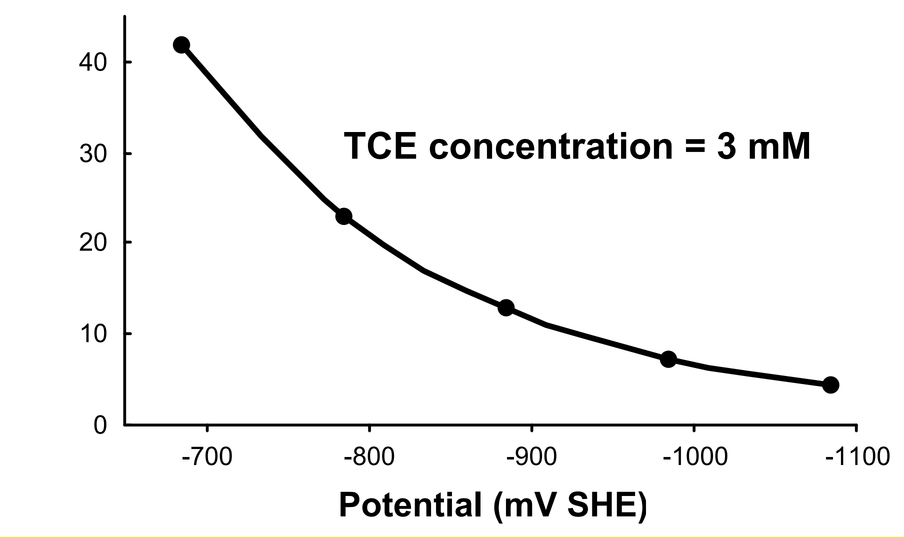
$+ 4\ e^- + 4\ H^+ \longrightarrow C_2H_4$

Fast -
no impact on overall rate

Current Efficiency

Current Efficiencies for Reductive Dechlorination of CT and TCE



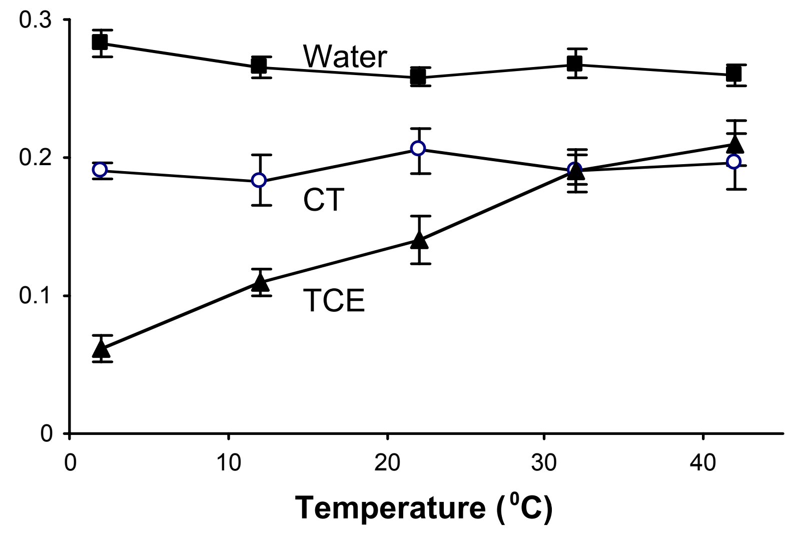


- current efficiency = fraction of the cell current going towards oxidation or reduction of the target compound.
- decreasing current efficiencies with decreasing voltage leads to a trade-off between rates of reaction and power costs.

Current Efficiency

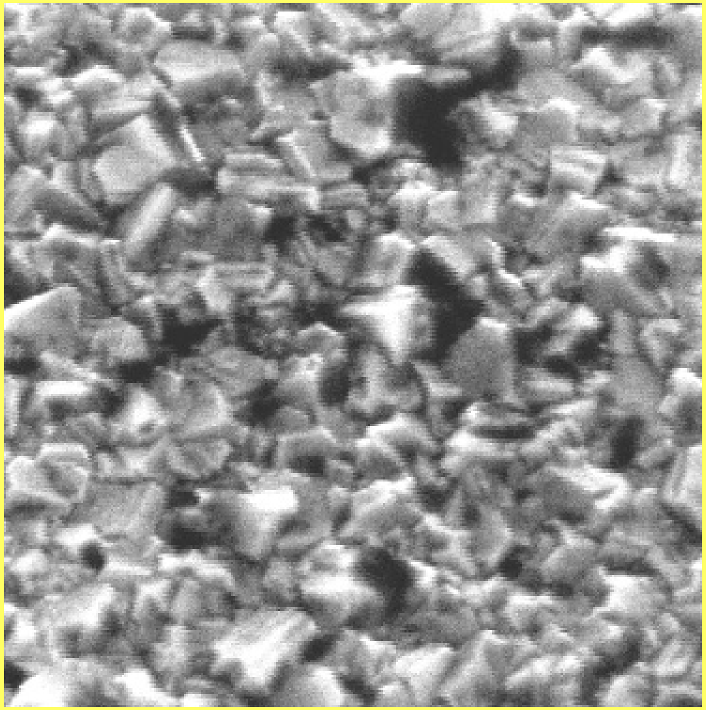
$$i = i_0[e^{-\alpha F(E-E_{eq})/RT} - e^{\omega F(E-E_{eq})/RT}]$$

forward reverse



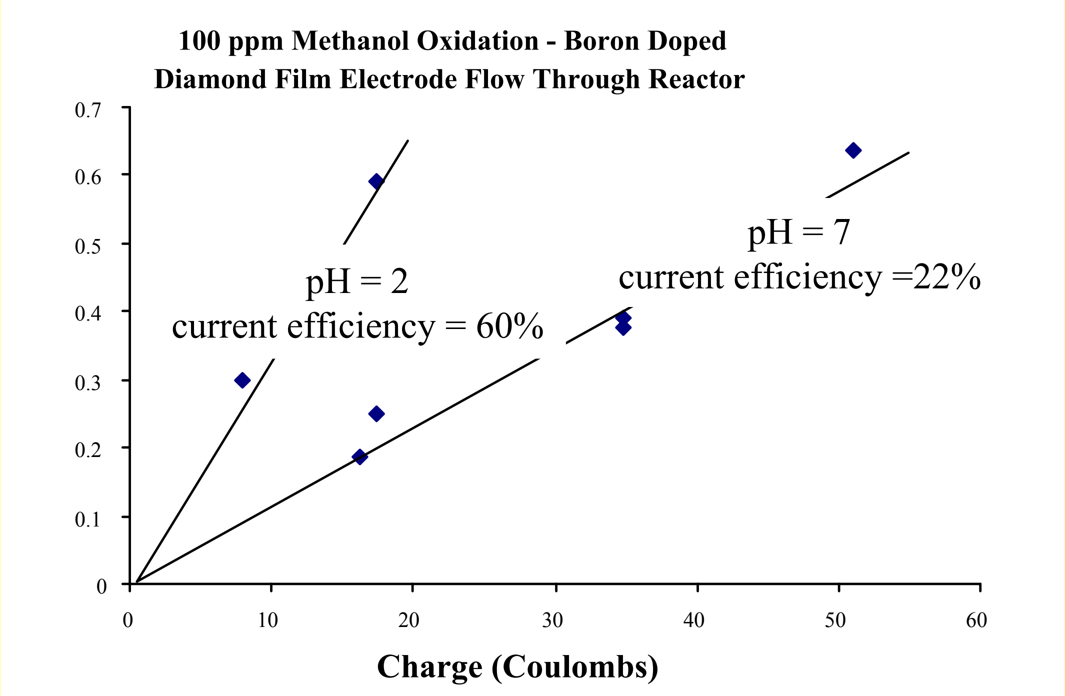
- decreasing current efficiency with decreasing potential due to $\alpha_{water} > \alpha_{CT}$ or α_{TCE}.

Oxidation at BDD Electrodes



- BDD electrodes: 1) resistant to oxidation; 2) have small exchange currents for H_2 and O_2 evolution; 3) resistant to fouling by *chemisorbed* compounds; 4) hydrophobic.

Methanol Oxidation



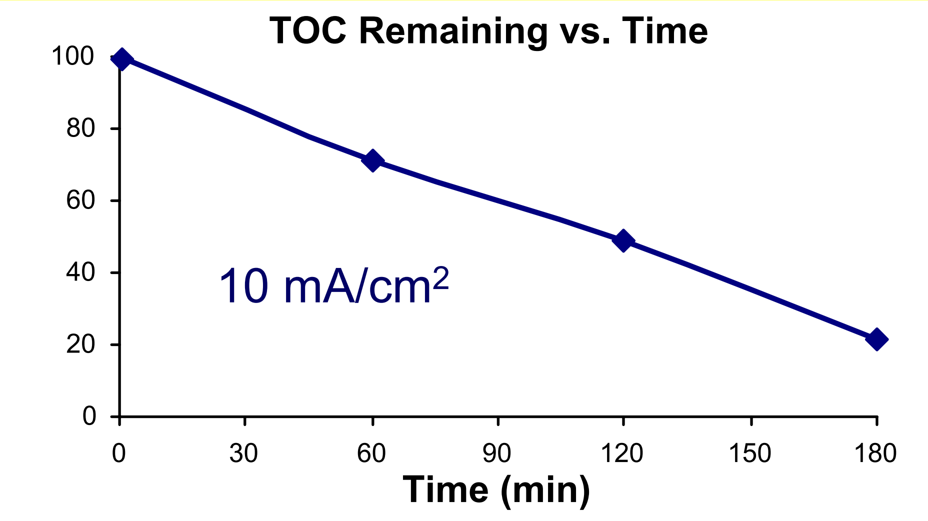
$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad anode$$

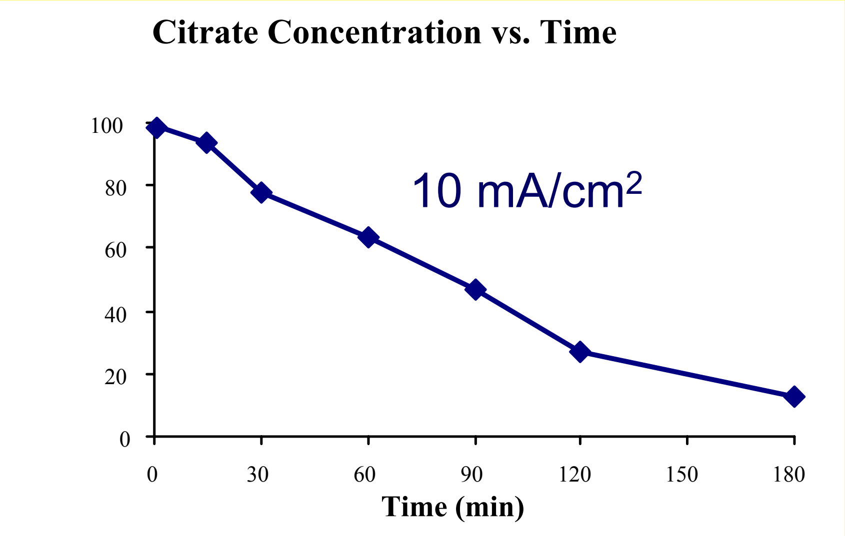
$$6e^- + 6H^+ \rightarrow 3H_2 \quad cathode$$

- To remove 100 mg/L methanol at pH = 7, electrical cost per m^3 treated = $0.60 for power at $0.10/kWhr.

Citrate Oxidation

Citrate Oxidation in Stirred Batch Reactor





- Similar TOC and citrate removal indicates mineralization to CO_2.
- Current efficiency at 10 mA/cm^2 was 180%, suggesting oxidation by O_2.

Possible Citrate Oxidation Mechanisms

Overall Oxidation Reaction

$$C_6H_8O_7 + 5\,H_2O \rightarrow 6\,CO_2 + 18\,H^+ + 18\,e^-$$

Likely Oxidation Reactions

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

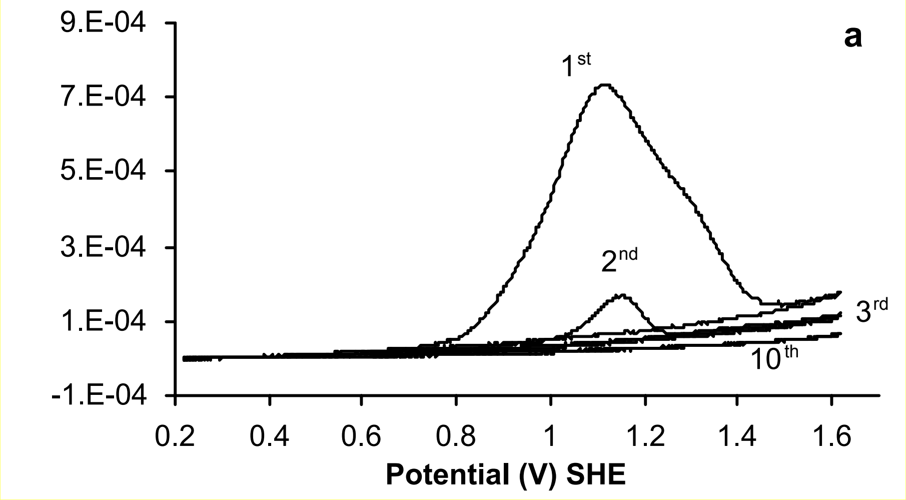
$$R_3CH + OH^\bullet \rightarrow R_3C^\bullet + H_2O$$

$$C^\bullet OOH + O_2 \rightarrow CO_2 + HO_2^\bullet$$

- Reactions of carboxyl radicals with atmospheric O_2 can produce current efficiencies greater than 100%.

Electrode Fouling

Cyclic Voltammetry Scans in 4 mM Triclosan Solutions with BDD Electrode

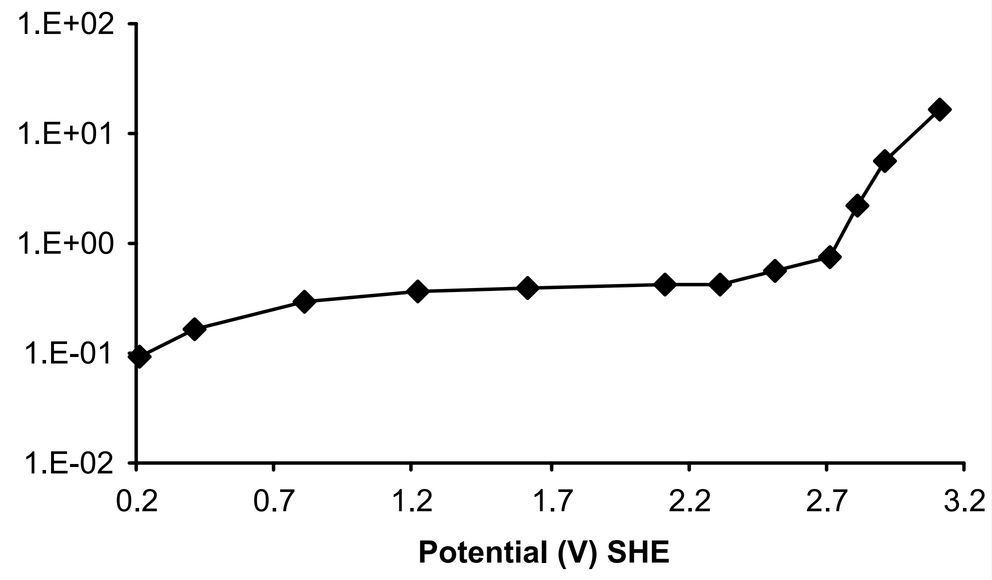


Effect of Anodic Stripping on Reactivation of BDD Electrode

- Decreasing currents indicative of fouling by polymerized organic compounds.
- Oxidation of polymer film by hydroxyl radicals reactivates the electrode.

Polymer Films Limit Potential Range

Current for BDD Rotating Disk Electrode in 4 mM Triclosan Solutions



Conclusions

- Electrochemical water treatment can be very cost effective.
- Cost per mole of electrons = 0.6 cents at 2.2 V ($0.10/kW hr).
- High current efficiencies for oxidation at BDD electrodes.
- Most difficult issues are in reactor design.

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