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Sonoelectrochemical deposition of Catalytically Active Iron Metal at Boron-Doped Diamond Electrodes: Aplication to electroreduction of chloroacetates

Veronica Saez[a], Jose Gonzalez-Garcia[a], M. Anbu Kulandainathanb[b] and Frank Marken[c]

[a]Universidad de Alicante, Departamento Química Física, Grupo Electroquim Aplicada, Ap Correos 99, Alicante, E-03080 Spain

[b]Central Electrochemical Research Institute, Karaikudi, Tamil Nadu 630006 India

[c]Department of Chemistry, University of Bath, Bath BA2 7AY, UK

Introduction

Properties Boron Doped Diamond (BDD) electrodes

- Quite stable physical and chemical
- Hardness and a mechanically robust nature suitable for high intensity sonoelectrochemical processes
- Very Low background current
- Wide electrochemical potential window in aqueous solutions (hydrogen evolution commences at about −1.25V versus SHE and oxygen evolution at +2.3V versus SHE)
- Long-term stability of the response.
- Excellent stability and high reproducibility

Applications:

(i) electro-synthesis, in which inorganic and organic compounds are produced by the application of electricity.

(ii) water treatment, which includes the purification of wastewater and the disinfection of drinking water and

(iii) electro-analysis and sensor technology

Example: Electrochemical oxidation of different organic compounds such as phenol, 4-chlorophenols, 3-methylpiridine and carboxylic acids.

Electrochemical reduction of oximes to amines and reduction of nitrate ions

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Introduction

Properties Iron nanoparticles

-Cheap

-Friendly environment

-Large surface areas and highly reactive

-Effective at reducing chlorinated organics

-Rapid formation of inert oxide coatings in aqueous enviroment

Applications: - dehalogenation and remediation processes:

a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides, and PCBs can be transformed by iron nanoparticles

$$C_2Cl_4 + 4Fe^0 + 4H^+ \rightarrow C_2H_4 + 4Fe^{2+} + 4Cl^-$$

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Objectives

1.- Electro-deposition active iron nanoparticles at BDD electrodes

- Deposition potential
- Deposition time
- Concentration effects of Fe(III)
- Mass transfer effects (ultrasound)
- Different electrolytes and electrodes

2.- Study of catalytic reactivity of electro-deposited iron towards chloroacetate

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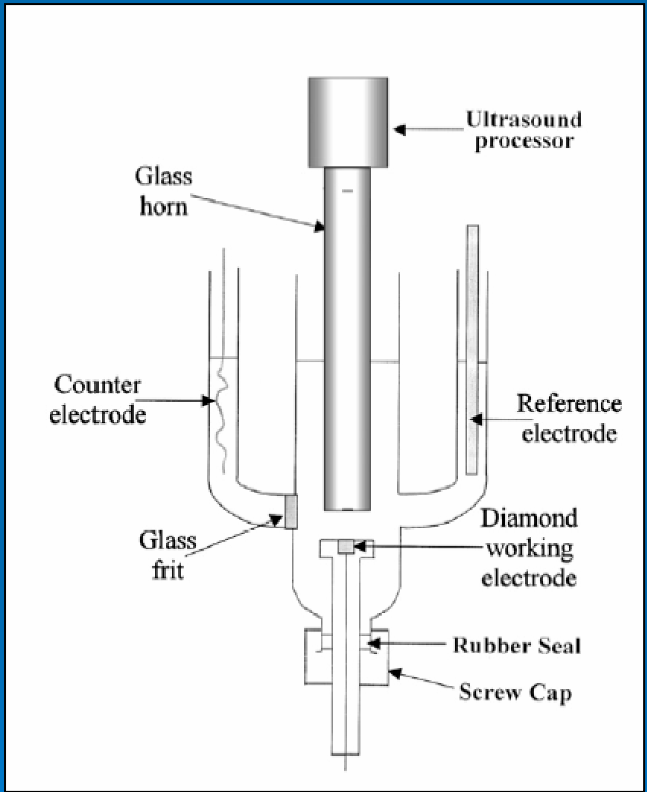
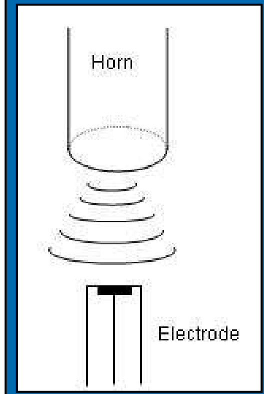
Experimental set-up





Face on

Sonoreactor Hielscher UP 200G
Frequency: 24 kHz
Maximum ultrasound intensity: 8 W cm^{-2} (calorimetric method)

Glass horn diameter: 13 mm

Working electrode Boron doped diamond (BDD)
3mm diam glassy carbon
Counter electrode platinum coil
Reference electrode satured calomel electrode (SCE)

Sonicated volume: $50cm^3$

0.5 M EDTA + 50 mM $Na_2S_2O_4$ → remove iron nanoparticles

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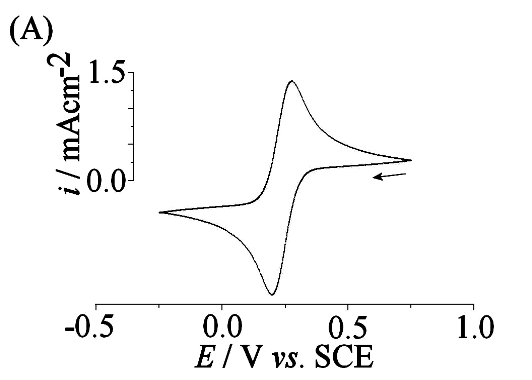
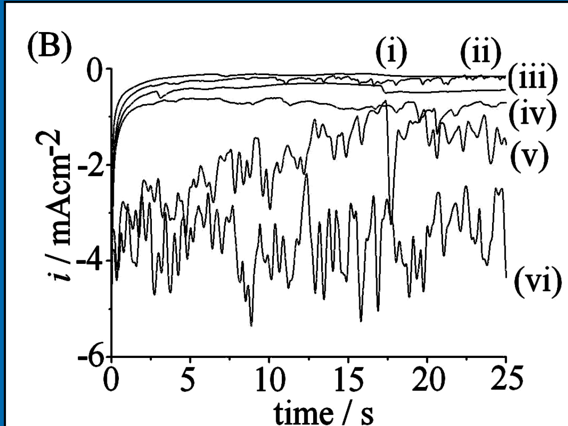
Sonoelectrochemical mass transport calibration

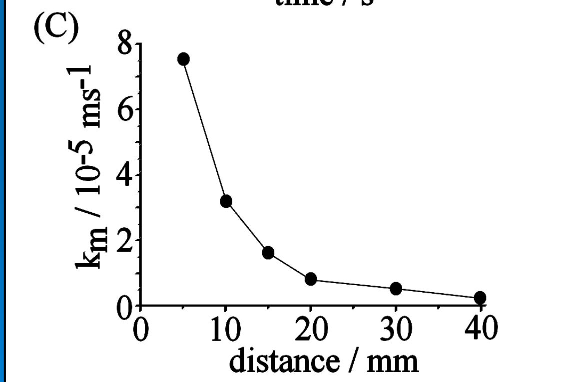
$Fe(CN)_6^{3-} / Fe(CN)_6^{4-}$ redox system



Cyclic voltammogram of 5 mM $Fe(CN)_6^{3-}$ in 1M NH_4F at a 3 mm BDD electrode 0.2 V s^{-1}



Chronoamperograms for the reduction of 5 mM $Fe(CN)_6^{3-}$ in 1M NH4F, applied potential 0.1 V vs. SCE, 8 W cm^{-2} ultrasound. Electrode to horn tip distance: (i) 40, (ii) 30, (iii) 20, (iv) 15, (v) 10 and (vi) 5 mm.



Mass transport coefficiend versus electrode to horn tip distance.

$$i_{lim} = nFk_m c$$

horn – electrodo distance 5mm

k_m = 7.5 x10^{-5} m s^{-1}

Strongly mass transport to the electrode surface!!

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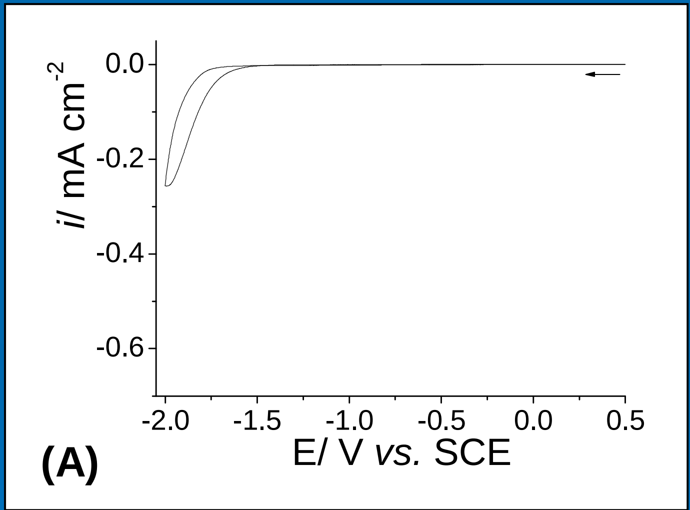
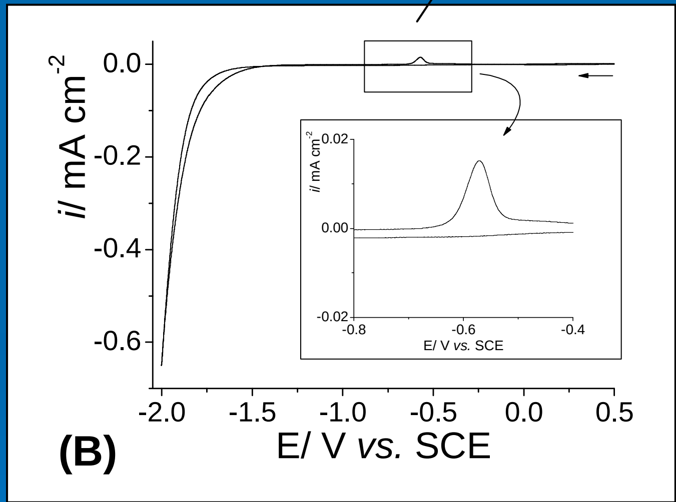
Electro-deposition and stripping of iron: reactivity in aqueous fluoride media

$$\mathrm{Fe(metal)} + 6\mathrm{F}^-(\mathrm{aq}) \longrightarrow \mathrm{FeF}_6^{3-}(\mathrm{aq}) + 3\mathrm{e}^-$$



(A)



(B)

Highly sensitive to Low concentration of Fe(III)

Require:
BDD electrode
1M NH_4F

BDD electrode
1M NH_4F
100 mV s^{-1}

BDD electrode
1M NH_4F + 10 μM Fe (III)
100 mV s^{-1}

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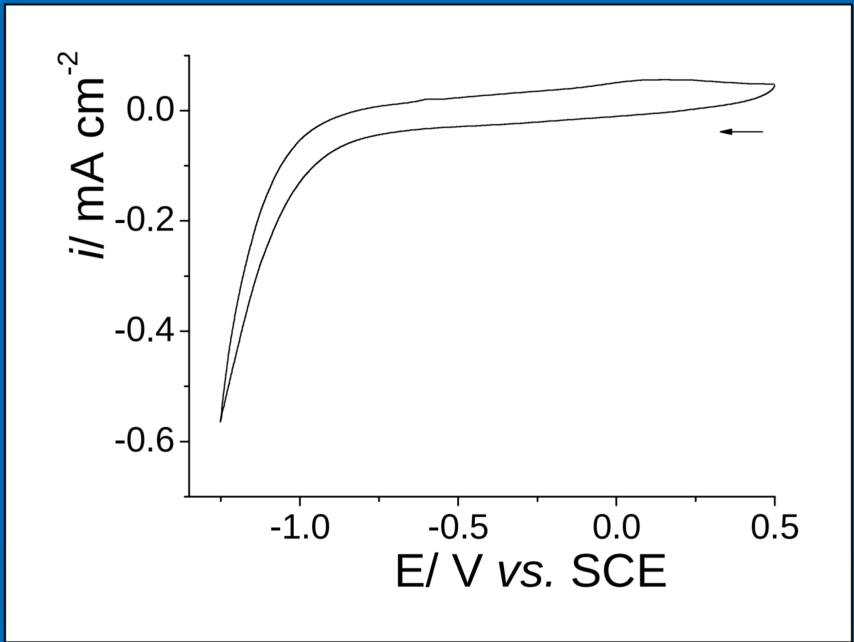
Electro-deposition and stripping of iron: reactivity in aqueous fluoride media



Glassy carbon electrode
1M NH_4F + 1 mM Fe (III)
20 mv s^{-1}

Experiments with a glassy carbon electrode

↓

no Fe stripping peak

Experiments with other electrolytes (NaOH, KCl) or lower concentration of NH_4F

↓

no Fe stripping peak

F^- importance!

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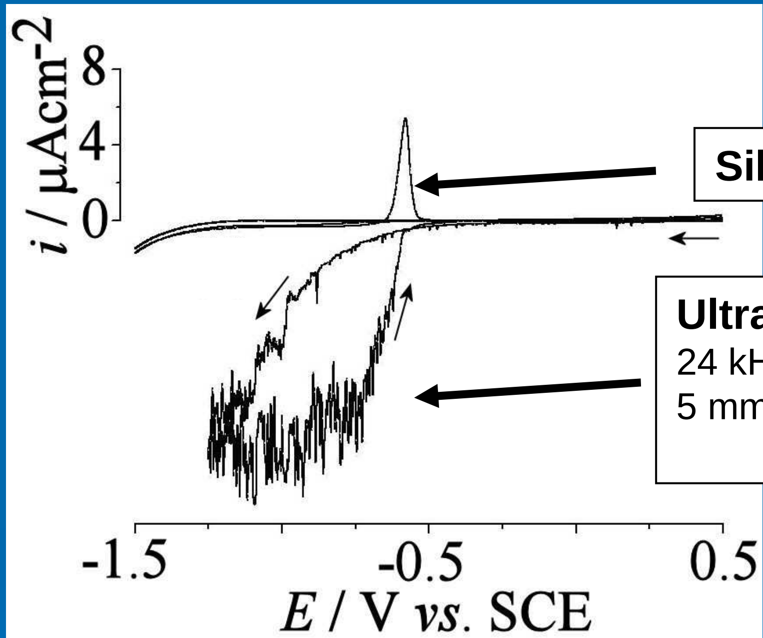
Electro-deposition and stripping of iron: reactivity in aqueous fluoride media



Silent conditions

Ultrasound conditions
24 kHz, 8 W cm^{-2} ultrasound
5 mm horn to electrode distance

BDD electrode
1M NH_4F + 10 µM Fe (III)
20 mV s^{-1}

Ultrasound

Enhanced mass transport conditions

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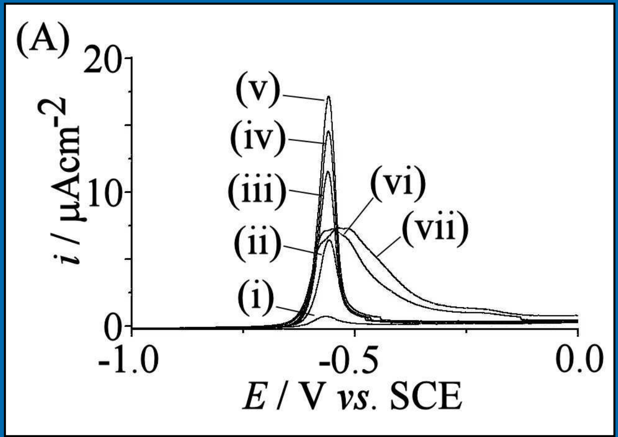
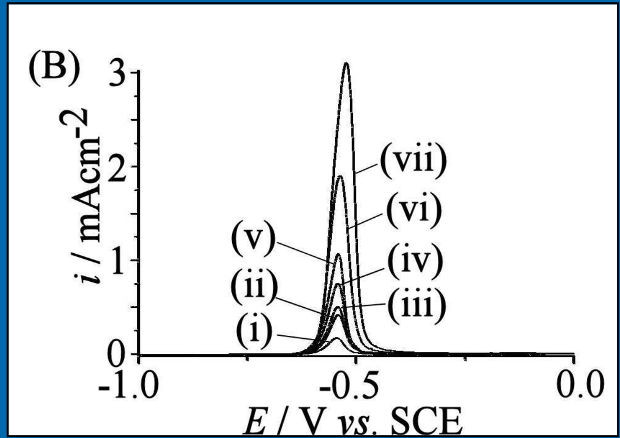
Electro-Deposition and Stripping of Iron: 2.2) Deposition Potential Effects

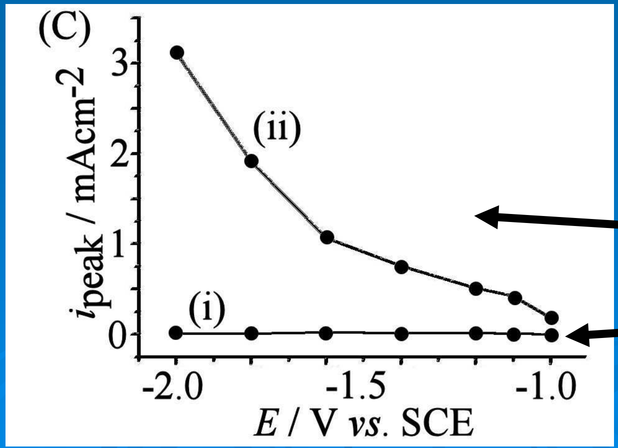


Without ultrasound

Linear scan voltammograms for the stripping of iron deposited in 10 µM Fe(III) + 1M NH_4F, scan rate 0.1 V s^{-1}, deposition time 30s depostion potential: (i) -1.0, (ii) -1.1, (iii) -1.2, (iV) -1.4, (v) -1.6V, (vi) -1.8 and (vii) -2.0 V vs. SCE.



With continuos 8 W cm^{-2} ultrasound, 5 mm horn to electrode distance



Ultrasound conditions

Silent conditions

Under ultrasound stripping peak increases 50-fold!

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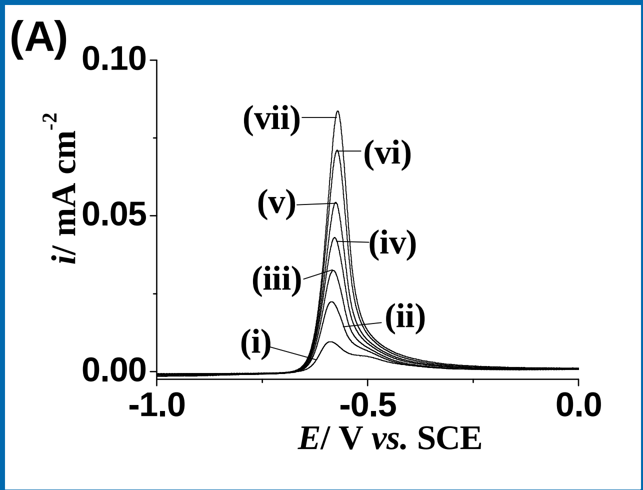
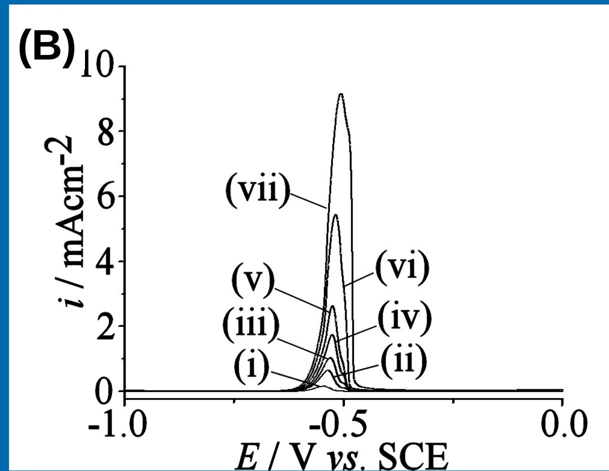
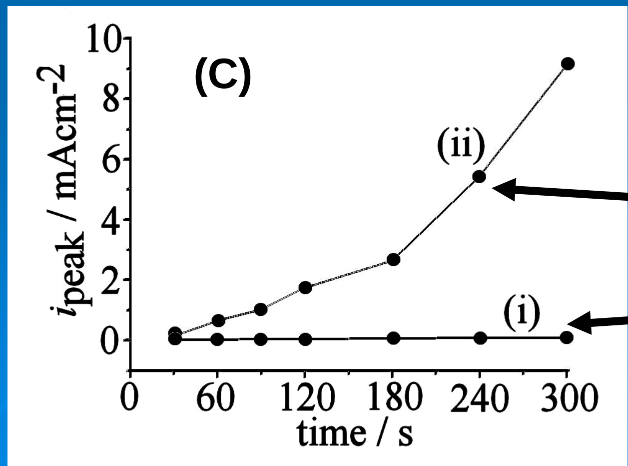
Electro-Deposition and Stripping of Iron: 2.3) Time Effects



Linear scan voltammograms for the stripping of iron deposited in 10 μM Fe(III) + 1M NH_4F, scan rate 0.1 V s^{-1}, deposition potential -1.5 V *vs.* SCE deposition time: (i) 30, (ii) 60, (iii) 90, (iV) 120, (v) 180, (vi) 240 and (vii) 300 s.



Without ultrasound



With continuos 8 W cm^{-2} ultrasound, 5 mm horn to electrode distance

Ultrasound conditions

Silent conditions

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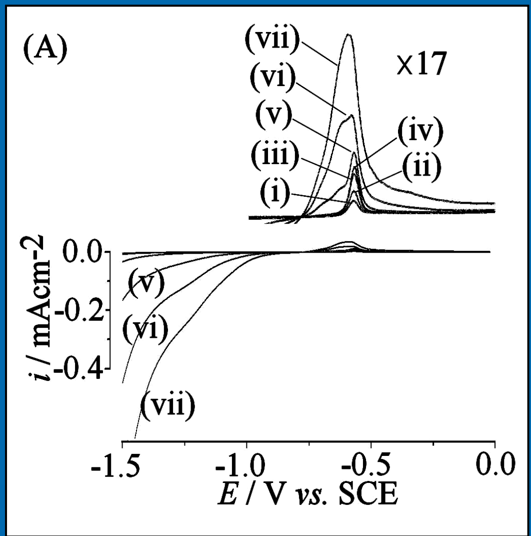
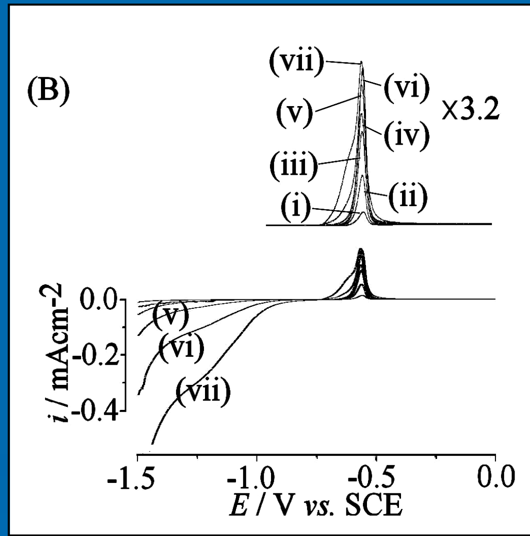
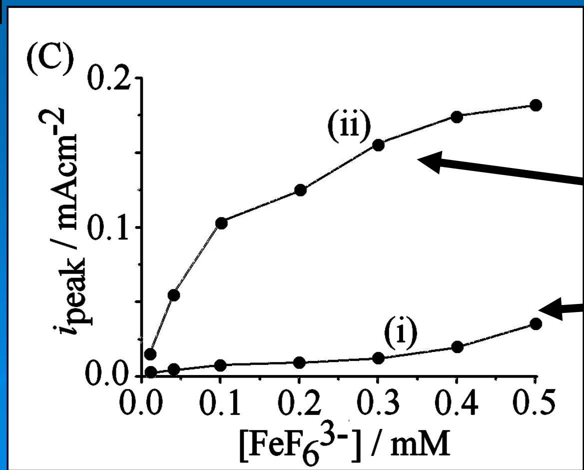
Electro-Deposition and Stripping of Iron: 2.4 Concentration Effects



Linear scan voltammograms for the stripping of iron deposited in (i) 10, (ii) 40, (iii) 100, (iV) 200, (v) 300, (vi) 400 and (vii) 500 µM Fe(III) + 1M NH4F, scan rate 0.1 V s^{-1}, deposition potential -1.5 V *vs*. SCE, deposition time 30 s



Without ultrasound



With continuos 8 W cm^{-2} ultrasound, 5 mm horn to electrode distance

Ultrasound conditions

Silent conditions

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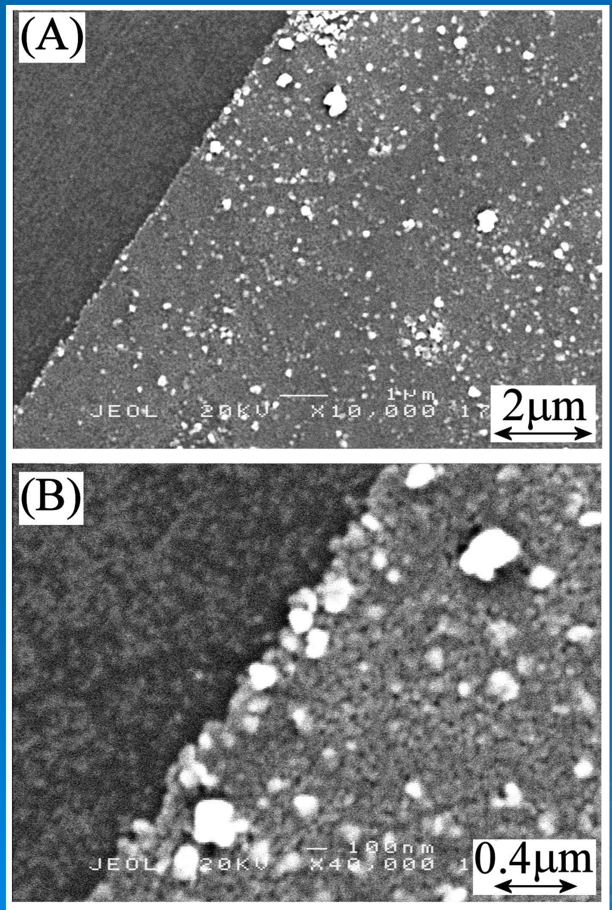
Electro-Deposition and Stripping of Iron:

Scanning Electron Microscope (SEM) images



Scanning electron micrographs for an iron deposit on boron doped diamond (generated by deposition at -1.5 V vs. SCE for 600s with 8 Wcm^{-2} ultrasound immersed in 10 µM Fe (III) in 1 M NH_4F.

Higher magnification image showing individual nanoparticles. Samples were scratched and gold sputter coated prior to imaging to improve image quality.

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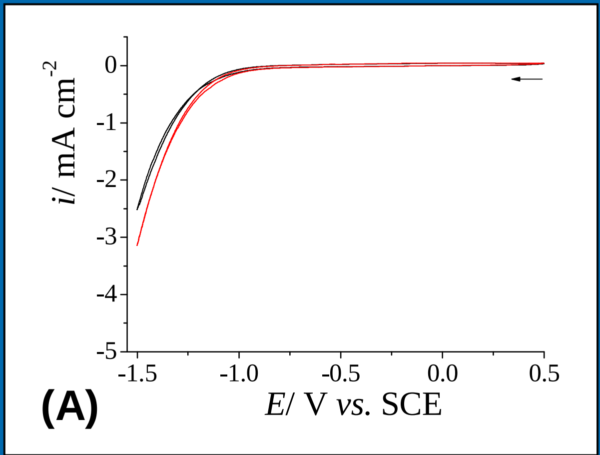
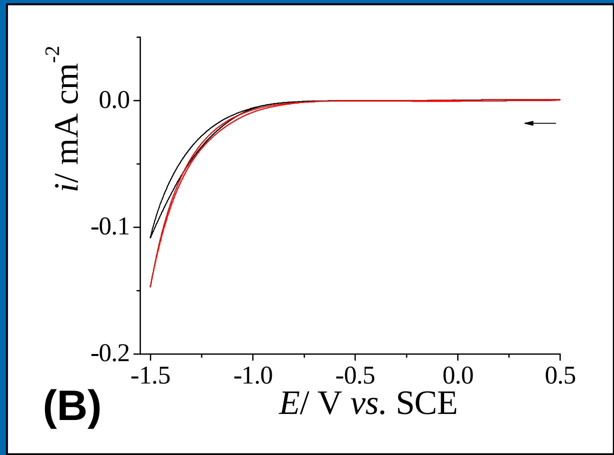
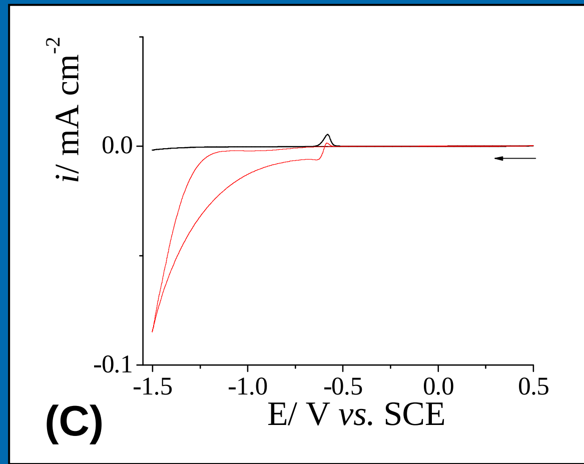
Catalytic reactivity of electro-deposited iron: Trichloroacetate anion reduction







Glassy carbon electrode without iron particles 20 mV s^{-1}

BDD electrode without iron particles 20 mV s^{-1}

BDD electrode 20 mV s^{-1}

__ 1M NH_4F

__ 5 mM TCA + 1M NH_4F

__ 1M NH4F + 10 µM Fe(III)

__ 1 mM TCA + 1M NH4F + 10 µM Fe(III)

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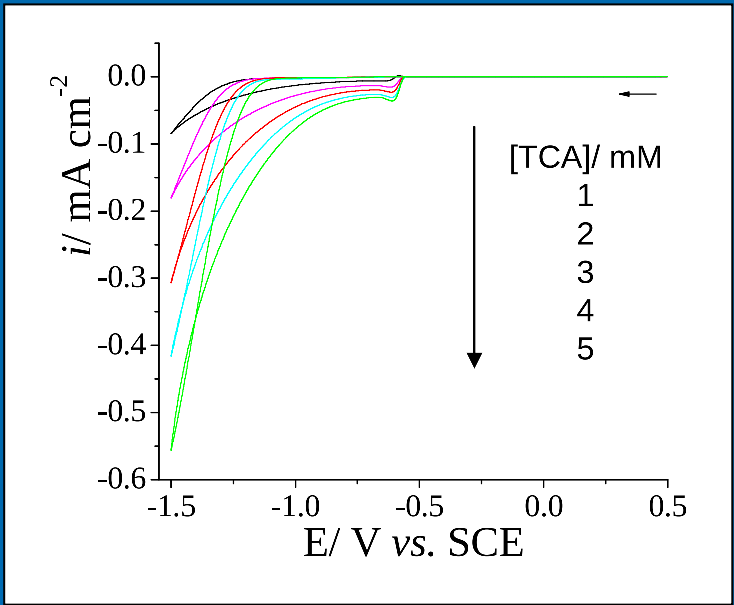
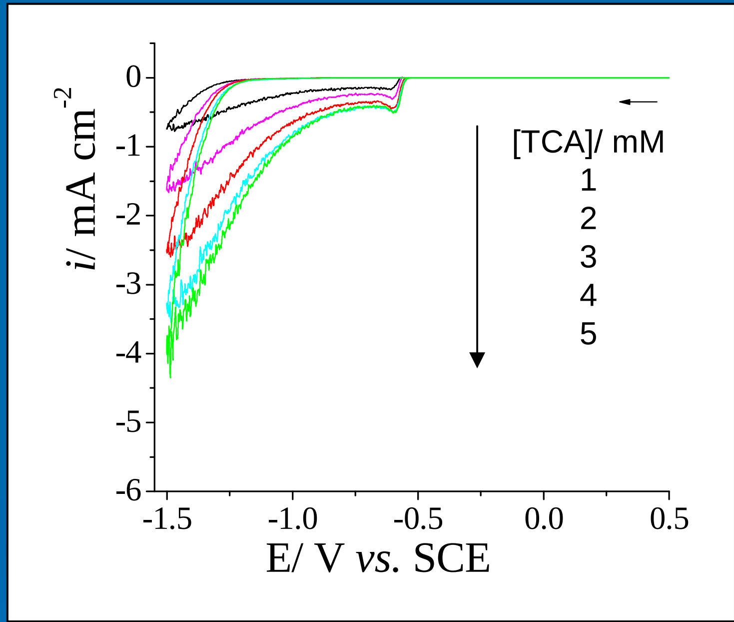
Catalytic reactivity of electro-deposited iron: Trichloroacetate reduction



Cyclic voltammograms for the reduction of trichloroacetate anion in 1M NH_4F + 10 μM Fe(III) at a BDD electrode ,20 mV s^{-1}



Cyclic voltammograms for the reduction of trichloroacetate anion in 1M NH_4F + 10 μM Fe(III) at a BDD electrode ,20 mV s^{-1}

With continuos 8 W cm-2 ultrasound, 5 mm horn to electrode distance

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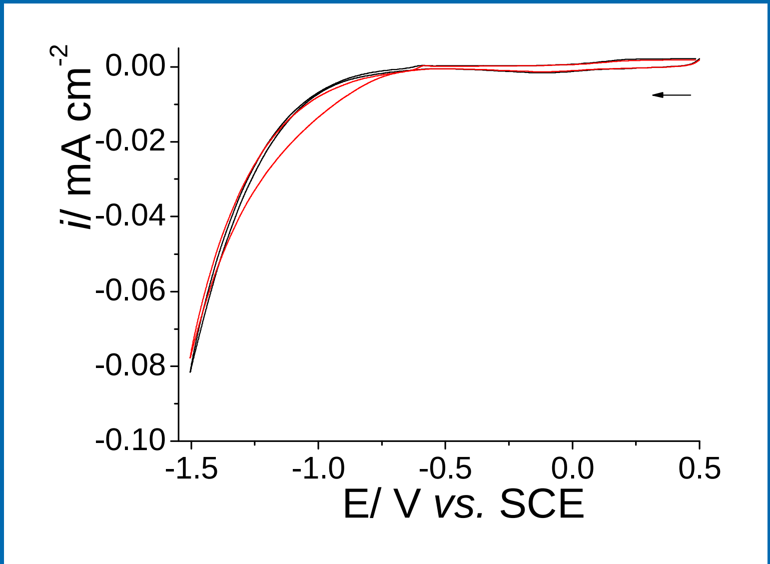
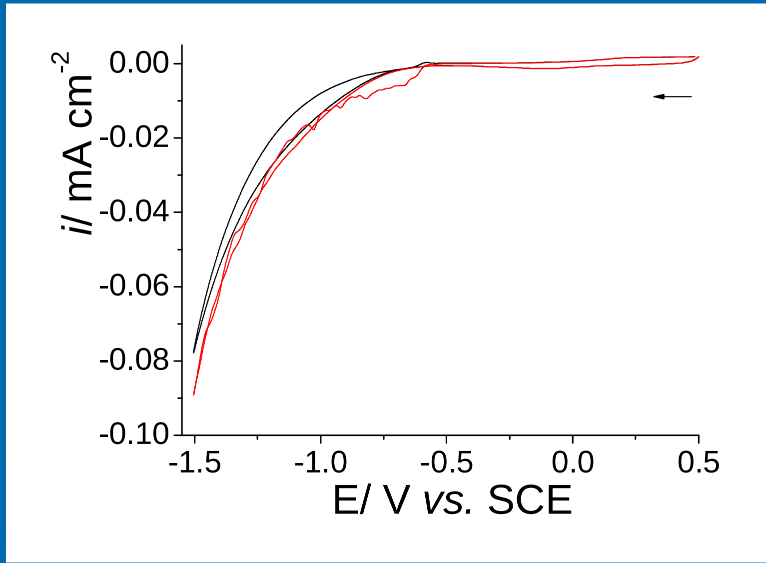
Catalytic reactivity of electro-deposited iron: Dichloroacetate reduction



BDD electrode
without iron particles
100 mV s^{-1}

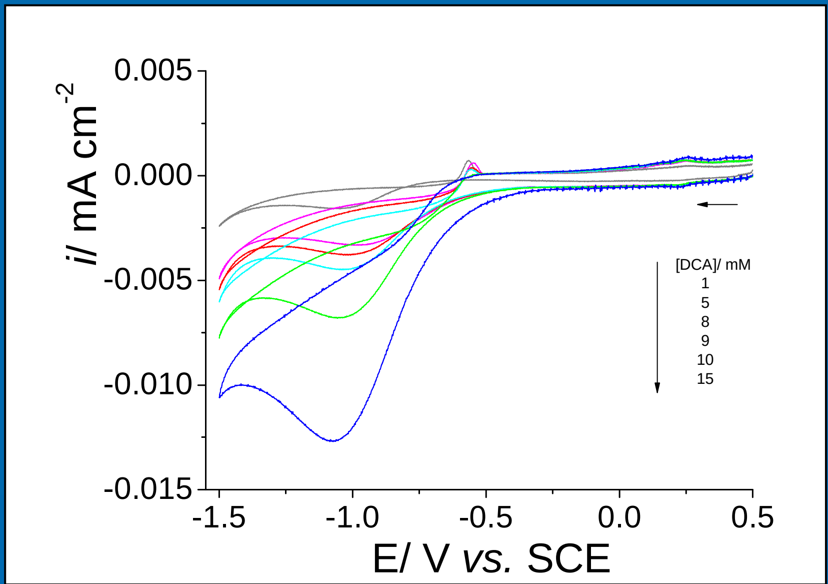
__ 1M NH_4F
__ 10 mM DCA + 1M NH_4F



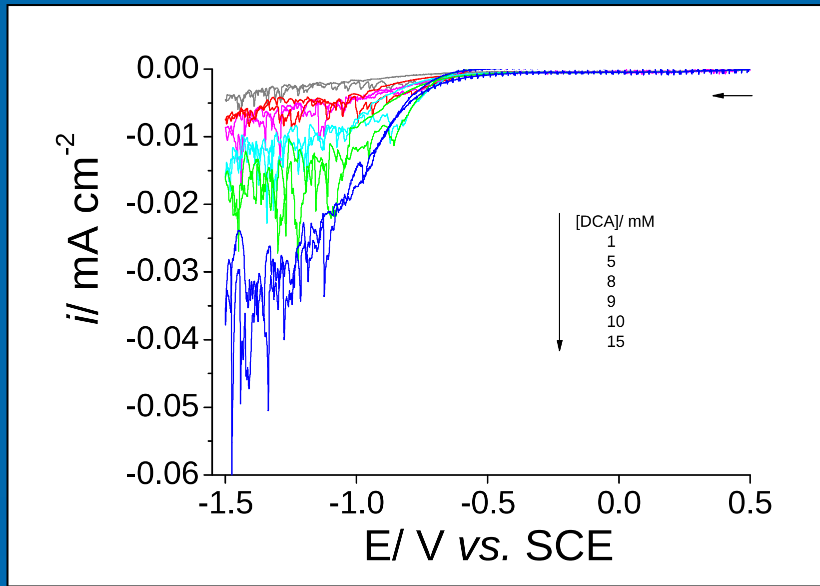
BDD electrode
without iron particles
100 mV s^{-1}
1M NH_4F + 10mM DCA

__ silent conditions
__ 8 W cm^{-2} ultrasound, 5 mm horn to electrode distance

Catalytic reactivity of electro-deposited iron: Dichloroacetate reduction



Cyclic voltammograms for the reduction of dichloroacetate anion in 1M NH_4F + 10 µM Fe(III) at a BDD electrode ,100 mV s^{-1}



Cyclic voltammograms for the reduction of dichloroacetate anion in 1M NH_4F + 10 µM Fe(III) at a BDD electrode ,20 mV s^{-1}

With continuos 8 W cm-2 ultrasound, 5 mm horn to electrode distance

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Conclusions

In this study it is demonstrated that the presence of fluoride in aqueous media allows both iron metal formation and iron stripping processes at BDD electrodes

The iron deposit has been demonstrated to provide electro-catalytic activity towards cathodic dehalogenation processes

Iron.. Is shown to act as an efficient electrocatalyst for the reduction of chloroacetate.

It has been shown conventional anodic stripping voltameetry with trace amounts of aqueous iron is possible and iron deposits at BDD electrodes are shown to be durable and catalytically active in electro-dehalogenation processes.

Further work

Mas trabajo con el di y el mono.. Estudiar el mecanismo de reduccion

Probar estos electrodos con otras moleculas de interes mediambiental (…)

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