

VOLTAMMETRIC/AMPEROMETRIC DETECTION OF SULFIDE IN SIMULATED SEAWATER USING BORON-DOPED DIAMOND AND CARBON NANOFIBER-EPOXY COMPOSITE ELECTRODES

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3rd regular meeting of the international team of the project

“HYDROGEN PRODUCTION FROM BLACK SEA WATER BY SULFIDE-DRIVEN FUEL CELL-HYSULFCEL

Outline

- Sulfide detection by electrochemical methods;
- Carbon-based electrode material for the electrochemical detection;
- Boron-doped diamond (BDD) and carbon nanofiber (CNF)-epoxy composite electrodes for sulfide detection.

Sulfide detection by electrochemical methods

- Potentiometry- Ag/Ag₂S ion-selective electrode;
- Voltammetry;
- Amperometry

Carbon-based electrode material for the electrochemical detection

Advantages:

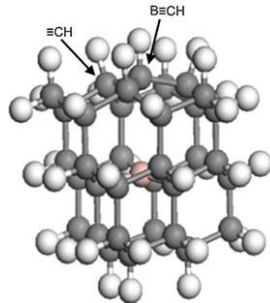
- good corrosion resistance;
- high electrical conductivity;
- low cost;
- wide potential window in aqueous solutions;

Disadvantages:

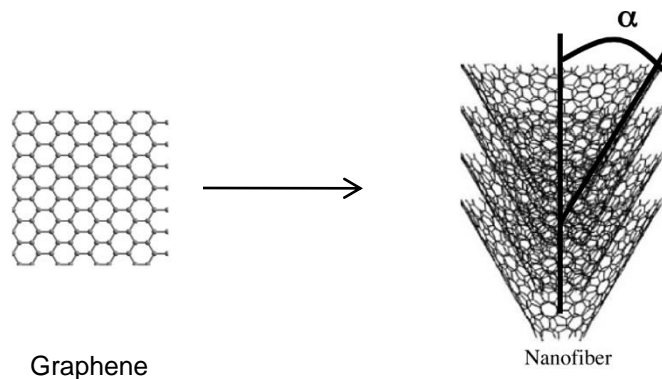
- low sensitivity;
- low selectivity;

Advanced carbon-based electrodes for electrochemical sensing

- Boron-doped diamond electrode- sp^3 -bonded carbon



- Carbon nanofiber-based electrode- sp^2 -bonded carbon with stacking shapes of graphene



Boron-doped diamond (BDD) and carbon nanofiber (CNF)-epoxy composite electrodes for sulfide detection

- Two types of carbon-based electrodes:
 - boron-doped diamond electrode (BDD)
 - carbon nanofiber-epoxy composite electrode (CNF)
- Electrochemical set-up:
 - Autolab potentiostat-galvanostat PGSTAT 302 (Eco Chemie, The Netherlands), controlled by a PC using the GPES 4.9
 - Classical three-electrode cell
- Electrochemical techniques:
 - Cyclic voltammetry;
 - Differential-pulsed voltammetry;
 - Chronoamperometry

Electrochemical behaviour of carbon-based electrodes in the presence of various sulfide concentrations

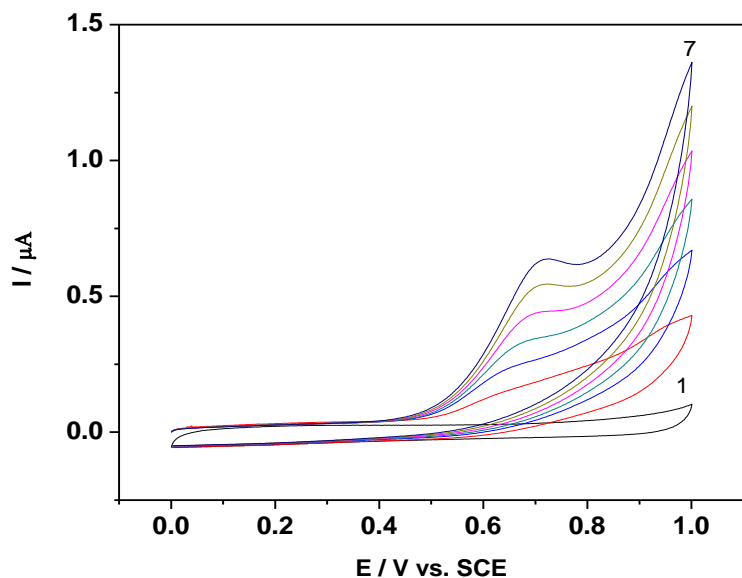


Fig. 1. Cyclic voltammograms recorded on BDD electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6 mM sulfide (curves 2-7); scan rate of 0.05 Vs^{-1} ; potential range: 0 to 1 V/SCE

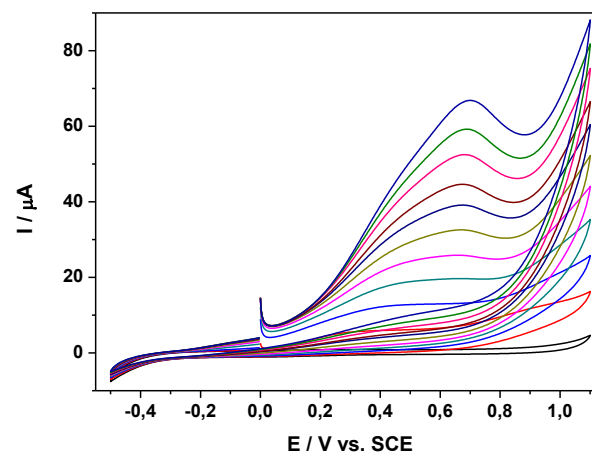


Fig. 2. Cyclic voltammograms recorded on CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte (curve 1) and in the presence of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6 mM sulfide (curves 2-7); scan rate of 0.05 Vs^{-1} ; potential range: 0 to 1 V/SCE

Calibration plots of the currents versus sulfide concentrations

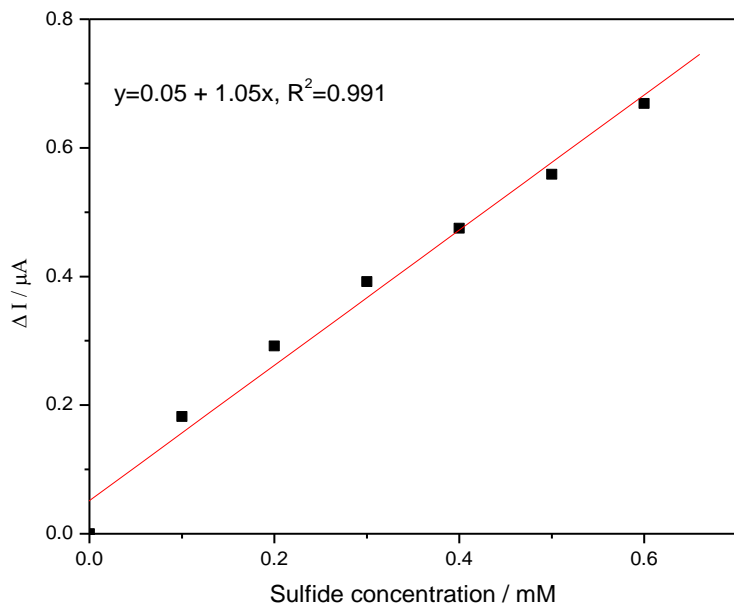


Fig. 3. The calibration plots of the currents corresponding to the sulfide anodic oxidation peaks recorded at +0.8 V/SCE with BDD electrode and the sulfide concentrations

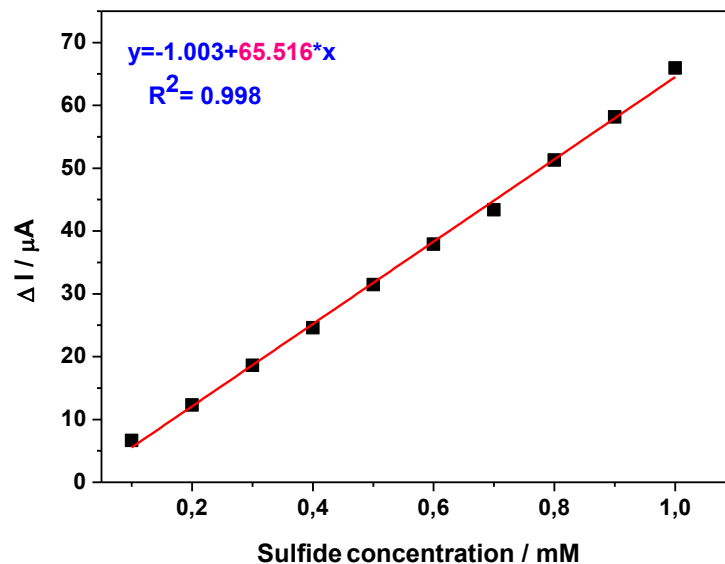


Fig. 4. The calibration plots of the currents corresponding to the sulfide anodic oxidation peaks recorded at +0.6 V/SCE with CNF electrode and the sulfide concentrations

Comparative electrochemical behaviour of carbon-based electrodes in different supporting electrolytes

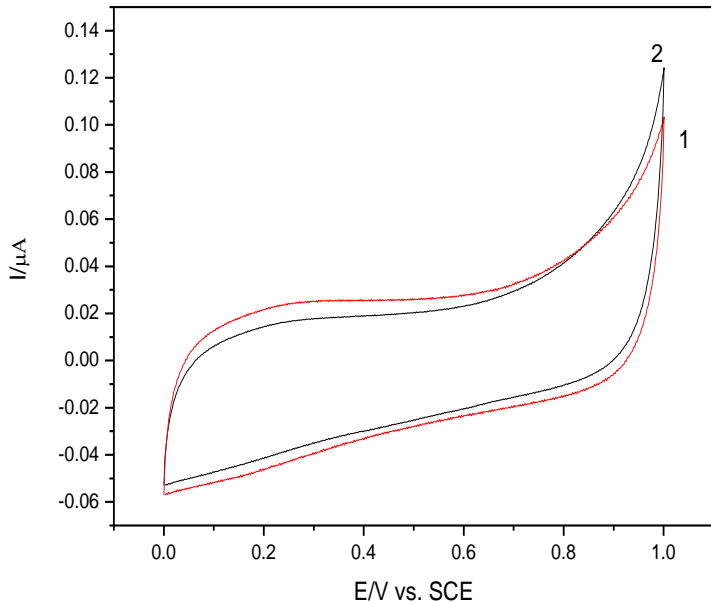


Fig. 5. Cyclic voltammograms recorded on BDD electrode in different supporting electrolyte: 1- 0.1 M Na_2SO_4 (curve 1) and 2- simulated seawater (curve 2)

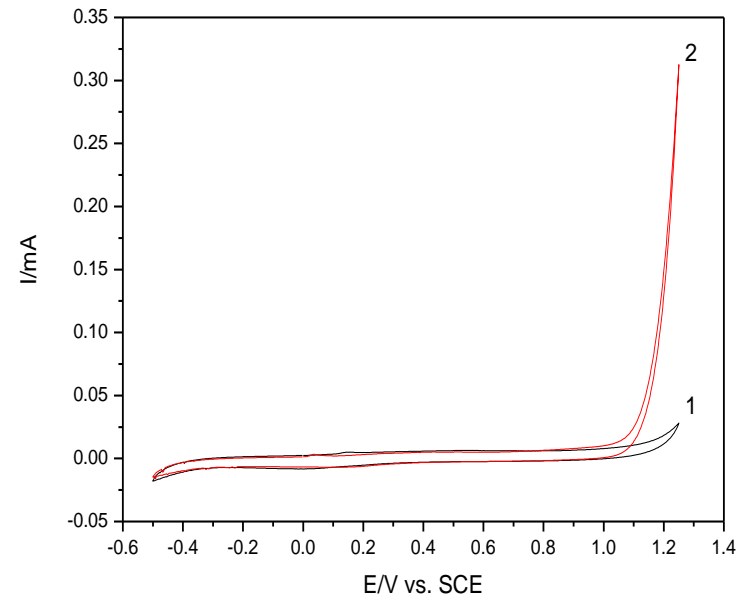


Fig. 6. Cyclic voltammograms recorded on BDD electrode in different supporting electrolyte: 1- 0.1 M Na_2SO_4 (curve 1) and 2- simulated seawater (curve 2)

Detection measurements in simulated seawater

Cyclic voltammetry

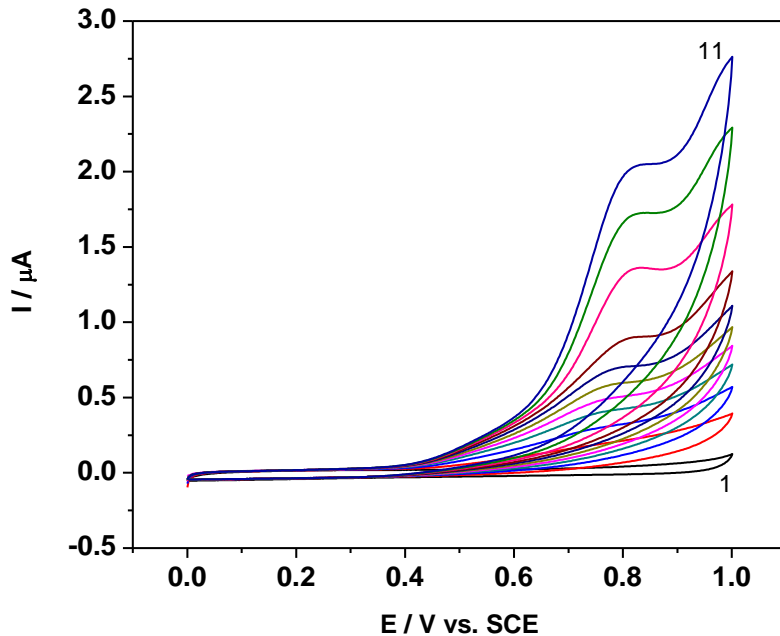


Fig. 7. Cyclic voltammograms recorded on BDD electrode in simulated seawater supporting electrolyte (curve 1) and in the presence of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1 mM sulfide (curves 2- 11); scan rate of 0.05 Vs⁻¹

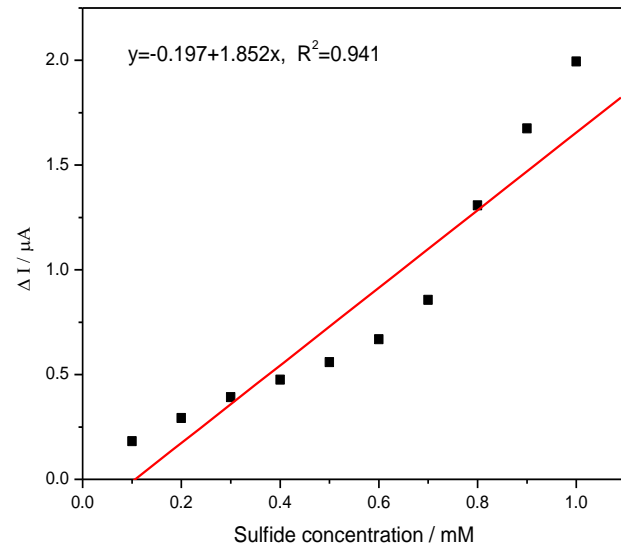


Fig. 8. The calibration plots of the currents corresponding to the sulfide anodic oxidation peaks recorded at +0.8 V/SCE and the sulfide concentrations

Detection measurements in simulated seawater

Cyclic voltammetry

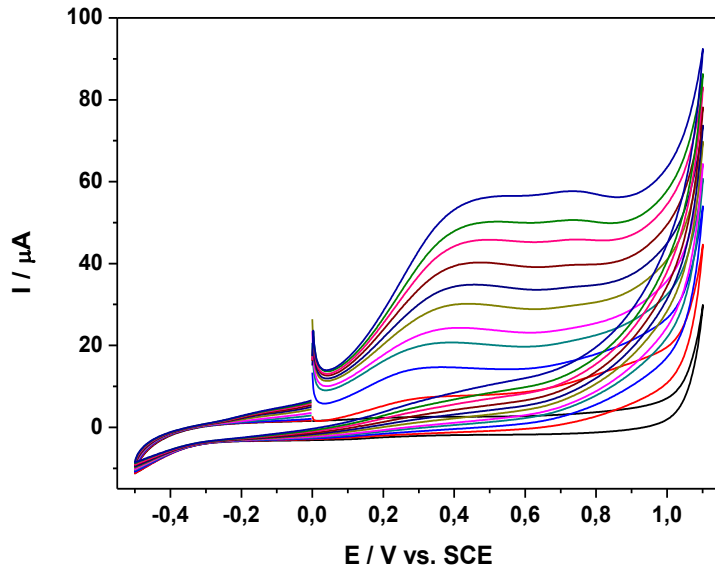


Fig. 9. Detail of cyclic voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte (curve 1) and in the presence of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1 mM sulfide (curves 2-11); scan rate of 0.05 Vs⁻¹.

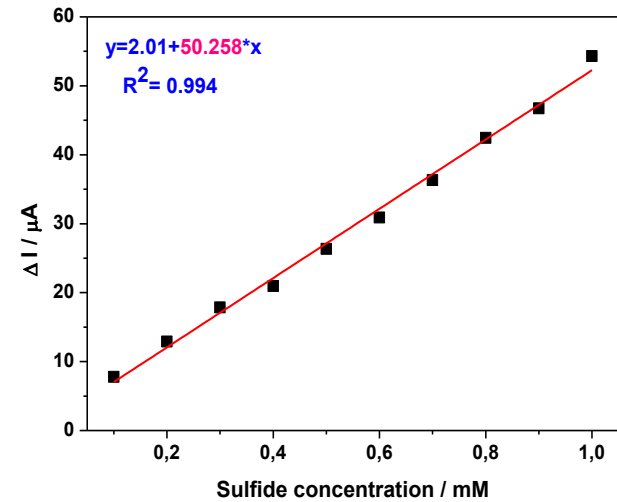


Fig. 10. The calibration plots of the currents corresponding to the sulfide anodic oxidation peaks recorded at +0.6 V/SCE and the sulfide concentrations

Detection measurements in simulated seawater

Differential-pulsed voltammetry (DPV)

Optimization of the DPV operating conditions

The dependence of the sensitivity on the operating DPV parameters:
modulation amplitude (**a**), step potential (ΔE_s) and scan rate (**v**)

a (V)	ΔE_s (V)	v(Vs ⁻¹)	E _{detection} /V	Sensitivity(μA/ mM)
0.05	0.01	0.05	0.7	15.66
0.1	0.01	0.05	0.66	32.50
0.1	0.02	0.05	0.66	35.84
0.2	0.02	0.1	0.15	75.86
0.2	0.05	0.05	0.15	78.19

Detection measurements in simulated seawater

Differential-pulsed voltammetry

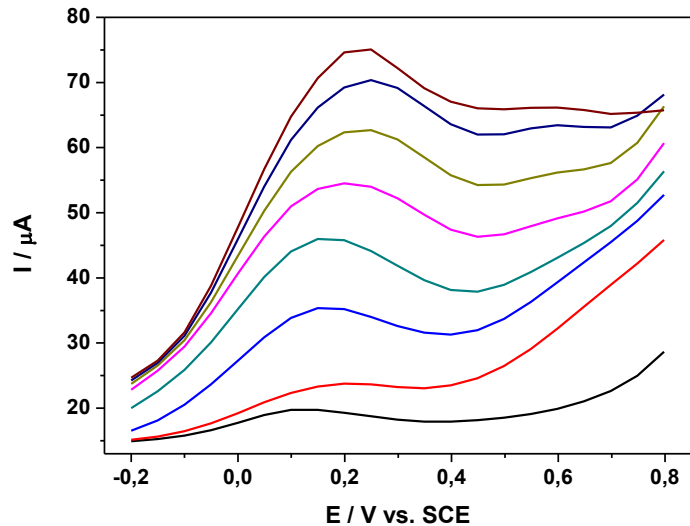


Fig. 11. Differential-pulsed voltammograms recorded on CNF electrode in simulated supporting electrolyte (curve 1) and in the presence of 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1 mM sulfide (curves 2-11); scan rate of 0.05 Vs⁻¹.

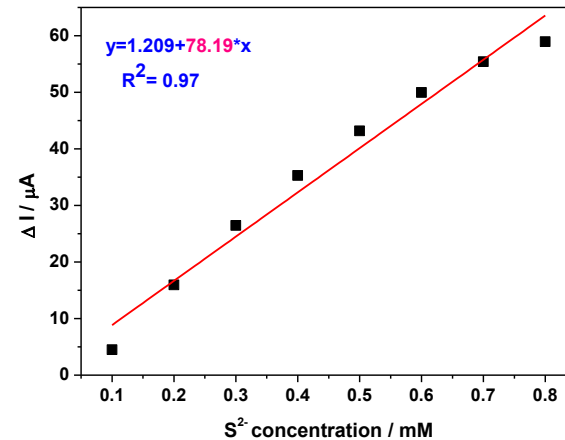


Fig. 12. The calibration plots of the currents corresponding to the sulfide anodic oxidation peaks recorded at +0.15 V/SCE and the sulfide concentrations

Detection measurements in simulated seawater

Chronoamperometry

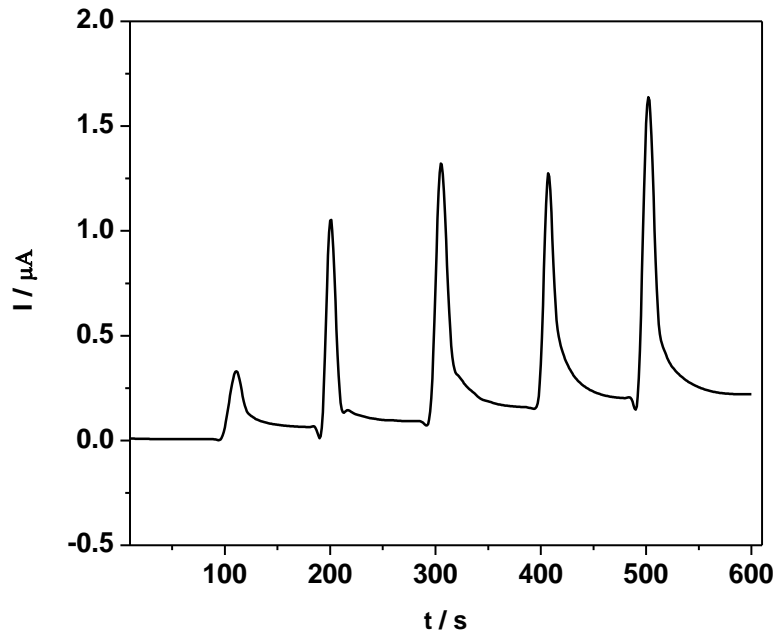


Fig. 13. Chronoamperograms recorded on BDD electrode in simulated seawater and in the presence of continuous 0.2 mM sulfide adding

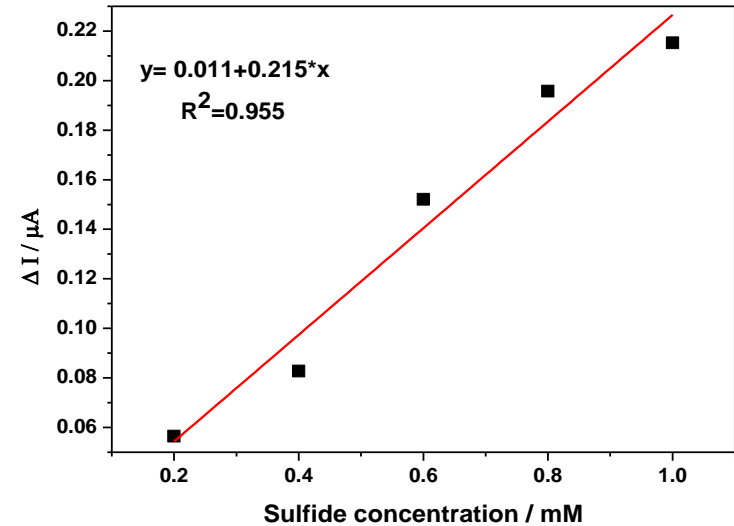


Fig. 14. The calibration plots of the currents corresponding to each sulfide concentration adding recorded at +1 V/SCE and the sulfide concentrations

Detection measurements in simulated seawater

Chronoamperometry

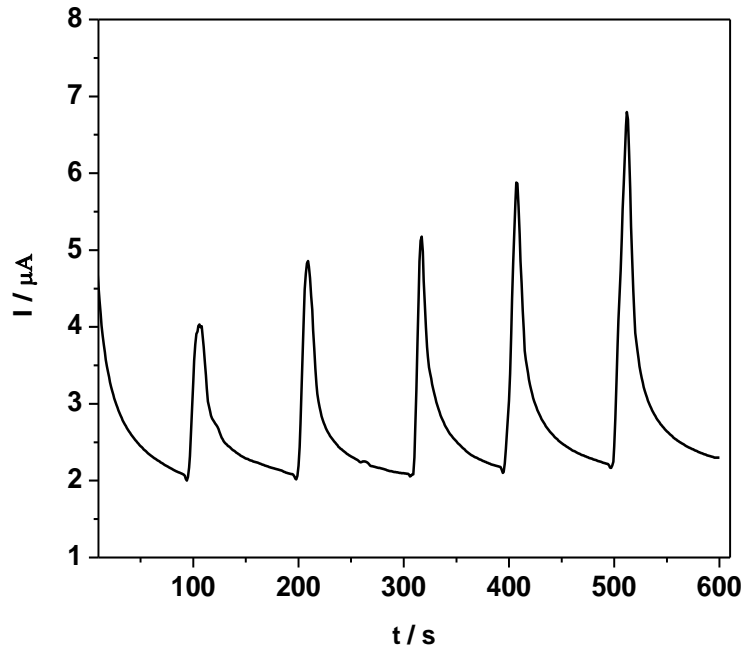


Fig. 15. Chronoamperograms recorded on CNF electrode in simulated seawater and in the presence of continuous 0.2 mM sulfide adding

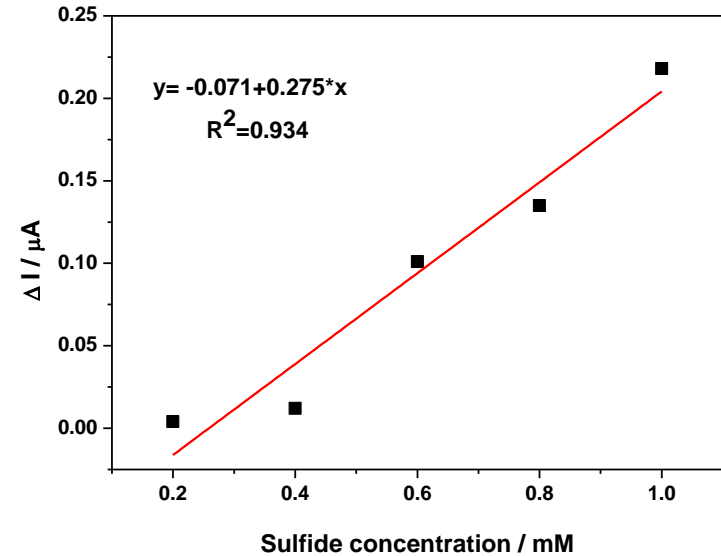


Fig. 16. The calibration plots of the currents corresponding to each sulfide concentration adding recorded at +1 V/SCE and the sulfide concentrations

The electroanalytical parameters for sulfide detection using BDD and CNF-composite electrodes

Technique	Electrode	Electrolyte	E / V vs. SCE	Sensitivity($\mu\text{A}/\text{mM}$)	R ²
CV	BDD	0.1M Na ₂ SO ₄	0.8	0.848	0.999 0.999
		Simulated seawater	0.8	1.852	0.941 0.979
	CNF	0.1M Na ₂ SO ₄	6	65.52	0.991
		Simulated seawater	0.6	50.26	0.990
DPV	CNF	Simulated seawater	0.15	78.19	0.970
CA	BDD	Simulated seawater	1.00	0.215	0.955
	CNF	Simulated seawater	1.00	0.275	0.934

Conclusions

- Both boron-doped diamond (BDD) and carbon nanofiber-composite (CNF) electrodes exhibited the suitable electrochemical features for the direct voltammetric/amperometric detection of sulfide in simulated seawater without chloride interference;
- Carbon nanofiber composite electrode allowed achieving better sensitivity in comparison with boron-doped diamond electrode using cyclic voltammetry, while chronoamperometry technique led to almost similar sensitivities, much lower in comparison with CV;
- Differential-pulsed voltammetry allowed achieving the best electroanalytical parameters related to sensitivity and the detection potential (0.15 V vs. 0.7V for CV);
- These results informed about the real utility potential of both electrodes for sulfide detection in seawater.

THANK YOU FOR YOUR ATTENTION!