

SIMULTANEOUS DETECTION OF OXYGEN AND HYDROGEN PEROXIDE ON FLUORINE DOPED TIN OXIDE ELECTRODES

ELECTROCHEMICAL CHARACTERIZATION OF OXYGEN AND HYDROGEN PEROXIDE

Tomasz Swebocki¹, Daniel Firganek¹, Karolina Dziąbowska¹, Żaneta Kłostowska², Anna Wcisło¹, Tadeusz Ossowski¹

¹University of Gdansk, Faculty of Chemistry,
Department of Analytical Chemistry, Laboratory of Supramolecular Chemistry
63 Wita Stwosza St., 80-308, Gdansk, Poland

²Polish Academy of Sciences, Institute of Oceanology,
Department of Marine Chemistry and Biochemistry, Laboratory of Marine Biochemistry
55 Powstańców Warszawy St., 81-712, Sopot, Poland

tomasz.swebocki@etoh.chem.univ.gda.pl



INTRODUCTION TO RESEARCH

Hydrogen peroxide is an unstable oxidizer that occurs naturally in the marine environment. In surface ocean waters, H₂O₂ concentration oscillate from 10⁻² to 10⁻¹ mM. Its transient character in sea water is determined mainly by the protonation of the superoxide anionic radical (O₂^{•-}), and the disproportionation of the hydroperoxyl radical (HO₂[•]).

Apart from the H₂O₂ present and generated in the marine environment, it is used in aquaculture in higher concentrations. There is a lot of data on the use of this compound in the fish farming industry. It is an agent against various groups of pathogenic organisms, mainly outer parasites, bacteria and fungi. However, despite the rapid decomposition of hydrogen peroxide in the presence of organic material and aeration, concentration values and toxicity to fish are determined by the sensitivity of a given species.

The methodology for determining the concentration of H₂O₂ covers: photometric-DPD method, colorimetric method, iodometric techniques, luminol chemiluminescence, and more.

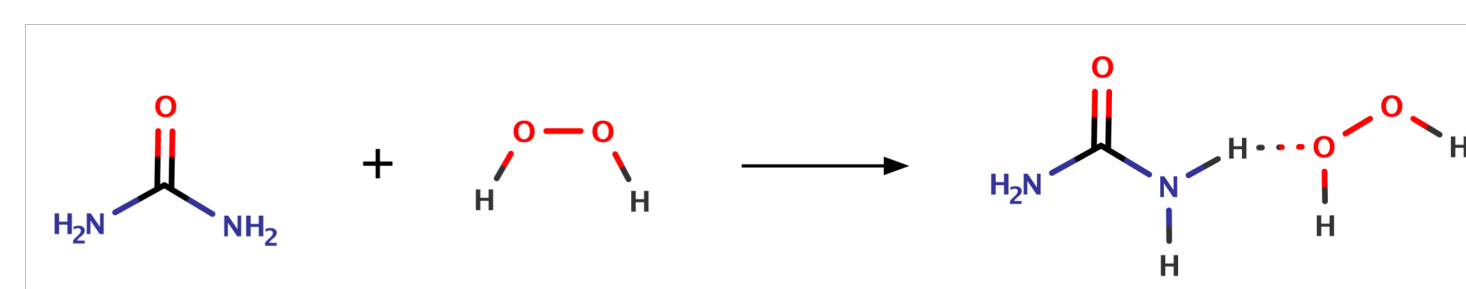


Fig. 1 The synthesis of H₂O₂-urea complex

Cyclic voltammetry (CV) was implemented to inspect the redox processes of investigated compounds. All measurements were carried out by using M204 potentiostat (Metrohm, NL). The system consisted of non-modified glass printed FTO electrode (WE), silver chloride electrode (RE) and glassy-carbon electrode (CE). Supporting electrolyte was 0,5M (ca. 28 PSU) sodium chloride (NaCl).

CV was carried out with: V=100mV/s and step +0,003V

MEASUREMENTS

Recent needs of fish farming industry require new techniques that would allow to carry out *in situ* measurements of hydrogen peroxide and oxygen simultaneously. Following studies focused on construction of sensor capable of detection of both molecules separately. First step of our research focuses on choosing the right electrode material.

Stable H₂O₂ was added to the system in form of H₂O₂-urea complex (pur. 99%). Oxygen was provided directly from gas cylinder (pur. 99,99%). Synthesis of H₂O₂-urea complex is carried out by dissolving urea in 30% hydrogen peroxide in molar ratio of 3:2 in temperature of 50°C. White flakes of complex participate on colling and are not a subject of further purification.

The obtained complex is one of the most stable well dissolving complex of H₂O₂. Urea is not electrochemically active on FTO electrodes, thus the complex is a good source of hydrogen peroxide for electrochemical measurements.

RESULTS

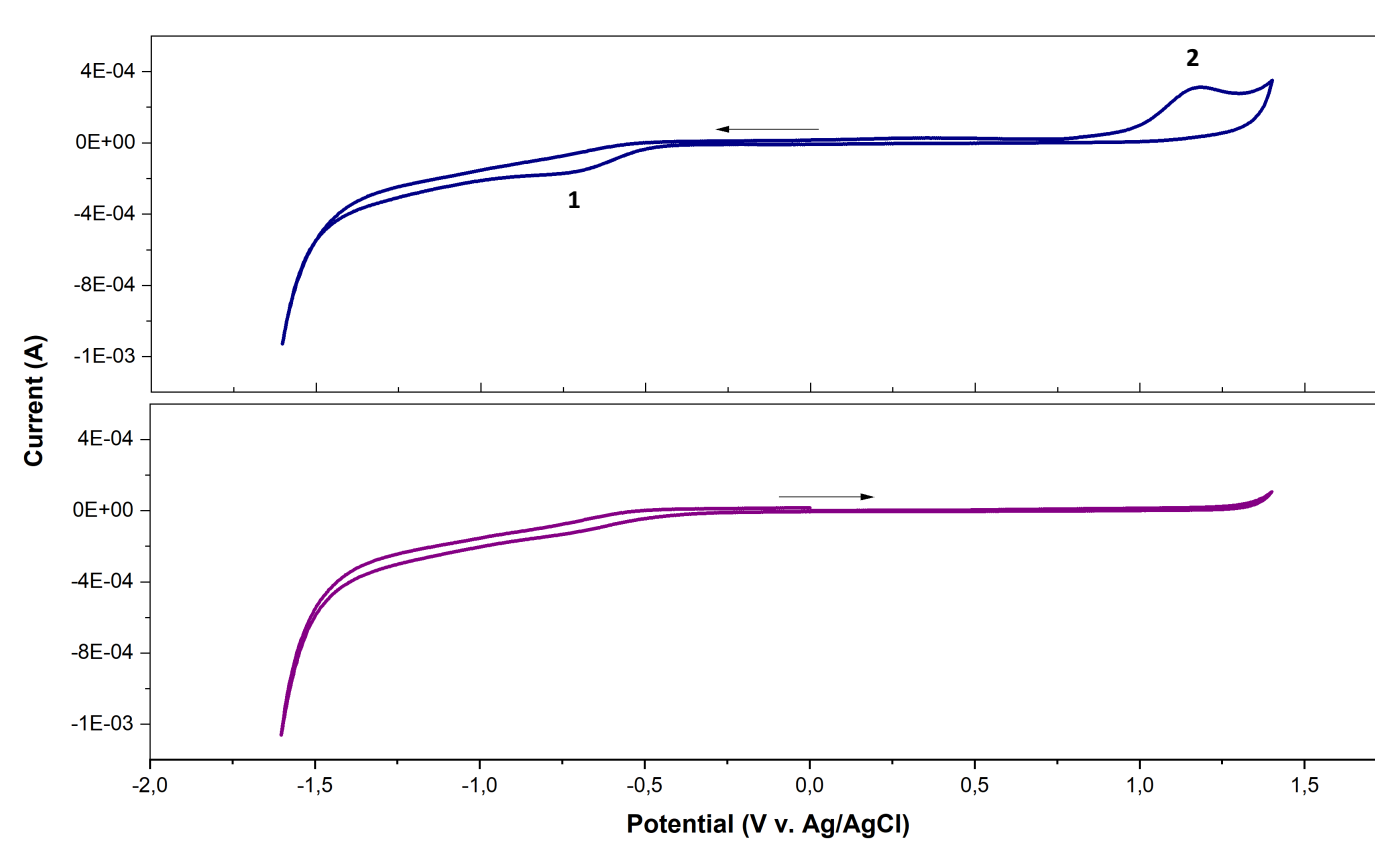
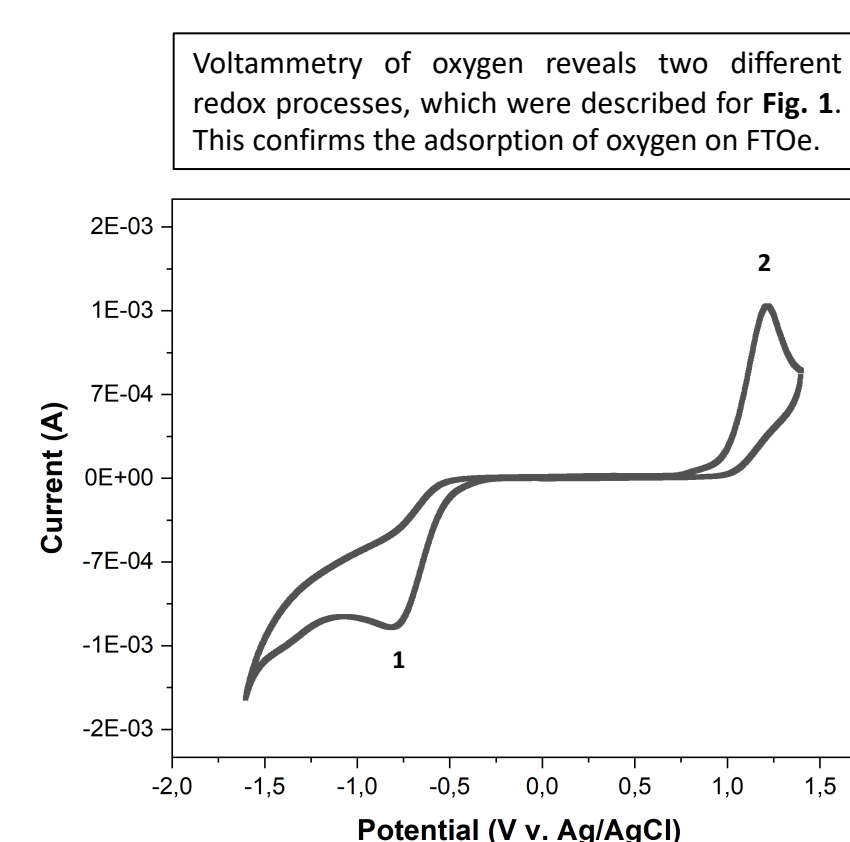


Fig. 2 Electrochemical window of FTOs, beginning with: cathodic scan (upper) and anodic scan (bottom)



Voltammetry of oxygen reveals two different redox processes, which were described for Fig. 1. This confirms the adsorption of oxygen on FTOs.

Fig. 3 Cyclic voltammetry of oxygen on FTOs

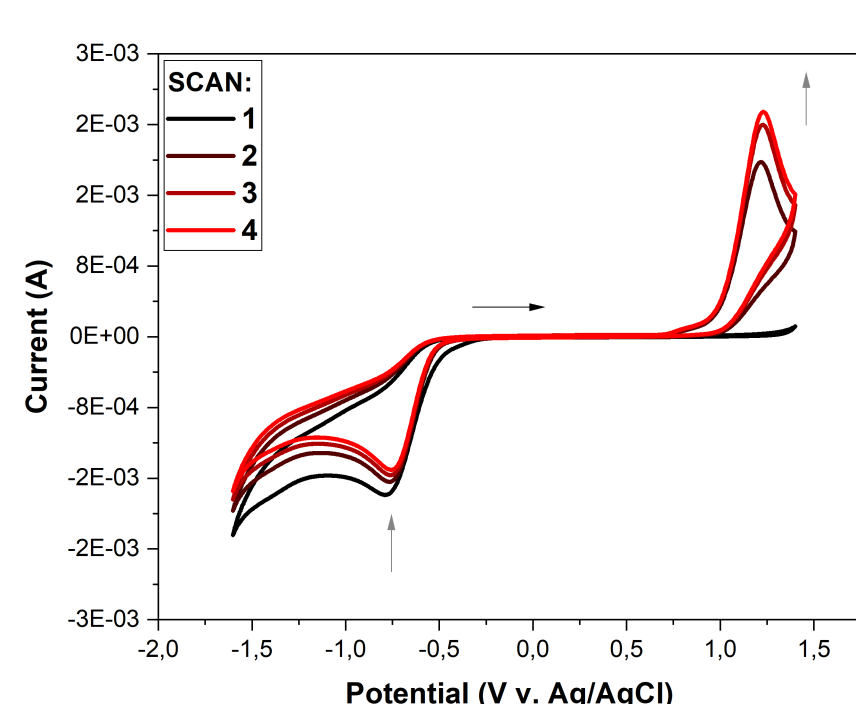


Fig. 4 Cyclic voltammograms of oxygen on FTOs (4 scans)

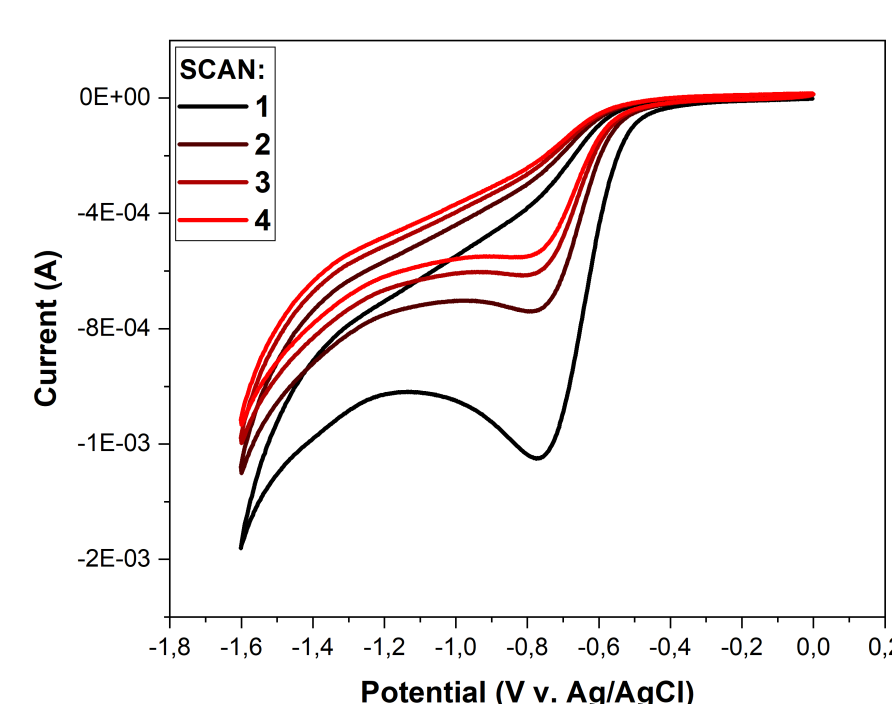


Fig. 5 Cathodic scans of oxygen on FTOs (4 scans)

The decrease of cathodic current and increase of anodic current of peaks were observed with increasing number of scans (Fig. 2 and Fig. 3). Thus pointing towards the equilibrium of two reactions.

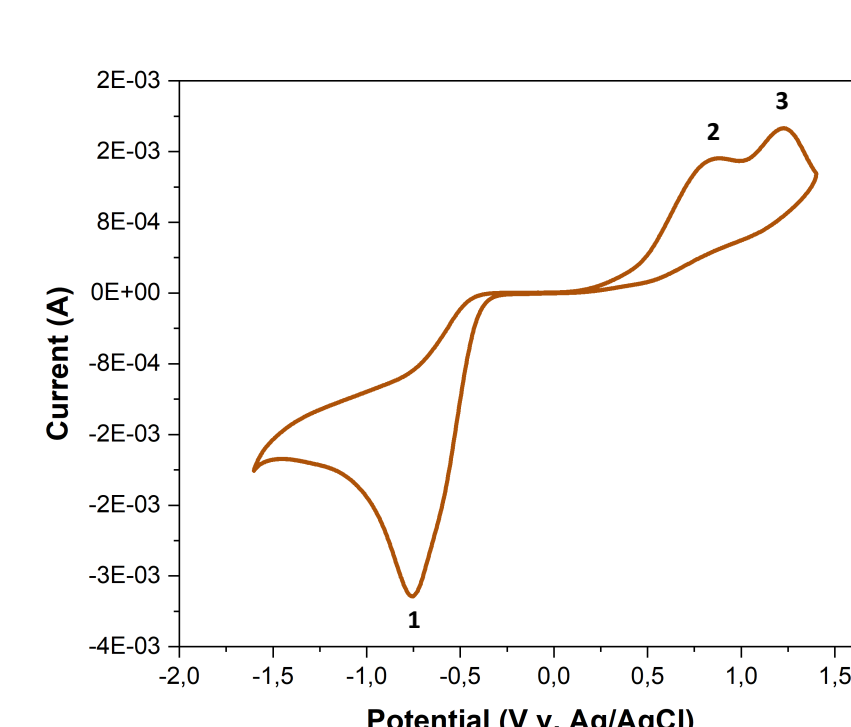


Fig. 6 Cyclic voltammogram of hydrogen peroxide (244ppm) on FTOs

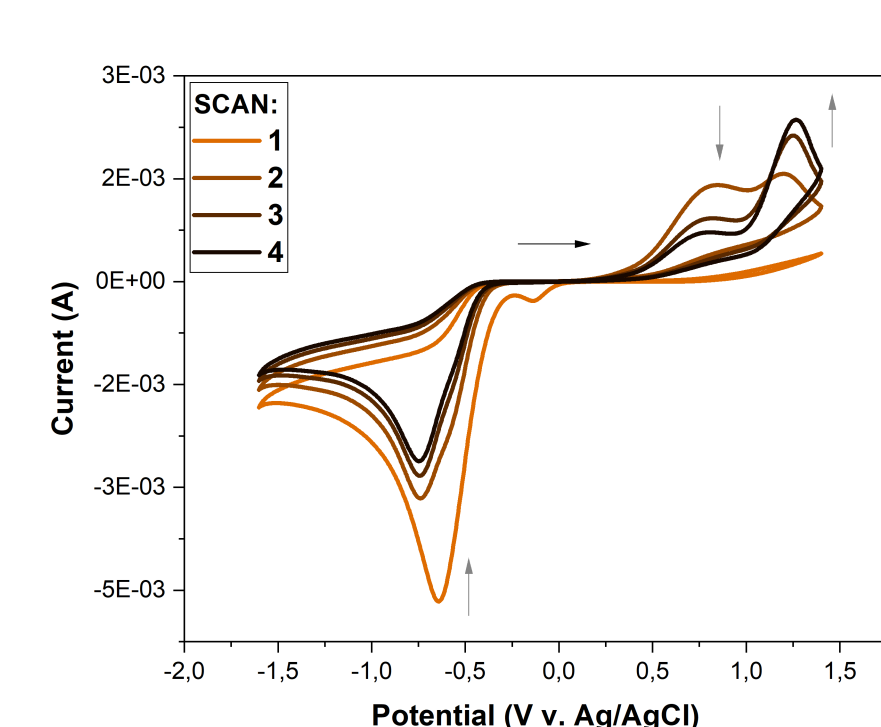


Fig. 7 Cyclic voltammograms of hydrogen peroxide (244ppm) on FTOs (4 scans)

Voltammogram of H₂O₂ reveals three peaks (Fig. 6). Two corresponding to oxidation at E=+0,75V (2) and E=+1,48V (3) and one peak of reduction at E=-0,72V (1). Same as for oxygen with following scans the change in currents occurs (Fig. 7). The decrease of (1) and (2) with increase of currents for (3).

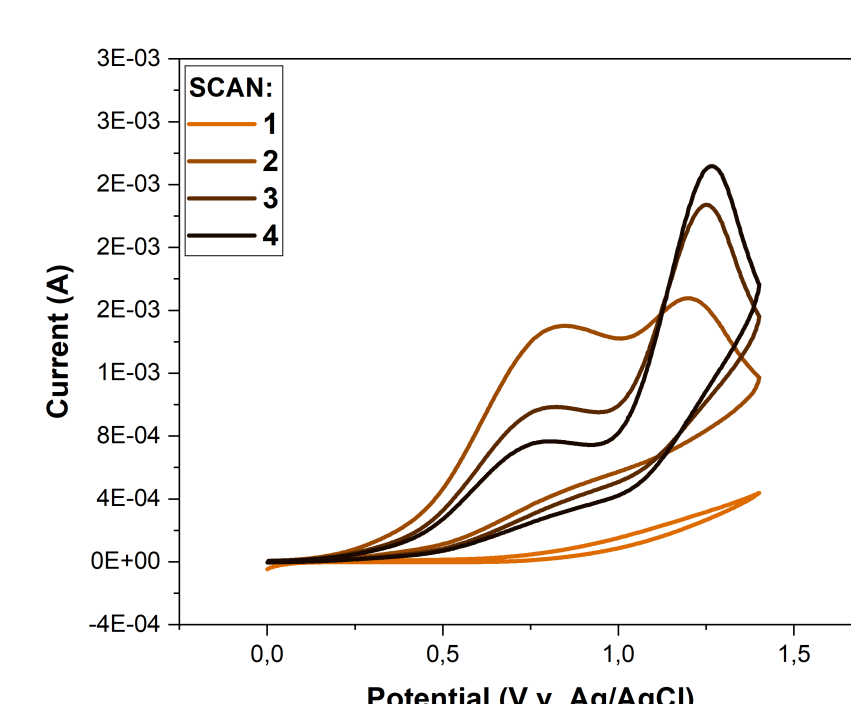


Fig. 8 Anodic scans of hydrogen peroxide on FTOs (4scans)

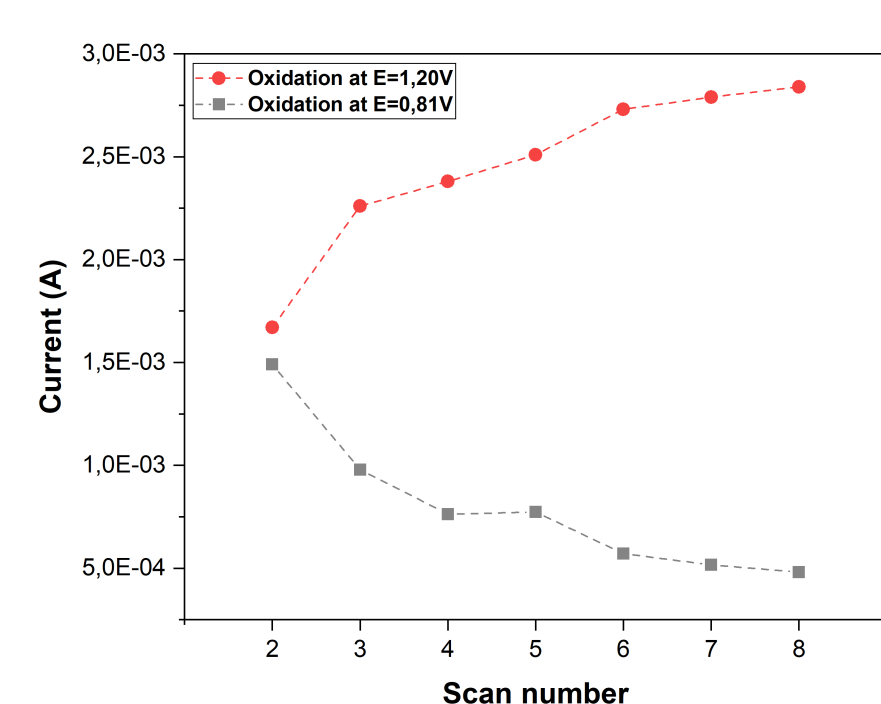


Fig. 9 Current changes of oxidation peaks of hydrogen peroxide on FTOs

After studying the oxidation processes (Fig. 8, Fig. 9) the correlation of (2) and (3) was found. The decrease of (2) caused currents of (3) to increase at almost same proportion. This points towards second equilibrium that may lead to potential correlation of whole process of H₂O₂ and O₂ redox activity.

SURFACE REUSABILITY

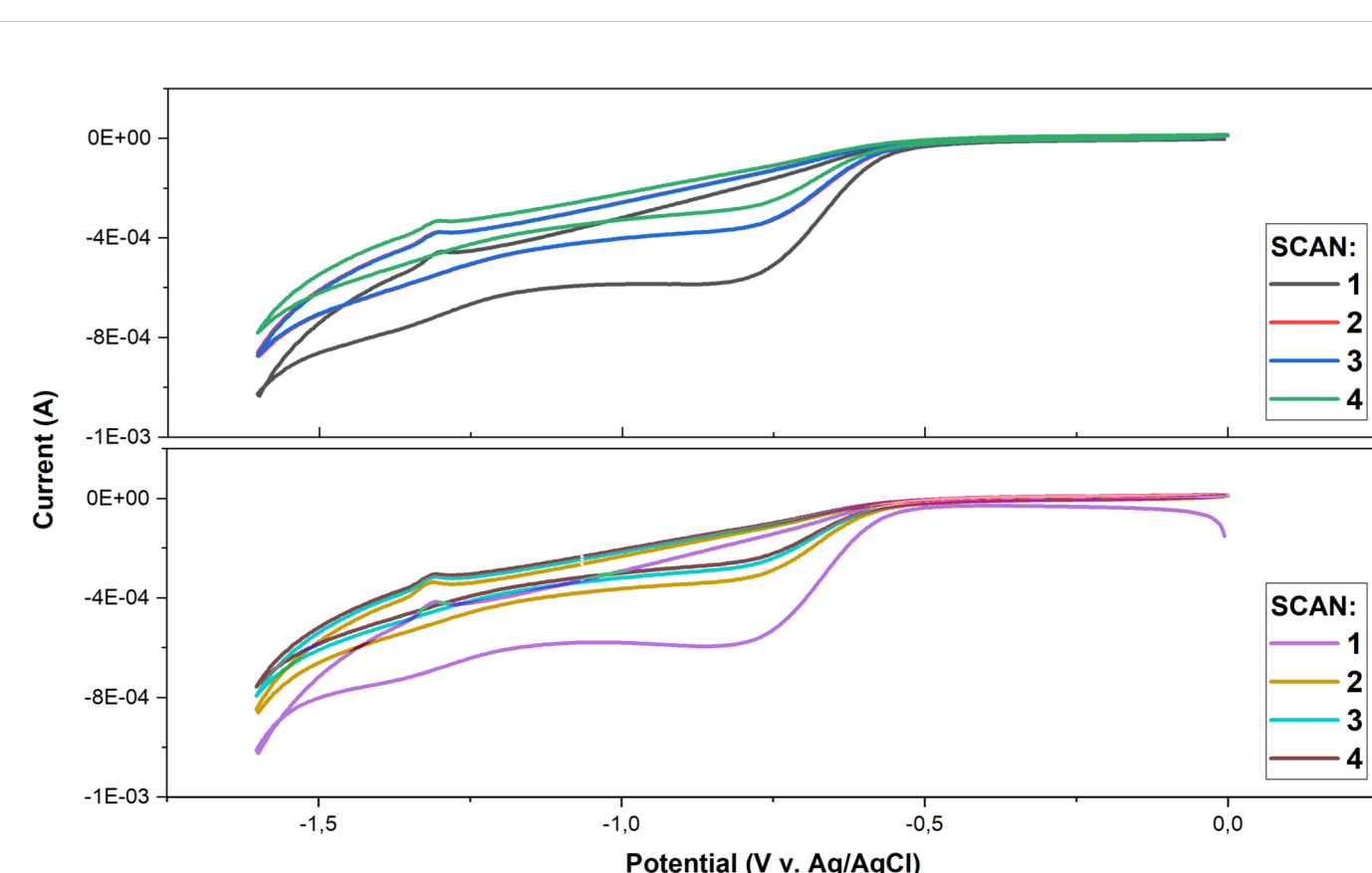


Fig. 10 Cathodic voltammograms of oxygen on FTOs before conditioning (top) and after conditioning in +1,4V (below).

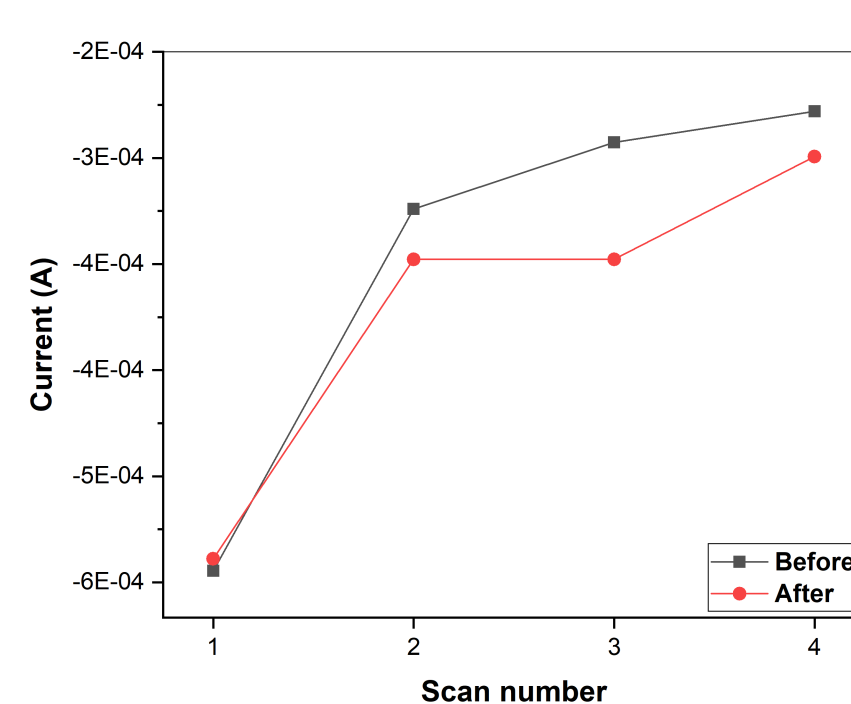


Fig. 11 Current changes of reduction peak of oxygen before and after conditioning at 1,4V

CONCLUSIONS AND FURTHER RESEARCH

- FTO electrodes are capable of sensing both oxygen and hydrogen peroxide
- Fluorine doped tin oxide electrodes adsorb the oxygen
- In order to restore the surface after sensing the oxygen conditioning at +1,4V shall be applied
- Further investigation towards redox mechanisms shall be done in order to describe the reactions on the surface of electrode
- We would like to perform the analysis in buffered solutions in range of pH 2-6

Bibliography

1. N. Lane, *Oxygen: the molecule that made the world*, Oxford University Press, Oxford, 2003, 117
2. D.T. Sawyer, *Oxygen Chemistry*, Oxford University Press, Oxford, 1991, 19-50
3. Y. Saygi, *The Israeli Journal of Aquaculture*, 2003, 55 (2), 107-113
4. S.A. Rusak et al., 2011, *Mar. Chem.*, 127 (1-4), 155-169
5. F. Terzi et al., 2016, *Electrochim. Acta*, 188, 327-335
6. W.J. Cooper et al., 2000, *Mar. Chem.*, 70 (1-3), 191-200
7. G.B. Avery et al., 2005, *Mar. Chem.*, 97 (3-4), 236-244



Acknowledgements

All the drawings were done using MarvinSketch by ChemAxon