

Study of Electrochemical Generation of Hydroxyl Radicals on Ti/SnO₂-Sb₂O₅ Anode by Spin-Trapping

Q.Ni¹, D.W.Kirk¹, S.J.Thorpe²

¹Dept. Chemical Engineering & Applied Chemistry
University of Toronto
200 College Street, Toronto, ON Canada M5S 3E5

²Dept. Materials Science & Engineering
University of Toronto
184 College Street, Toronto, ON Canada M5S 3E4

Introduction

Electro-oxidation was proposed as a possible technique to treat municipal wastewater containing organic compounds and pathogens. The process economy relies on decreasing the energy consumption, which is significantly affected by catalysis at the anode. The electro-catalysis of the oxidation was believed to involve the highly active hydroxyl radical, (OH·), generated from the electrolysis of water (1). In the presence of organic compounds, (OH·) can completely oxidize them to CO₂ and H₂O. Otherwise, it can be further oxidized to produce O₂. The competition between these two reactions is a major factor that determines the current efficiency in the electrochemical treatment of wastewater. Under this schematic, the difference in efficiency between different anodes can be explained by classifying the anodes as “active” or “inactive”. For example, electrodes made with platinum group metals often exhibit low efficiency because they are efficient O₂ evolution. Boron-doped diamond (BDD) has shown efficient degradation of organics, because it is “inactive”. In addition to this, Zhu’s group has proposed another theory to account for the differences between the anodes under the “inactive” category (2). The theory states hydroxyl radicals can leave the anode surface and react in the bulk electrolyte, and this promotes the oxidation kinetics. Such is the case of BDD.

The antimony-doped tin oxide (Ti/SnO₂-Sb₂O₅) is an “inactive” anode which was found to be suitable for wastewater treatment. It has modest efficiency, but compared to BDD, it is easier to fabricate and install, in a way similar to the widely used Dimensionally Stable Anode (DSA). To improve its efficiency, it is necessary to understand the relation between its surface structure and chemistry in the production and activity of hydroxyl radicals.

Due to the short life of the (OH·), it is often very difficult to study it directly. Therefore a spin-trapping compound can be used. N,N-dimethyl-*p*-nitrosoaniline (RNO) is a compound that selectively binds to the hydroxyl radical (1). It is used for this study to gain a closer understanding of the processes.

Experiments and Results

First, linear voltammetric scans were performed with 1mM of RNO. The voltammogram is shown in Figure 1. Two major peaks were found. There is a small peak at 0.5V, which may be the re-oxidation of the reduced RNO at lower voltages. There is another reaction with an onset potential of 0.9V. The slope of this was found to be 104mV/decade. Applying this to Butler-Volmer equation, the charge transfer coefficient was

found to be 0.567, probably indicating a single-electron transfer reaction.

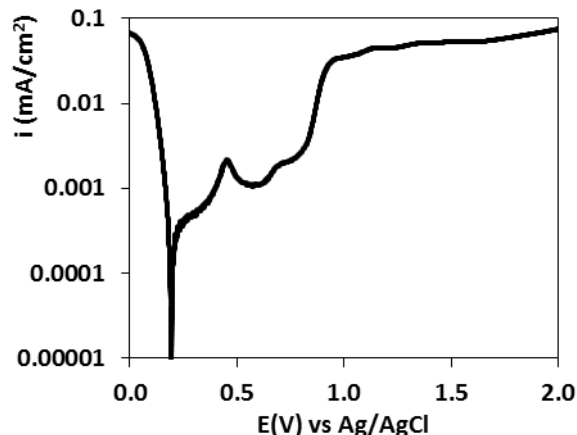


Figure 1. The voltammetry (1mV/s) curve in 1mM RNO. Supporting Electrolyte: 0.1M Na₂SO₄ and 0.01M H₂SO₄

Cyclic voltammetry was also performed. The voltammograms were taken after 5 cycles so that it represents a reasonably steady-state. The results in Figure 2 showed that the first peak near 0.5V was reversible while the other at 0.9V was only partially reversible.

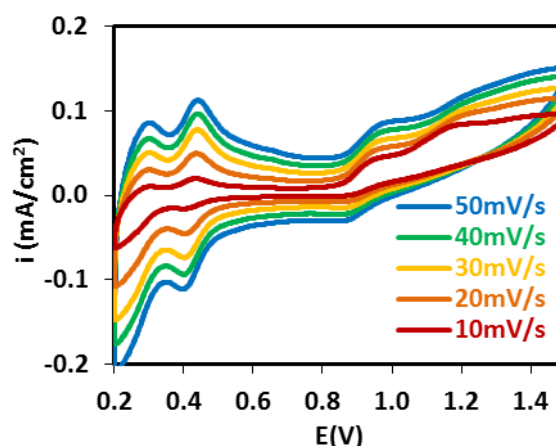
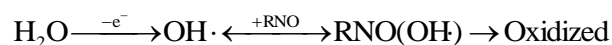


Figure 2. The CV in the presence of 1mM RNO

Based on the observations, a possible reaction pathway can be postulated as follows. Hydroxyl radicals bind to the spin trap, and this binding is reversible. However, (OH·) can oxidize RNO due to its strong mineralization power.



Summary and Further Work

In this work, the response of RNO towards the electrochemically generated hydroxyl radical was studied. Ongoing work is focusing on the kinetic model of OH· generation and destruction, and how the surface structure and chemistry of the Ti/SnO₂-Sb₂O₅ anode affects its reactions.

This work was supported by University of Toronto, with the funding source from Xogen Technologies Inc, OCE, SDTC and NSERC.

References

1. Ch. Cominellis, *Electrochim. Act.*, **39**, 1857 (1994)
2. X. Zhu, et al, *Env. Sci. Tech.*, **42**, 4914 (2008)