Electrochemical Chloride behavior at Ti/SnO_2-IrO_2-Sb_2O_3 electrode

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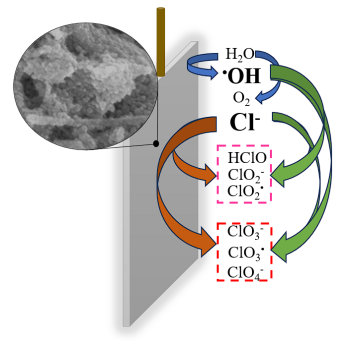

This research assesses the effect of chloride concentration at different pH during the electrolysis of the aqueous medium using a DSA electrode (IrO_2-SnO_2-Sb_2O_3). The elemental and morphological characterization of DSA electrode was performed by Energy-dispersive X-Ray spectroscopy (EDS) and scanning electron microscopy (SEM), respectively, while its electrochemical properties were obtained by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV and EIS overcomes were used to study the effects of chlorides in solutions at pH 2, 6 and 13 with concentrations between 10^{-4} and 2 M of chloride. The results reveal that specific active chlorine species are produced under different experimental conditions, intensifying the oxidation power of the solution. Chlorine species were identified and quantified by Mohr volumetric method and ion chromatography.

Introduction

Chlorine is a versatile chemical substance with the highest supply-demand in the commercial and industrial sector. Its market is substantially involved in the manufacture of polymers, organic and inorganic excipients, solvents, water sanitation supplies and others. The annual compound growth rate of the chlorine market worldwide is around 4.5% (2015 - 2023), with a projection for 2030 of 128.95 million metric tons, which represents an opportunity in its production chain [1]. However, an excessive amount of chlorine in aqueous systems treated by Advanced Electrochemical Oxidation Processes (AEOPs) becomes a problem when the oxidation of chloride ions towards "free" or "active" chlorine species (Cl_2, HClO, ClO^-) in solution, as well as chlorates and perchlorates (ClO_3^- and ClO_4^-, respectively), which have been shown to be toxic to human health, specifically in neurological, cardiovascular, thyroid and respiratory areas, also affecting the immune system. Therefore, health protection agencies as the United States Environmental Protection Agency (US EPA) have taken regulatory action to limit the amount of ClO_3^- and ClO_4^- to 56 ppb [2]. Hence, it is important to control the experimental conditions in the chlorine oxidation processes in order to favor or not the formation of reactive chlorine species of interest [3-5]. The aim of this work is to characterize the elemental, morphological and electrochemical characterization of DSA. To identify the number of electrochemical processes in acid, alkaline and neutral pH bulk solutions by the presence of chloride in different concentrations. Finally, quantify the chlorides consumed before and after anodic polarization curves.

Material and Methods

All chemical reagents were used as received, without further purification and solutions were prepared with Milli-Q purified water (≥ 18.2 MΩcm, Millipore at 25 °C). Electrochemical measurements were carried out in Autolab potentiostat/ galvanostat model PGSTAT302N with a single-body glass cell configured for three electrodes with 10 mL of capacity. IrO_2-SnO_2-Sb_2O_3 was employed like WE positioned at 1.0 cm distance between Ag/AgCl and Pt wire used as reference and counter electrodes, respectively. 7 mm^2 was the geometrical exposed area of WE. Cyclic voltammograms were executed with 50 mV s^{-1} scan rate and 2.4 mV step potential, meanwhile, linear sweep voltammetry (LSV) with 5 mV s^{-1} scan rate and 0.45 mV step potential. For the sinusoidal potentiodynamic impedance measurements (Nyquist and bode), 1.30 V (vs. Ag/AgCl) was applied in between 0.1 MHz and 0.1 Hz at 0.125 s integration time. The tests were performed with NaCl solutions of 0.1 mM - 2.0 M in H_2SO_4 0.5 M (pH 2), Na_2SO_4 0.1 M (pH 6) and Na_2SO_4 0.5 M + 0.25 M NaOH (pH 13). Chloride concentration in bulk solutions at pH 2, 6 and 13 was determined by argentometry (Mohr's method) using $AgNO_3$ (0.05 M), $K_2Cr_2O_4$ (5%) like titrant and indicator, respectively.

Results and Discussion

The voltammetric profiles of Figure 1 show the anodic and cathodic processes of SnO_2-IrO_2-Sb_2O_3 WE at pH 2, 6 and 13 with chloride ion concentrations in solution from 10^{-4} to 2.0 M at 1.0 mV s^{-1}. In the cathodic process in Figure 1 (A and B), one peak at 0.86 V (vs. Ag/AgCl) is observed at pH 2, two at pH 6 at ca. 0.7 and 0.96 V (vs. Ag/AgCl), whose intensity increases proportionally with Cl^- concentration starting from 0.1 M.

However, at pH 13 there is no peak formed in this region, in fact, the curves in Figure 1C almost overlap with increasing Cl^- concentration.

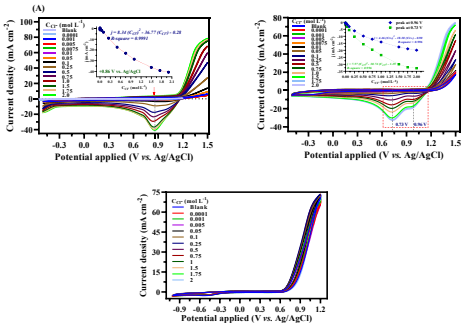

Figure 1. Voltammetric profiles of IrO_2-SnO_2-Sb_2O_3 WE in presence of different chloride concentration (10^{-4} to 2 M) at 1.0 mV s^{-1} scan rate. Supporting electrolytes were **(A)** H_2SO_4 (0.5 M) at pH 2. Inserted graph correlates j and CCl^- at 0.86 V (*vs*. Ag/AgCl); **(B)** Na_2SO_4 (0.5 M) at pH 6. Inset plot shown j *vs.* C_{Cl^-} at ca. 0.7 and 0.9 V (*vs*. Ag/AgCl); and **(C)** Na_2SO_4 (0.5 M) + NaOH (0.25 M) at pH 13.

Figure 2 demonstrates that the presence of Cl^- favors charge transport and improves the ability of capacitor to store and distribute charge at pH 2, 6 and 13. In the inset graph is observed that when Cl^- is less than 0.1 M the resistance decreases rapidly from ca. 1.0 to 0.1 kΩ, and converges to zero. Whereas, the capacitance increases linearly at pH 6.

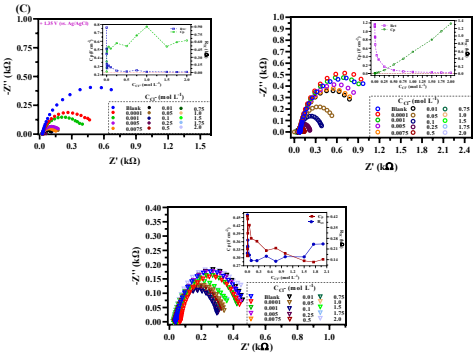

Figure 2. Nyquist plot at 1.35 V (*vs*. Ag/AgCl). Inset graphs correlates double layer capacitance (C_p) and charge transfer resistance (R_{ct}) with C_{Cl^-}. Frequency scan was 10 kHz - 0.1 Hz. Supporting electrolytes were **(A)** H_2SO_4 (0.5 M) at pH 2. Inserted graph correlates j and C_{Cl^-} at 0.86 V (*vs*. Ag/AgCl); **(B)** Na_2SO_4 (0.5 M) at pH 6. Inset plot shown j *vs.* C_{Cl^-} at ca. 0.7 and 0.9 V (*vs*. Ag/AgCl); and **(C)** Na_2SO_4 (0.5 M) + NaOH (0.25 M) at pH 13.

Figure 3 shows that at high Cl- concentrations at pH 2 there is a significant consumption of chlorides in the electrochemical polarization.

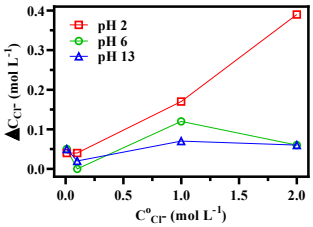

Figure 3. Initial chloride concentration versus change in chloride concentration post-polarization by LSV at pH2, 6 and 13. Cl^- amount was determined by Mohr's method.

Conclusions

A robust study of the chloride behavior in electrochemical processes was performed with the SnO_2-IrO_2-Sb_2O_3 electrode (DSA), whose composition is 20% Sn, 0.68% Ir and 0.45% Sb with an average particle size of 16nm ± at pH 2, 6 and 13. Briefly, we conclude that chloride concentrations below 0.1 M act as a mediator in REDOX processes favoring charge transport, while above this concentration chlorides participate in REDOX processes forming active chlorine species.

Acknowledgments

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