

## Production of Sodium Hypochlorite or Mixed Oxidant using Rhodium/Rhodium Oxide Mixed Modified Electrode

H.H. Shaarawy and M.S. Shalaby

Chemical Engineering & Pilot Plant Dept., National Research Center, Cairo, Egypt

**Abstract:** In the present work, the produced mixed oxidant was studied during the electrolysis of water containing chloride ions ( $\text{Cl}^-$ ). Titanium based rhodium/ rhodium oxide (Rh /Rho) thermally activated modified electrode was successfully used for the production of mixed oxidant solution generated via brine electrolysis (35g/l sodium chloride) at optimum conditions of initial pH 2.7, applied current density of  $250\text{mA}\cdot\text{cm}^{-2}$ , electrolysis temperature of  $25^\circ\text{C}$ , electrolysis duration of 2hrs, cathode to anode area ratio of 1:1, gap distance between the anode and cathode of 3cm, and rate of stirring of 300rpm at membrane less electrolysis cell. The detected active chlorine species at the above mentioned conditions was 2.1g/l, while the active oxygen was 0.9g/l. At higher current densities, the rate of production of active chlorine is about 4 times greater than of active oxygen. This shows how the chlorine production rate is highly influenced by current density. However the concentration of mixed oxidant gives a sharp decrease with temperature increase for chlorine more than that of oxygen. The used modified electrode displays a porous structure with small-sized crystal particles and a very compact crystalline structure. Oxidants, such as hydroxyl radical, hydrogen peroxide and hypochlorite ion were obtained through electrolyses process using the produced mixed electrode. The generated mixed-oxidant solution can be used to address water quality issues that chlorine gas or hypochlorite, and indeed other oxidant disinfectants as well, simply cannot.

**Key words:** Modified electrodes, Mixed oxidants, electrochemical water disinfection, and Rhodium oxide.

### INTRODUCTION

For several decades chlorine gas has been widely used as the main disinfecting agent because of its availability with cheap cost. Chlorine is the most commonly used chemical compound of disinfection providing both primary and residual disinfection. Despite chlorine's effectiveness as a method of water disinfection, it has several disadvantages, which are the cause of consumer and regulatory pressure on water supply companies. These include; unfavorable taste and odor associated with the use of chlorine in drinking water, ineffectiveness when used alone against resistant microorganisms such as *Cryptosporidium parvum*, occasional regulatory failures, and the generation of potentially toxic disinfection by-products (Driedger *et al.*, 2000; Hallam *et al.* 2003; Bull *et al.*, 2001).

As a result of these disadvantages a number of alternatives to chlorine for water disinfection have been suggested. The alternatives are wide ranging including chemical systems, such as ozone (L. Joseph Bollyky 1979), and potassium permanganate; physiochemical systems, such as titanium photo-catalysis (R. Armon *et al* 2004), photodynamic disinfection (Qilin Li *et al* 2008), and electrochemical disinfection (Alexander Kraft 2008), and physical systems, such as ultraviolet irradiation (Vilhunen S *et al* 2009), Ultrasonication (K.K. Jyoti, A.B. Pandit 2003), pulsed electric fields (Renuka Narsetti *et al* 2004), irradiation, magnetic enhanced disinfection, and microwave systems. Whilst alternatives such as ozone and ultraviolet irradiation have gained acceptance within the water treatment process, most of the alternatives at present do not fulfill the requirements for an alternative to chlorine for primary and residual water disinfection (Bergmann *et al.*, 2002).

Electrochemical disinfection has been studied and utilized for several decades as an effective water purification method, because it is an easy, low-cost method that has been proven to inactivate variety of microorganisms, including different types of bacteria and viruses (Casteel *et al.*, 2000; Drees *et al.*, 2003; Diao *et al.*, 2004). Electrochemical disinfection can be done by either of two methods: direct in-line electrolysis and onsite generation of reactive oxygenated species. Direct in-line electrolysis disinfects drinking water by interfacing directly with electrochemical cells using the chloride ions ( $\text{Cl}^-$ ) naturally contained in or added to water for active chlorine formation (i.e., dissolved  $\text{Cl}_2$ ,  $\text{HOCl}$  and  $\text{OCl}^-$ ) (Bergmann, 2010). Specific problems in treating water with direct in-line electrolysis are scaling (calcareous deposits) and fouling effects mainly occurring on the cathode surface (Yan *et al.*, 1993). The second method uses a mixture of disinfecting species, including several oxidizing compounds, generated in an on-site electrochemical cell and added to a water stream (Kerwick *et al.*, 2005). To date, the majority of the literature related to the electrochemical process has dealt

**Corresponding Author:** H.H. Shaarawy, Chemical Engineering & Pilot Plant Dept., National Research Center, Cairo, Egypt.

E-mail: marwashalaby\_4@yahoo.com

with the oxidation of harmful organic compounds and the disinfection of microorganisms in water (Kerwick *et al.*, 2005; Saracco *et al.*, 2000; Petersen *et al.*, 2007).

The efficiency of mixed oxidant generation in the electrochemical process differs depending on the electrode material, which is known as mediators (Jeong *et al.*, 2009). Mixed oxide mediators( electrodes) are used in many applications as hydrogen production (Chandra Babu *et al* 1990) through electrolysis of sea water, production of glucose from rice starch (Shaarawy *et al.*2009), and metals electrowinning (Flavio *et al.*2006). The aim of our work was to use rhodium/rhodium oxide/titanium mixed oxide; thermally treated modified electrode, in the production of mixed oxidant which could be used in the disinfection of drinking water or in feed water of reverse osmosis desalination plants. Several operating parameters will be investigated within this study as the effect of applied current density, solution pH, electrolysis temperature, electrolysis duration, cathode to anode area ratio and gap distance between the two electrodes. The main species formed within mixed oxidants are hypochlorite and reactive oxygen, but low concentrations of undesired by-products, such as chlorite ( $\text{ClO}_2^-$ ,  $\text{ClO}_3^-$ , and  $\text{ClO}_4^-$ ) were produced at the same time will be neglected with rhodium modified electrode. The mechanism of the formation of the above mentioned species will be discussed in details within our work. The kinetic studies on the formation of mixed oxidants under various operating conditions were thoroughly investigated utilizing the suggested kinetic model equation.

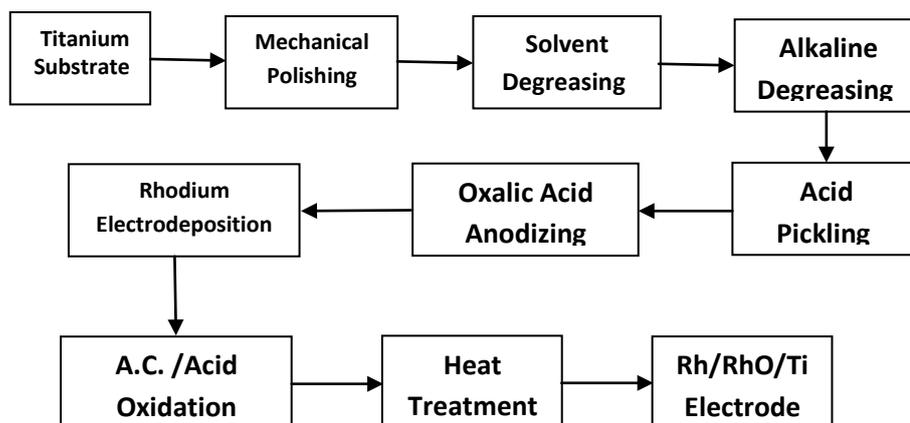
## 2. Experimental Work:

### 2.1 Materials and Stock Solutions:

Titanium sheets of 99.9% purity were purchased from alumisr Company. Rhodium sulfate produced by Degussa Co. was used for the preparation of rhodium/rhodium oxide/titanium modified electrode; sodium chloride, Sodium hydroxide and sulfuric acid were purchased from El-Gomhoria Co. for chemicals.

### 2.2 Preparation of Modified Electrode:

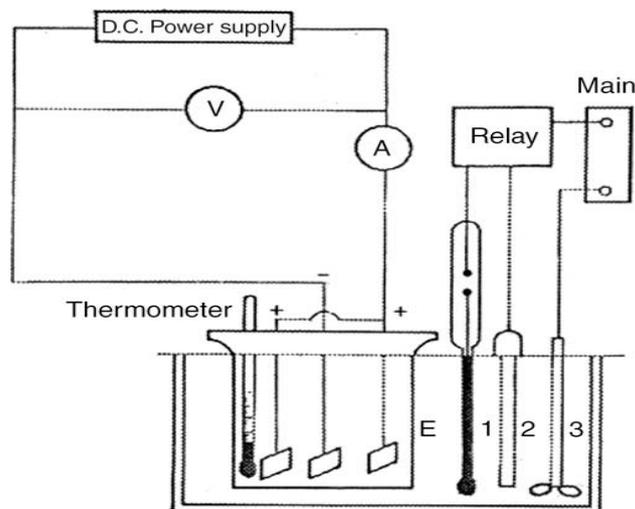
The development of Rhodium/Rhodium oxide thermally treated electrode which will be used in this study is shown in Fig. 1.



**Fig. 1:** Flow chart for the preparation of Rhodium/Rhodium oxide thermally treated electrode.

Titanium substrate was mechanically polished via different grades of sand paper followed by solvent degreasing via butyl glycol, water rinsing, and alkaline cleaning for complete removal of oil and grease. The substrate was then subjected to acid pickling for 5 minutes in 36% hydrochloric acid. Then acid pickled substrate was subjected to anodizing in 5% oxalic acid at 40°C for 5 minutes. The anodized titanium substrate was coated with rhodium thin film by the electro-deposition in rhodium sulfate bath with the composition and operating conditions as expressed above. The obtained coated titanium substrate with rhodium thin film is then subjected to oxidation process via alternating current (3A/cm<sup>2</sup>, 30 volt, 50 Hz, for 60mins.) in concentrated sulfuric acid (98%). After completing the oxidation process, the electrode was rinsed in distilled water and then it was thermally treated with hot air at 450°C for 30mins. The details for the preparation of the modified electrode were explained via (Baraka *et al* 2002, and Baraka *et al* 2003).

Mixed oxidant generation electrochemical setup and procedure: Figure 2 represents the experimental set-up used for the preparation of mixed oxidant via sodium chloride solution electrolysis using Rh/RhO/Ti electrode.



**Fig. 2:** Electro-catalytic mixed oxidant preparation circuit.

#### 2.4 Analytical Measurements:

The concentration of the generated hypochlorite ion was determined via DPD colorimetric method described in standard methods for the examination of water and wastewater 1998. The concentration of total oxidants in the same solutions was determined by iodometric titration as the method described by Jara, *et al* 2007. The concentration of active oxygen was obtained as difference between the concentration of total oxidants and hypochlorite.

#### 2.5 Electrode Morphology and Structure:

The surface morphology and structure of obtained electrodeposited rhodium thin film over anodized titanium substrate and the acid oxidized rhodium thin film followed by thermal activation (Rh/RhO/Ti modified electrode) were examined using a scanning electron microscope (SEM) JEOL (Tokyo, Japan) JSM T330A equipped with KEVEX (Tokyo, Japan) electron diffraction equipped (EDAX) X-ray microanalyzer. The operating conditions were accelerating voltage of 25 Kev. Beam/sample incidence angle of  $90^{\circ}$ , and X-ray window incidence angle of  $22.7^{\circ}$ . The phases and crystal structure of the deposited rhodium and rhodium oxide on the pre-anodized titanium substrate were examined by x-ray diffraction (XRD). The measurements were carried out using a Philips (USA) diffractometer (40 Kev, 30 mA) with a nickel filter and copper radiation. The scanning angular range was from  $4-90^{\circ}$ . The diffraction pattern was recorded at room temperature.

## RESULTS AND DISCUSSIONS

#### 3.1 Mixed Electrode Quality Assessment:

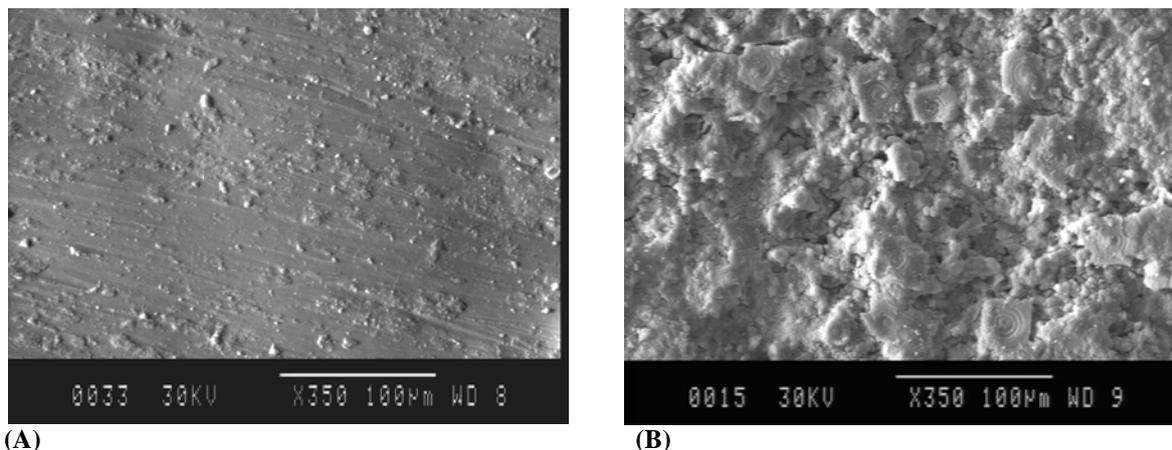
The produced Rhodium/Rhodium oxide thermally treated electrode was subjected to SEM (Campari *et al.* 2002) to show its surface morphology with a magnification of 350 as shown in figure3.

Figure3 (A) and (B) show, respectively, SEM photographs of the morphology of the electrodeposited rhodium metal of the pre-anodized titanium substrate and the oxidized rhodium oxide thin film formed due to the A.C. treatment of the rhodium thin film in concentrated sulfuric acid followed by thermal activation. As it is clear from the photograph that deposited was in the form of large crystal this large crystal divided into small porous structure with small-sized crystal particles with sharp boundaries and a very compact crystalline structure. This gave the chance for the formation of active oxygen, hydroxyl radicals and hydrogen peroxide.

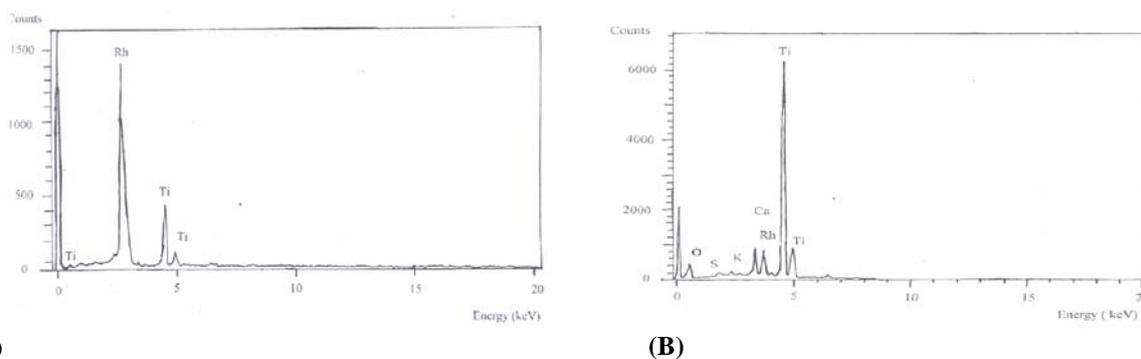
Figure 4 (A) and (B) represents respectively the EDIX charts for the electrodeposited rhodium metal of the pre-anodized titanium substrate and the oxidized rhodium oxide thin film formed due to the A.C. treatment of the rhodium thin film in concentrated sulfuric acid followed by thermal activation. The presence of the Ti peak at 4.5Kev for the EDAX chart assure the porous structure of the electrodeposited rhodium thin film and the oxidized rhodium oxide thin film.

Figure5 (A) and (B) shows the XRD pattern for the electrodeposited rhodium thin film over the pre-anodized titanium substrate and that of oxidized rhodium thin film after treatment of concentrated sulfuric acid using A.C. followed by thermal activation. The peaks in this figure were represented for titanium, rhodium and rhodium oxide. The identification of the crystals is empirical: the American Society for Testing and Materials (ASTM) provides Keysort and IBM cards that provides d-spacing and relative line intensities for pure compounds for over than 25000 crystalline materials. It is clear from the X-ray pattern that rhodium and

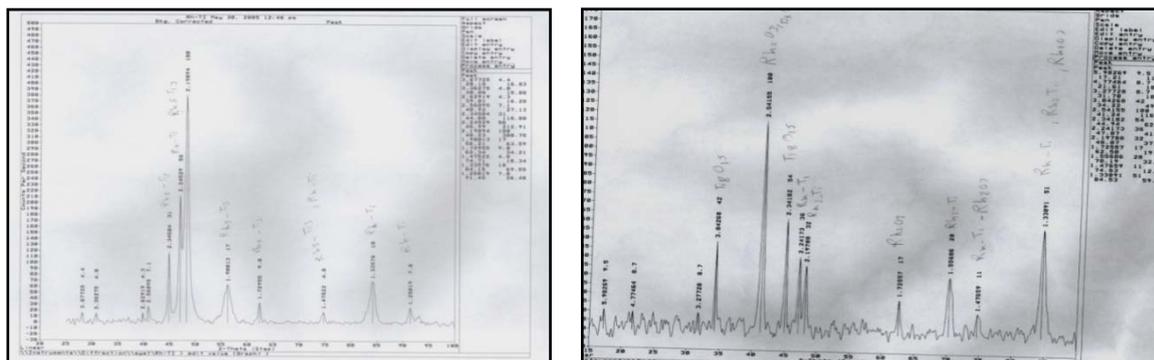
rhodium oxide are present over the pre-anodized titanium substrate. However, the presence of Ti peaks could mean that noble metal films are very thin, Perhaps 1  $\mu\text{m}$ .



**Fig. 3:** SEM photographs showing (A) rhodium thin film over titanium substrate (B) rhodium/rhodium oxide thin film over titanium substrate after chemical treatment with sulfuric acid using A.C. Current and thermal activation (Rhodium/rhodium oxide/titanium thermally activated modified electrode).



**Fig. 4:** SEM-EDIX charts (A) for the electrodeposited rhodium thin film over anodized titanium substrate, while (B) for the Rhodium/rhodium oxide/titanium mixed oxide modified electrode after treatment in sulfuric acid and heat treatment.



**Fig. 5:** XRD patterns of (A) for the electrodeposited rhodium thin film over anodized titanium substrate, while (B) for the Rhodium/rhodium oxide/titanium mixed oxide modified electrode after treatment in sulfuric acid and heat treatment.

### 3.2- Mixed Oxidant Formation Mechanism:

During the electrolysis of water, besides active chlorine, reactive species, such as  $\text{OH}^\cdot$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$ , are produced by electrochemical and/or chemical reactions using rhodium/rhodium oxide/titanium thermally activated modified electrode which diffuse to the bulk solution (Wabner and Grambow, 1985; Pletcher and

Walsh, 1993; Marselli *et al.*, 2003; Kerwick *et al.*, 2005; Jeong *et al.*, 2009).  $\text{OH}^\bullet$  and  $\text{O}^\bullet$  can be formed by reaction (1) and reaction (2), respectively.

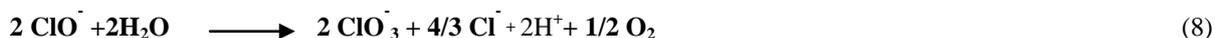
$\text{O}_3$  can be generated by the reaction of  $\text{O}_2$  with  $\text{O}^\bullet$  according to reaction (4); then it can form hypochlorite together with ozone and hydrogen peroxides as mixed oxidants, which are the main purpose of electrolysis due to the high disinfecting ability of these species.



Since this investigation is dealing with electrocatalytic production of mixed oxidant disinfecting agent using rhodium/rhodium oxide/titanium thermally activated modified electrode, it is not out of space to summarize the reaction mechanism involved in this regard. It has been reported (Schmittinger, 1986) that if sodium chloride solution is electrolyzed in an individual cell,  $\text{Cl}_2$  formed at the anode disproportionate in the presence of  $\text{OH}^-$  ions generated at the cathode resulting in the formation of hypochlorite.



The resultant hypochlorite can be further oxidized to chlorate:



However, this leads to the requirement of nine Faradays per mole of chlorate, whereas only six are needed if a chemical disproportionate route is followed:



**Cathode:**



**Anode:**



On the basis of the above reactions, we can see that from reaction (8), the hypochlorite is favored by keeping the chloride concentration as high as possible. In addition to chlorine generated by electrolysis it was suggested that ozone and chlorine dioxide or hydrogen peroxide could be generated (Eqs. (11) to (15)) summarize the important reactions that can occur between chlorine and each subsidiary oxidant under acidic conditions (Son *et al.*, 2004).

Recently (Anodo & Tanaka, 2004; Sudoh, Kitaguchi, & Koide, 1985a; Sudoh, Kitaguchi, & Koide, 1985b) the production of hydrogen peroxide by electrolysis have been examined. Peroxide ion is produced on the cathode of the electrolysis cell by the reduction of oxygen gas (Eqs. (16) to (18)).

### 3.3 Formation of Active Oxygen and Active Chlorine and Effect of Current Density:

It was shown from figures (6 & 7); that by increasing current density, the concentration of the obtained mixed oxidant regarding to its contents (active chlorine and active oxygen) was increased too.

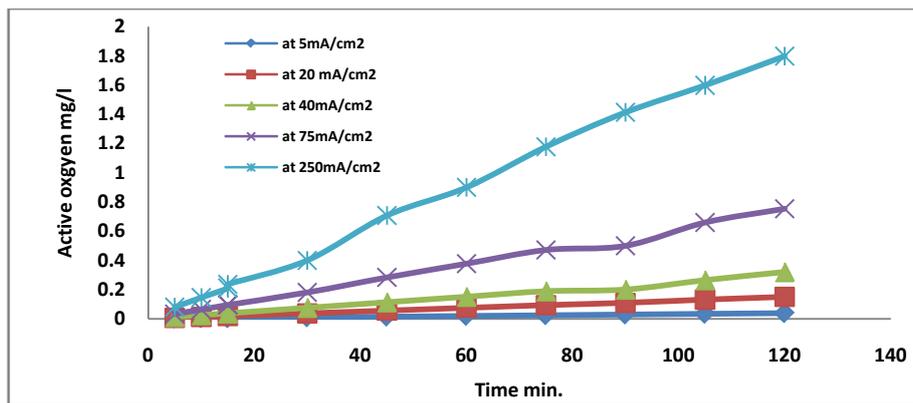


Fig. 6: Effect of current density on concentration of active oxygen at different electrolysis time.

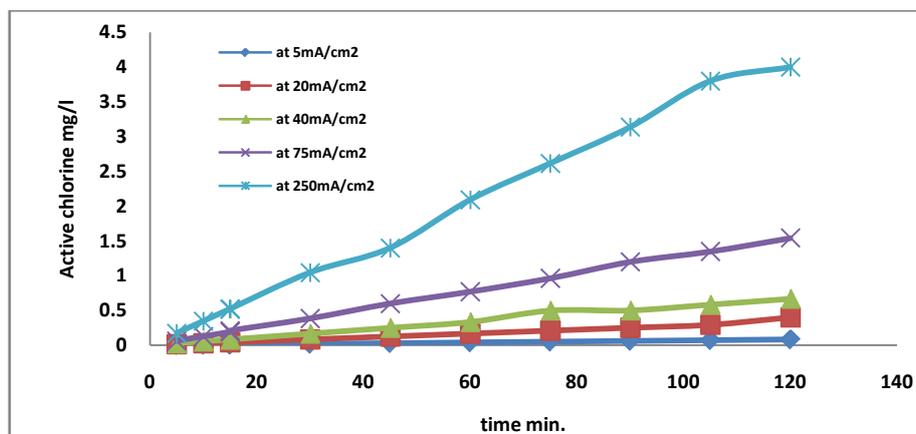


Fig. 7: Effect of current density on concentration of active chlorine at different electrolysis time.

The concentration of these oxidants was determined by the aforementioned analytical techniques and then reported versus electrolysis time at constant reaction temperature 25°C. At higher current densities the rate of production of active chlorine is about 4 times greater than that of active oxygen, while at low current densities it is only about double the production rate of active oxygen as clear in figures 6 to 8.

It was obvious from the previous figure that the concentration of produced mixed oxidants recorded as active oxygen or active chlorine is highly affected by current density; that at constant optimum operating parameters of time (2 hrs), temperature, pH, gap distance and electrode dimensions, the concentration of active oxygen in mg/l, reaches about 0.0188 at 5 mA/Cm<sup>2</sup> which rises to be 0.9 at 250 mA/Cm<sup>2</sup>.

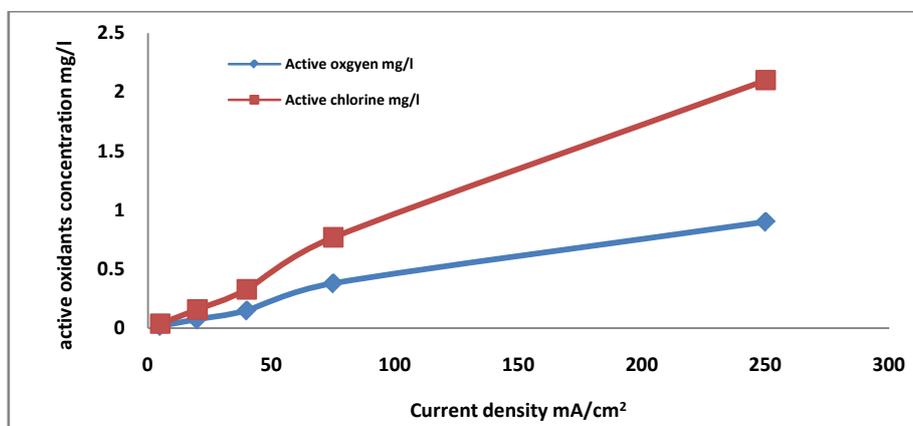
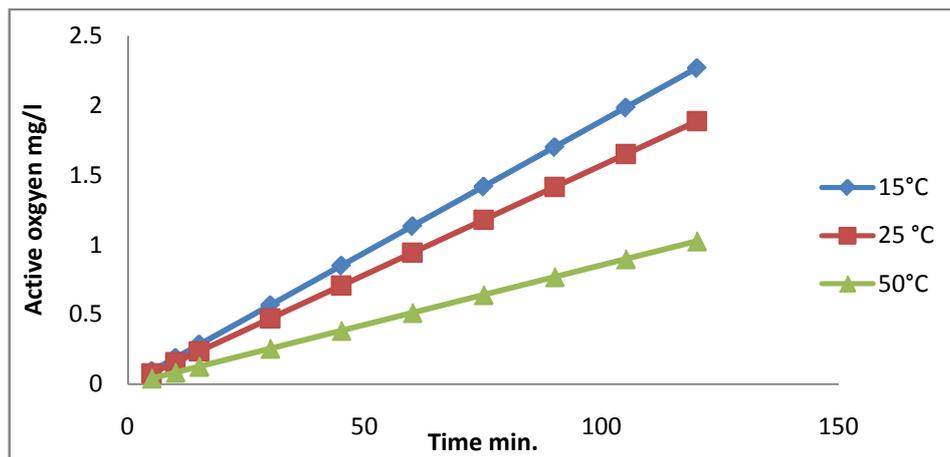


Fig. 8: Effect of current density on the concentration of active oxidants at optimum electrolysis time.

At higher current densities the rate of production of active chlorine is about 4 times greater than that of active oxygen, while at low current densities it is only about double the production rate of active oxygen as shown in figure 8.

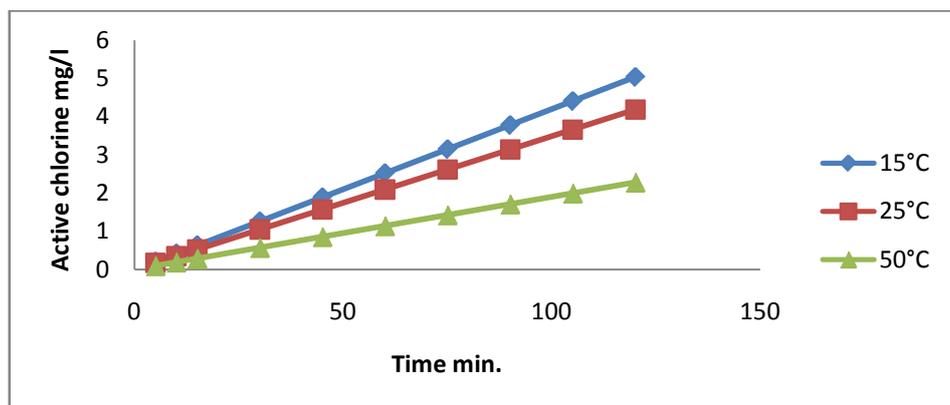
**3.4 Effect of Temperature:**

Again with respect to temperature; as it is clear from figures 9 and 10 as electrolysis time increases, the concentration of both active chlorine and active oxygen increases too. Although the increase in reaction temperature leads to the dramatic decrement of the active chlorine and active oxygen concentration obtained at the same operating conditions as clear from figure 11. In case of uncontrolled electrolysis temperature; the increment of electrolysis time or applied current density will lead to decrement of active chlorine and active oxygen concentration, which illustrates clearly the effect of temperature as an important controlling parameter for electrolysis process.

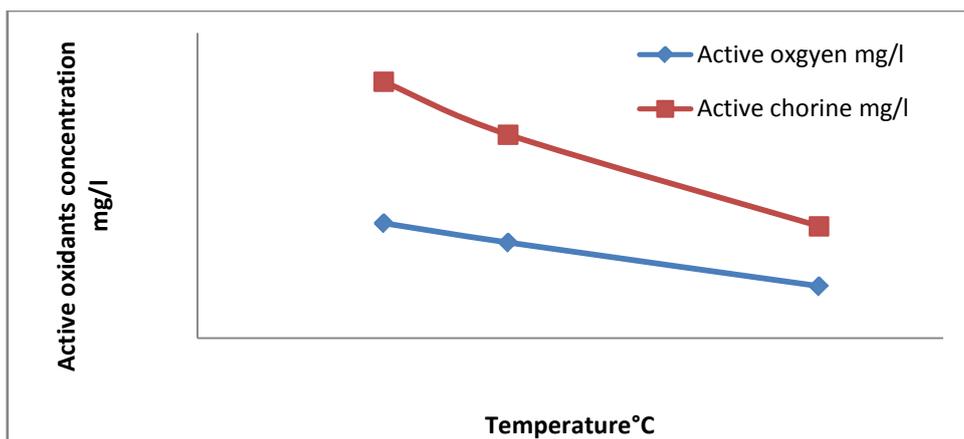


**Fig. 9:** Variation of concentration of active oxygen with time at different temperatures.

As the applied current efficiency does not reach 100% conversion to chemical change, always loss in current is converted to heat which in turn increases the reaction temperature. Although any rise in temperature above 35° C will lead to decomposition of formed mixed oxidant, or does not formed at all, for this the electrolysis temperature must be controlled below 35°C. It was clear from figure 9 that concentration of mixed oxidant decreases as temperature increases reaching its minimum value at 60°C. It was concluded that the temperature is an important factor controlling the efficiency and concentration of mixed oxidant so electrolysis temperature have to be controlled at value less than 35°C and preferably 25°C, that could be considered the optimum temperature for the production of mixed oxidant mixture, taking into consideration optimum current efficiency (250mA/Cm<sup>2</sup>) with low cost production technique that the operation will be at ambient conditions.



**Fig. 10:** Variation of concentration of active chlorine with time at different temperatures.

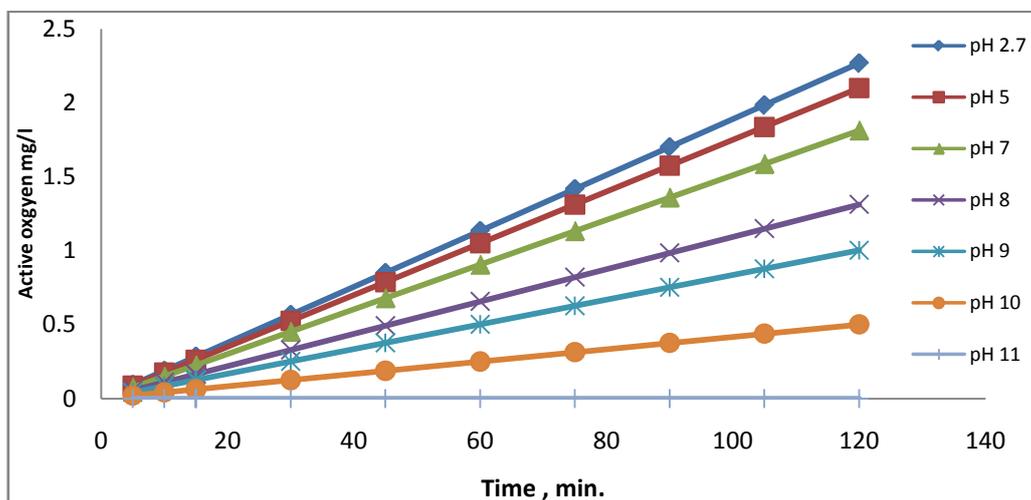


**Fig. 11:** Effect of temperature on the concentration of active oxidants at optimum electrolysis time.

The concentration of mixed oxidant gives a sharp decrease with temperature increase for chlorine more than that of oxygen. The concentration of oxygen at 15°C was 1.13 mg/ lit decreases to reach 0.51 mg/l. At 50°C, on the other hand the concentration of chlorine decreases from 2.52 to 1.1 mg/l as the temperature increases from 15 to 50°C at electrolysis time of 2 hours.

### 3.3 Effect of pH of Medium:

The most important factor affecting the formation of the mixed oxidant through brine electrolysis is the adjustment of pH of electrolytic cell. The effect of pH was studied over electrolysis time from 0 to 120mins, to show its effect on formed active oxygen and chlorine which in turn combine to form different active oxidants. The effect of pH was studied at constant operating conditions of temperature 25°C, gap distance between cathode and anode of 3cm, and anode to cathode area ratio of 1 with constant stirring rate of 300rpm at constant current density of 250mA/cm<sup>2</sup>. It was observed from figures (12 and 13) that the concentration of active oxygen increased from 0.51 to 2.268 mg/ l at electrolysis time of 2 hours as the pH was decreased from 10 to 2.7 respectively. This means that the electrolytic reaction is greatly enhanced in acidic medium as it falls to reach zero at pH of 11 as shown in figure 10, which is due to presence of sodium hydroxide comes out from combination of reaction 1 and 6.



**Fig. 12:** Variation of concentration of active oxygen with time at different pH.

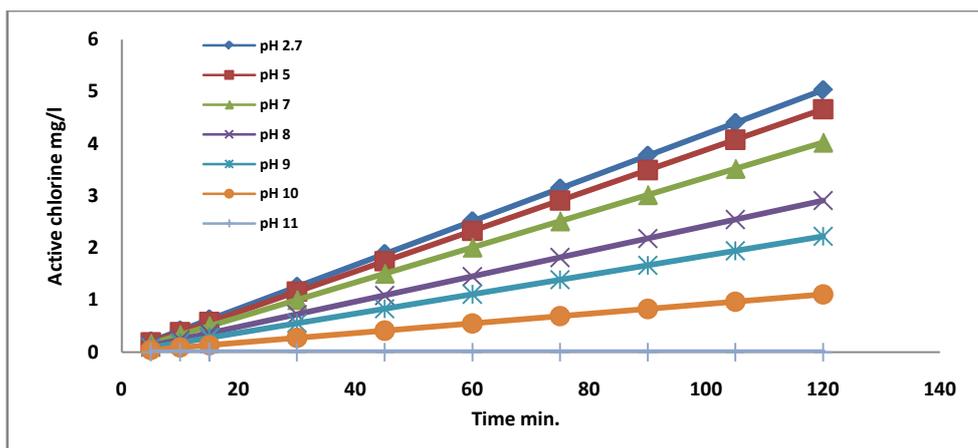


Fig. 13: Variation of concentration of active chlorine with time at different pH.

It was concluded then that reaction pH leads to a variation in the mixed oxidants formed in the reaction medium and the mode of interaction of the formed active species with each other as shown in the proposed mechanism. Figures 9 and 10 show increase of concentration of active chlorine and active oxygen species by increasing electrolysis time till reach 2 hours giving a maximum of 5 mg/l and 2.3 mg/l at 250 mA/cm<sup>2</sup>. while Figure (14) shows that as reaction medium pH increases, the active species concentration (chlorine and oxygen) decreases reaching to zero at pH of 11, and it was maximum at pH 2.7, so pH value of 2.7 was selected as the optimum medium pH for the production of mixed oxidant using Rh/RhO/Ti electrode.

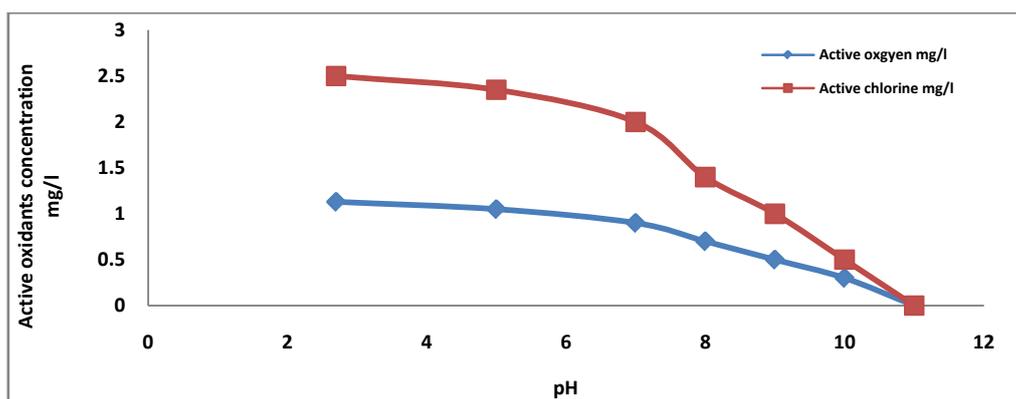
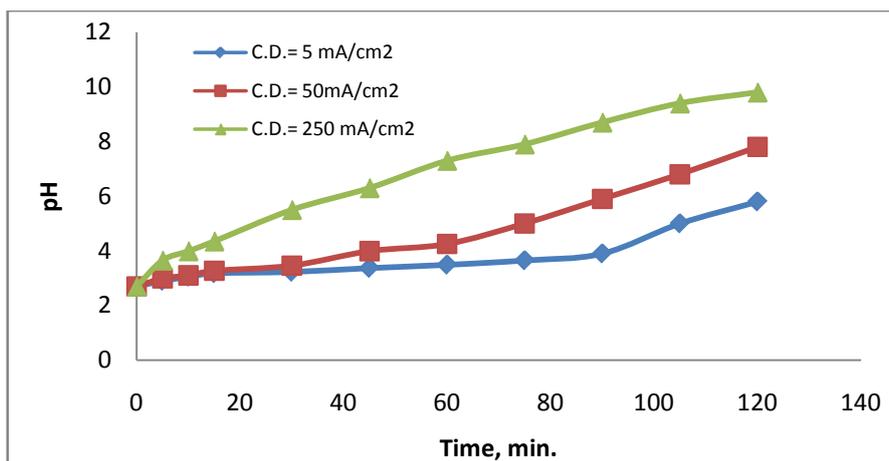


Fig. 14: Effect of medium initial pH on the concentration of mixed oxidants at optimum parameters.

### 3.4 Effect of Current Density on Produced Mixed Oxidants pH:

In the following figure, the authors studied the effect of different applied current densities over electrolysis time from 0 - 120 min. on the produced active oxidants concentration expressed as product pH. It was clear that produced mixed oxidants increases the pH of product medium at 120 min from 5.8 to 9.8 at 5 and 250mA/Cm<sup>2</sup> respectively, this means that concentration of mixed oxidants which increases by increasing applied current density is not optimum at 120 min because of the presence of hypochlorite which raises the pH to 9.8.

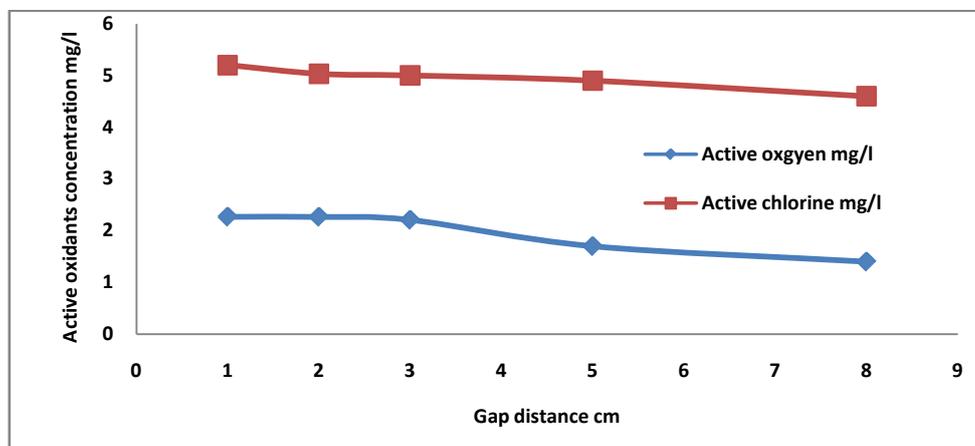


**Fig. 15:** Variation of produced mixed oxidant pH with time at different current densities.

While at electrolysis time of 60 min, the concentration of mixed oxidants gives a pH of 7.3 which is neutral giving an evidence of absence of any strong alkali. The increase in pH of reaction medium with time could be attributed to the increase of the concentration of hypochlorite, which is alkaline in nature.

**3.5 Effect of Gap Distance Between Electrodes on Produced Mixed Oxidants Concentration:**

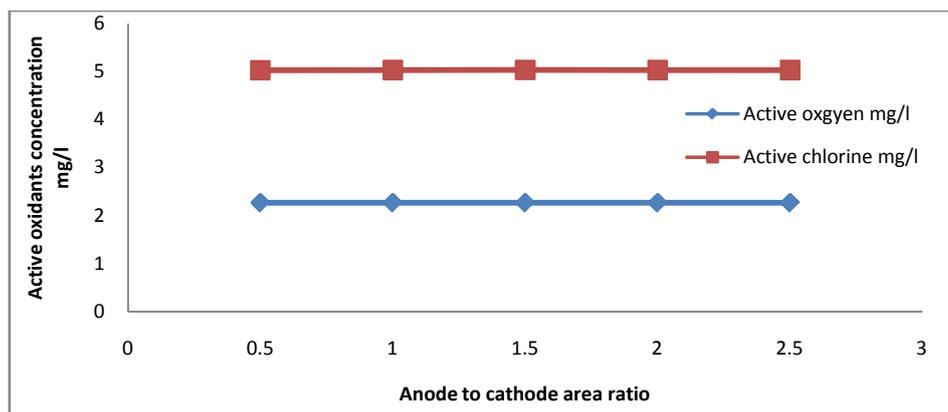
Figure 16 represents the effect of variation of gap distance between cathode and anode on the concentration of the produced active chlorine and active oxygen during the production of the mixed oxidants via brine electrolysis using Rh/RhO/Ti thermally modified electrode, at optimum pH 2.7 and temperature 25<sup>0</sup>C which are studied and illustrated in the previous sections. It is clear that as the gap distance increases, nearly no change was obtained for both active chlorine and active oxygen till gap distance reach 3cm. By increasing the gap distance above 3cm; slight decrement was noticed for active chlorine, while significant decrement was obtained for active oxygen concentrations. And so 3cm gap distance was selected as the optimum distance between cathode and anode.



**Fig. 16:** Effect of gap distance on the produced mixed oxidant concentration at optimum operating conditions.

**3.6 Effect of Anode to Cathode Area Ratio on Produced Mixed Oxidants Concentration:**

The effect of anode to cathode area ratio on the production of both of active chlorine and active oxygen obtained via brine electrolysis using Rh/RhO/Ti at the above mentioned pH, temperature, and gap distance was studied at this section. As clear from figure 17, there is no influence obtained by the change of the anode to cathode area ratio from (0.5:1 to 2.5:1) and so according to common design bases 1:1 was selected as optimum area ratio between anode and cathode.



**Fig. 17:** Effect of anode to cathode area on the produced mixed oxidant concentration at operating conditions.

#### 4. Conclusions:

Titanium based rhodium/ rhodium oxide thermally activated modified electrode was successfully used for the production of mixed oxidant solution generated via brine electrolysis (35g/l sodium chloride) at different operating conditions. The rate of change of active chlorine and active oxygen species increases with the increase of applied current density from 5 to 250 mA/cm<sup>2</sup> at constant temperature, pH, and other operating parameters to give 2.1mg/l and 0.9mg/l for chlorine and oxygen species at optimum electrolysis duration of 60 min as the increase in species concentration above can be neglected economically. However the rate of change in active species concentration expressed as oxygen and chlorine decreased with the increase in medium pH to illustrate clearly the acidic medium effect in the production of these mixed oxidants. It was clear from the above data in sections 3.7 and 3.8 that the electrolytic cell geometry as gap distance for electrodes and electrodes area ratio are insignificant as they didn't affect the concentration of produced active species especially for electrodes area as the concentration formed were around the same range; but for the gap distance, the concentration begin to drop by increasing the gap distance over 3 cm which is the optimum. The used modified electrode displays porous structure with small-sized crystal particles and a very compact crystalline structure. Oxidants, such as hydroxyl radical, hydrogen peroxide and hypochlorite ion were detected via electrolyses process using the obtained electrode. The generated mixed-oxidant solution can be used to address water quality issues that chlorine gas or hypochlorite, and indeed other oxidant disinfectants as well, simply cannot.

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