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## TRIALS FOR BEST OXYGEN EVOLUTION EFFICIENCY OF MnMo- OXIDE ANODE DEPOSITED ON IrO<sub>2</sub>/Ti SUBSTRATE AND ELECTROLYZED IN 0.5M NaCl

R. ABOU SHAHBA

*Chemistry Department, Faculty of Science (for Girls), AL- Azhar University, Nasr City, Cairo, Egypt*

E. ATTIA

*Chemistry Department, Faculty of Science (for Girls), AL- Azhar University, Nasr City, Cairo, Egypt*

N. ABDEL GANY

*National research Center, Dokki, Cairo, Egypt.*

A. EL-M ONEIM

*National research Center, Dokki, Cairo, Egypt.*

N. DEIAB

*National research Center, Dokki, Cairo, Egypt.*

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ELECTROLYZED IN 0.5M NaCl**

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R. M. ABOU SHAHBA<sup>a</sup>, E.M. ATTIA<sup>a</sup>, N. A. ABDEL GANY<sup>b</sup>, A. A. EL-M ONEIM<sup>b</sup>  
AND N. M. DEIAB<sup>b</sup>

<sup>a</sup>*Chemistry Department, Faculty of Science (for Girls), AL- Azhar University, Nasr  
City, Cairo, Egypt*

<sup>b</sup>*National research Center, Dokki, Cairo, Egypt.*

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**Abstract**

Hydrogen is produced in this study by direct electrolysis at 1000 Am<sup>-2</sup> in 0.5M NaCl solution of pH 2 at room temperature. Direct and pulse current electro-deposition methods have been applied to the preparation of MnMo-oxide anode deposited on IrO<sub>2</sub>/Ti substrate. The beneficial effects of pulse deposition and timings on the performance of MnMo-oxide anodes during electrolysis and the physicochemical properties of the deposits were characterized using SEM and electrochemical techniques.

**Key words:** electrolysis, electro-deposition, oxygen evolution efficiency

**Introduction**

Hydrogen, future fuel, is considered as one of the possible alternative sources of energy to replace the fossil fuels in which their production is expected to decrease [1-6]. Seawater and oceans are used as abundant resources for the production of hydrogen via viable electrolysis process. The industrial seawater electrolysis produces poisonous chlorine on the anode at a vast amount of hydrogen production which is not preferable and represents major environmental problems [7,8]. Electro-deposition techniques are the basic technological prerequisites for industrial electrode materials.

It is known that the anodes coated with layer of IrO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub> are commercially used for oxygen evolution reaction from acidic media as in electro-flotation and metal electro-winning processes [9,10]. Despite the high cost of these anodes, they evolve chlorine gas on expense of oxygen gas during seawater electrolysis process. Thus, there is an urgent need for new anode materials producing only oxygen without chlorine in seawater electrolysis. First trial for developing oxygen evolving anode during seawater electrolysis was carried out by Bennet et al [7]. They demonstrated that manganese dioxide coating anodically deposited from acidified MnSO<sub>4</sub> was initially capable of evolving oxygen from seawater at 99% efficiency, and from saturated sodium chloride brine at 95% efficiency.

In spite of the fact that Mo addition to MnO<sub>2</sub> coating enhances beneficially oxygen evolution efficiency (OEE), the performance of dc MnMo-oxide anode is still unsatisfactory for industrial application. As a consequence, it seems interesting to examine the effect of basic pulse current conditions such as pulse current density (Ip), the on and off duration values on the performance of electrodeposited MnMo-oxide anodes during electrolysis.

## **Experimental**

### **1- Etching and polishing**

Punched titanium sheet was immersed in 0.5M HF solution for 5 mins. for removal of titanium oxide layer, and then rinsed with distilled water. To guarantee the anchor effect for the electrocatalysts by surface roughening of these electrodes, the punched titanium was immersed in 12M H<sub>2</sub>SO<sub>4</sub> at 80°C until hydrogen evolution was ceased. After etching was accomplished, titanium sulfate on expanded titanium surface was removed by washing by flowing tap water for about 60 mins.

### **2- IrO<sub>2</sub> coating and post treatment**

Punched titanium was coated with very thin layer of IrO<sub>2</sub> as an intermediate layer between the electro-catalytically active substances and the titanium substrate [11]. The coating was carried out as follows: 0.1 M chloroiridic acid butanol solution was coated on the punched-titanium substrate and the specimen was dried at 80°C for 10 mins, and then baked at 450°C for 10 mins. and cooled to room temperature. This procedure was repeated only three times so as to form about 5 gm<sup>-2</sup> IrO<sub>2</sub> layer on the titanium substrate. This specimen was finally baked at 450°C for 1h. Finally, the sheet was cut into 160 mm x 75 mm x 1mm as suitable electrodes and a titanium-wire was spot-welded to its edge. The IrO<sub>2</sub>/Ti electrodes were anodically polarized at 1000 Am<sup>-2</sup> for 5 mins. in 10M NaOH solution, then in 1M H<sub>2</sub>SO<sub>4</sub> stagnant solution for 5 mins. at room temperature and finally rinsed with distilled water before the anodic deposition of MnMo oxide.

### **3- Anodic deposition by direct and pulse current techniques:**

The electrolytes for anodic deposition were composed of reagent grade chemicals 0.2M MnSO<sub>4</sub>, 0.003M Na<sub>2</sub>MoO<sub>4</sub>, 0.00~0.006M H<sub>2</sub>IrCl<sub>6</sub>. The concentrations of Mn<sup>2+</sup> and Mo<sup>6+</sup> species were selected based on data reported elsewhere [12]. The pH of the solution was adjusted by adding 18M H<sub>2</sub>SO<sub>4</sub>.

A cell with separate anode and cathode compartments was used for anodic deposition. An anode compartment was a cylindrical alumina diaphragm and a

cathode was a pair of type 316 stainless steel sheets set outside the diaphragm in the cell containing 0.1M  $\text{MnSO}_4$  as a catholyte. The  $\text{IrO}_2/\text{Ti}$  anode was put in the cylindrical diaphragm in parallel with the stainless steel sheet cathodes.

Direct current (dc) anodic deposition was carried out on the  $\text{IrO}_2/\text{Ti}$  electrodes in stirred solutions at  $90^\circ\text{C}$  and current density was  $600 \text{ Am}^{-2}$  for 0.5-2 h. Pulse current (pc) electrodeposition method has been applied to the preparation of manganese based oxide deposits on  $\text{IrO}_2/\text{Ti}$  substrate. A computer connected to a dc source was used to generate a rectangular pulse current  $T_{\text{on}}$  and  $T_{\text{off}}$  respectively. The  $T_{\text{on}}$  and  $T_{\text{off}}$  were varied at constant peak current density and the temperature of deposition was  $90^\circ\text{C}$ .

#### 4- Electrode performance

The amount of oxygen evolved was determined as the difference between the total charge passed and the charge for chlorine formation during electrolysis. The electrolysis was conducted in stirred 0.5M NaCl solution of pH 2 at a constant current density of  $1000 \text{ Am}^{-2}$  until the amount of charge of 300 coulombs, that is  $10^6$  coulombs  $\text{m}^{-3}$ , was passed. In order to avoid reduction of sodium hypochlorite and formation of chlorine on the anode, the cathode used for the measurement of the oxygen evolution efficiency was a thin platinum wire of 0.25 mm in diameter. The amount of chlorine formed was measured by iodometric titration of chlorine and hypochlorite.

The change in the surface morphology and mapping images of deposited oxide specimens were observed by means of scanning electron microscopy (SEM), Jeol-JXA-480A.

### Results And Discussion

#### 1- Comparison between dc-deposited $\text{MnO}_2$ and MnMo-oxide anodes for best oxygen evolution efficiency

The change in the oxygen evolution efficiency (OEE) and loss in weight of dc-deposited  $\text{MnO}_2$  anode prepared in 0.2M  $\text{Mn}^{2+}$  electrolyte and MnMo-oxide anode prepared in 0.2M  $\text{Mn}^{2+}$ -0.003M  $\text{Mo}^{6+}$ , at  $600 \text{ Am}^{-2}$  for 1 h were compared. The  $\text{MnO}_2$  anode shows the initial 96% OEE. Afterwards, the OEE decreases along with steep increase in the loss in weight of  $\text{MnO}_2$  anode with electrolysis (Figure 1). Meanwhile, it is noted that the color of the solution turns into purple during the course of electrolysis. This is due to oxidative dissolution of insoluble  $\text{Mn}^{4+}$  species to soluble  $\text{Mn}^{7+}$  species which is not only detrimental to the electrode durability but also known to poison the proton exchange membrane by attaching to sulphonic

clusters and reducing its ionic conductivity [13]. Furthermore, visual observation of  $\text{MnO}_2$  anode surface after 1400 h of electrolysis revealed significant detachment of catalyst layer from the  $\text{IrO}_2/\text{Ti}$  substrate, which actively evolves chlorine. It can, therefore, be said that the decrease in OEE and significant loss in the anodic weight of  $\text{MnO}_2$  anode is attributed to oxidative dissolution and partial detachment of deposit layers from  $\text{IrO}_2/\text{Ti}$  substrate.

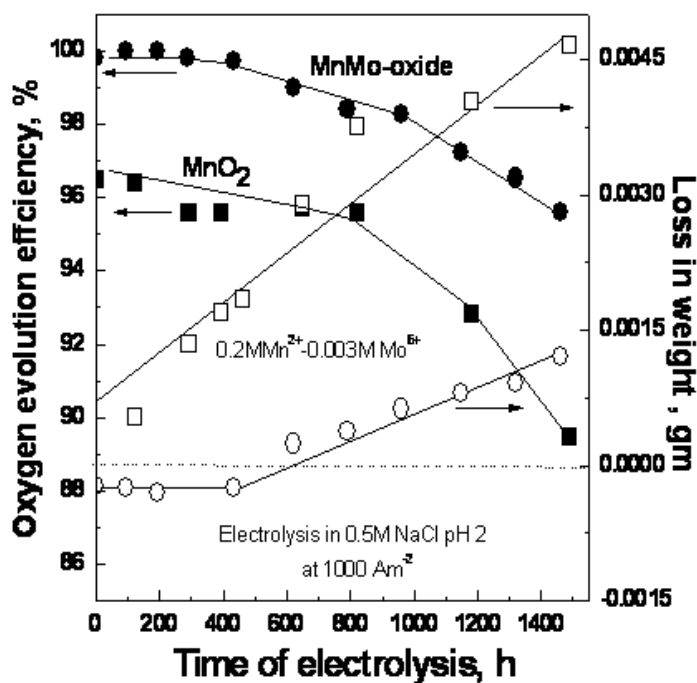


Figure 1: Variation in OEE and loss in weight with time of electrolysis for  $\text{MnO}_2$  and  $\text{MnMo-oxide}$  anodes.

On the other hand, data of Figure 1 reveal that  $\text{MnMo-oxide}$  anode generally shows better durability (OEE and stability) than  $\text{MnO}_2$  anode which displays the initial 100% OEE with little loss in weight. However, an extension in the electrolysis time is resulted in a clear decay in the OEE and an increase in the loss in electrode weight. Meanwhile, no change in the solution color was observed

during the course of electrolysis, assuming the decay in oxidative dissolution process of manganese  $Mn^{4+}$  species.

**2- Effect of on and off duration, pulse current density and Ip values on OEE of pc- deposited MnMo-oxide anode during electrolysis in 0.5M NaCl solution**

All MnMo-oxide anodes were prepared in 0.2M  $Mn^{2+}$ -0.003M  $Mo^{6+}$  electrolyte of pH 0.0 with total deposition time of 1h at  $600 Am^{-2}$ . The electrolysis was carried out in 0.5M NaCl solution of pH 2 at  $1000 Am^{-2}$ . Comparing with the dc-deposited MnMo-oxide, all pc-deposits show better performance for OEE during long term electrolysis. Meanwhile and regardless the  $T_{on}$  duration value; the increase in  $T_{off}$  up to 0.1 sec significantly enhances the OEE. The extension of  $T_{off}$  duration leads generally to a shorter life of the anodes (Figure 2). Similar results were observed for constant  $T_{on}$  values of 1 and 5 sec.

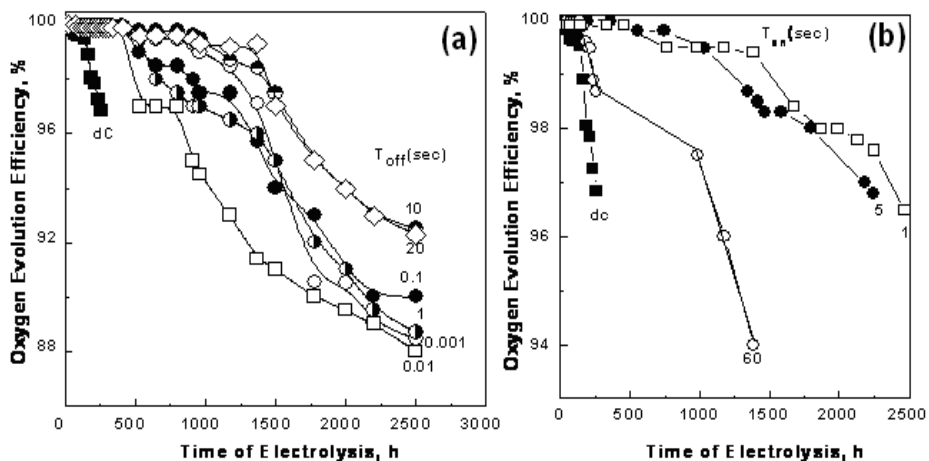


Figure 2: Variation in OEE of pc-deposited anode (a)  $T_{on} = 60$  sec and different  $T_{off}$  values, (b)  $T_{off} = 0.1$  sec and different  $T_{on}$  values, with the time of electrolysis, compared with dc-deposited anode.

The effect of  $T_{off}$  and  $T_{on}$  variation on loss in weight of MnMo-oxide anode reveal that, pulse deposition at  $T_{on} = 1$  sec and  $T_{off} = 0.1$  sec, provides anode with the best OEE leading to durable anode with no loss in weight during long term electrolysis (Figure 3).

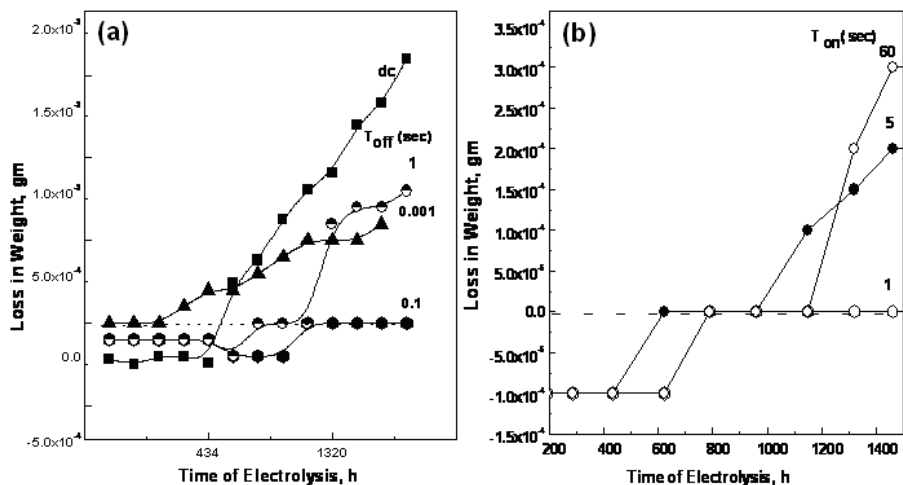
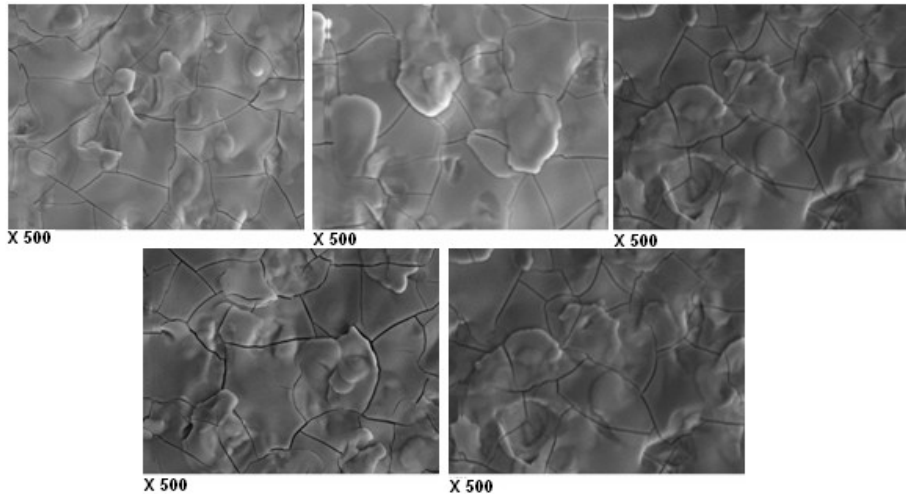


Figure 3: Loss in weight of pc -deposited anode with time of electrolysis (a)  $T_{on} = 1$  sec with different  $T_{off}$  values, (b)  $T_{off} = 0.1$  sec with different  $T_{on}$  values.

Regardless  $T_{off}$  value and mode of anodic deposition, the morphology of oxide surface for all deposits is almost the same; dull appearance and uneven surface with cracked-mud like structure (Figure 4).

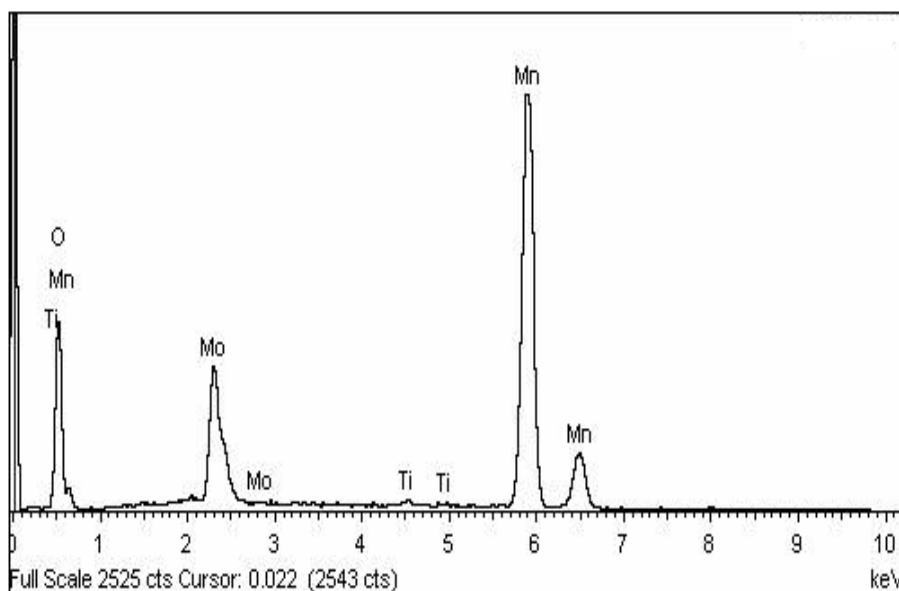
(a) (b) (c)

(d) (e)



**Figure 4:** SEM images (a), (b), (c) and (d) for pulse deposited MnMo- oxide anodes prepared in  $0.2\text{M Mn}^{2+}$ - $0.003\text{M Mo}^{6+}$  electrolyte of pH 0.0 at constant  $T_{\text{on}} = 1$  sec and different  $T_{\text{off}}$  values of 0.001, 0.01, 0.1 and 1 sec, respectively compared with SEM image (e) for dc- deposited MnMo-oxide anode.





**Figure 5: EDX spectrum of MnMo-oxide anode prepared in 0.2M  $Mn^{2+}$ -0.003M  $Mo^{6+}$  electrolyte of pH 0.0 for 1h at  $600Am^{-2}$  at  $T_{off} = 0.1$  sec and  $T_{on} = 1$  sec using pulse current deposition.**

As seen (in Figure 5), O, Mn, Mo are the main components of spectrum. In addition, weak peaks for elemental Ti are detected, although Ti species are not included in the starting deposition electrolyte. The source of Ti species might rise from dissolution of exposed edges of expanded Ti-substrate in the acidic medium of the deposition electrolyte.

The results of energy dispersive X - ray analysis which are summarized in Table (1) indicate clearly that Mo acts as an alloying element and Ti acts as a dopant. Comparing results obtained using direct current deposition with those obtained

using pulse current deposition generally; pulse current deposition increases the current efficiency of manganese deposition, thickness of deposit, content of alloying molybdenum and titanium dopant and decreases content of oxygen in the deposit.

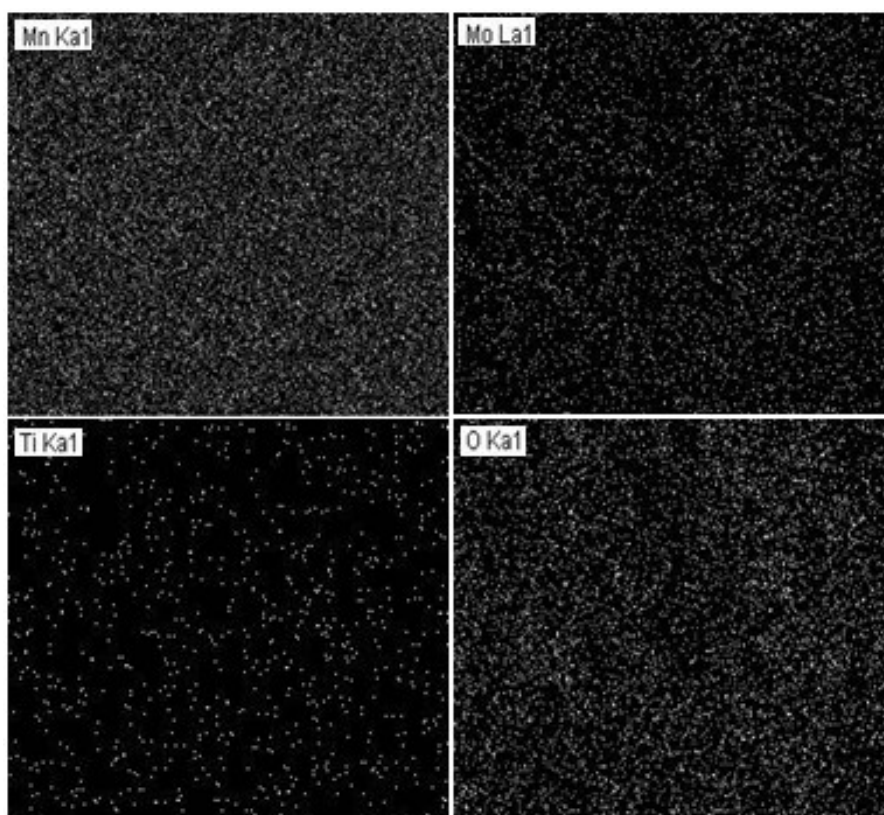
**Table 1: Variation in composition, current efficiency (CE %) and thickness ( $\delta$ ) of pc-deposited MnMo-oxide anode prepared in 0.2M Mn<sup>2+</sup>-0.003M Mo<sup>6+</sup> electrolyte of pH 0.0 at T<sub>on</sub> = 1 sec and different T<sub>off</sub> compared with dc-deposited MnMo-oxide anode**

T <sub>off</sub>	O%	Ti%	Mn%	Mo%	CE %	$\delta$ $\mu\text{m}$
0.001	79.32	0.13	18.02	2.62	5.39	13.94
0.010	77.21	0.12	15.70	2.55	4.99	13.39
0.100	78.84	0.17	18.41	2.57	6.58	17.37
1.000	79.79	0.21	16.68	3.31	5.09	13.51
dc	81.91	0.11	15.11	2.43	4.65	12.12

At this stage of characterization, the improvement in the performance of MnMo-oxide anode by pulse deposition can be attributed to optimizing deposit composition and thickness along with a reduction in the total oxygen content of the deposit. These results indicate that, pulse current deposition is more beneficial than direct current deposition for improving the performance of MnMo-oxide anode.

SEM image analysis illustrates that all elements constituting MnMoTi-oxide deposit were homogeneously distributed in oxide surface, referring to the formation of homogenous single-phase solid solution oxides (Figure 6).

The effect of  $I_p$  has been examined over deposition current density range from 300 to 900 Am<sup>-2</sup>. The results have revealed that  $I_p$  value of 600 Am<sup>-2</sup> presents the optimum deposition current density during pulse deposition for tailoring oxide anode with the best OEE.



**Figure 6:** Mapping images of elements constituting deposited MnMoTi-oxide anode prepared by using pulse anodic current deposition.

**3- Effect of addition of  $\text{Ir}^{4+}$  species on the performance of MnMo-oxide anode during electrolysis in 0.5M NaCl solution**

Figure 7 (a and b) show typical example for the variation in OEE and loss in weight with the time of electrolysis for MnMoIr-oxide anode in which the deposition bath was 0.2M  $Mn^{2+}$ -0.003M  $Mo^{6+}$ -xM  $Ir^{4+}$  electrolytes of pH 0.0 for 1 h at  $600Am^{-2}$  with electrolysis in 0.5M NaCl of pH 2 at  $1000Am^{-2}$ .

As seen in Figure 7(a), all anodes show the 100% initial OEE. However a decreasing in OEE for all anodes is noticed during electrolysis. In comparison to MnMo-oxide,  $Ir^{4+}$  addition up to 0.0005M consequently enhances the durability of anode for OEE; its approaches 98.5% OEE after 2000 h of electrolysis. Further increase in  $Ir^{4+}$  concentration results in shorter life of the anode.

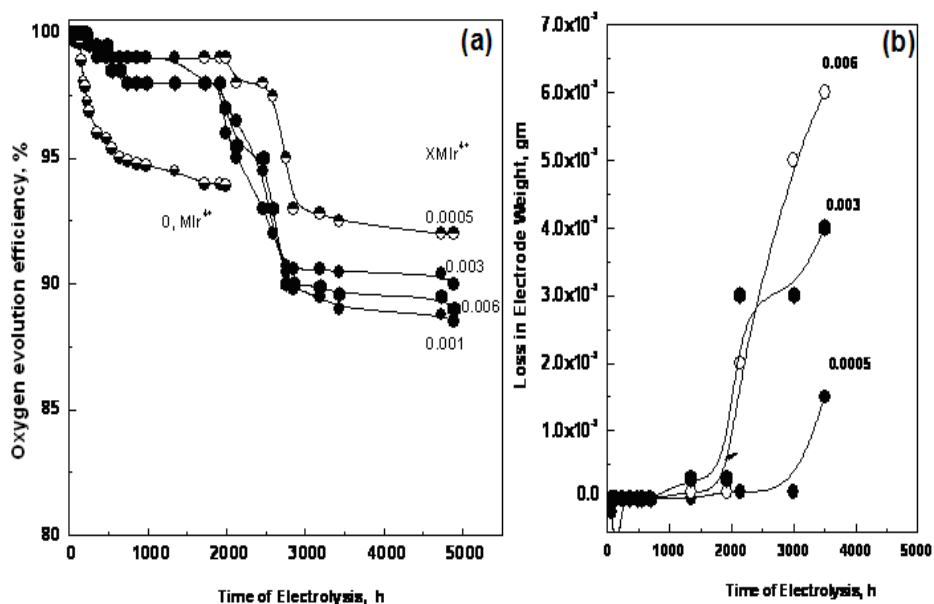


Figure 7: Variation in (a) OEE with time of electrolysis, (b) Loss in weight with time of electrolysis for MnMoIr-oxide anodes prepared in deposition electrolytes of different  $[Ir^{4+}]$ .

As seen in Figure 7(b), addition of  $Ir^{4+}$  to deposition electrolytes generally improves the stability of MnMo-oxide during long term electrolysis. Meanwhile, MnMoIr-oxide anode which shows the best performance for OEE by deposition at 0.0005M  $Ir^{4+}$  exhibits almost no loss in weight up to 3000 h of electrolysis.

## Conclusion

Pulse current deposition is more beneficial than direct current deposition for improving the performance of MnMo-oxide anode.

Pulse current value of  $600 \text{ Am}^{-2}$  presents the optimum deposition current density during pulse deposition for tailoring oxide anode with the best OEE.

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