
**TRIALS FOR BEST OXYGEN EVOLUTION EFFICIENCY OF MnMo-
OXIDE ANODE DEPOSITED ON IrO₂/Ti SUBSTRATE AND
ELECTROLYZED IN 0.5M NaCl**

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Abstract

Hydrogen is produced in this study by direct electrolysis at 1000 Am⁻² 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 IrO₂/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 IrO₂ and Ta₂O₅ 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 MnSO₄ 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 MnO₂ 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 H₂SO₄ 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- IrO₂ coating and post treatment

Punched titanium was coated with very thin layer of IrO₂ 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⁻² IrO₂ 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 IrO₂/Ti electrodes were anodically polarized at 1000 Am⁻² for 5 mins. in 10M NaOH solution, then in 1M H₂SO₄ 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 MnSO₄, 0.003M Na₂MoO₄, 0.00~0.006M H₂IrCl₆. The concentrations of Mn²⁺ and Mo⁶⁺ species were selected based on data reported elsewhere [12]. The pH of the solution was adjusted by adding 18M H₂SO₄.

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 MnSO_4 as a catholyte. The IrO_2/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 IrO_2/Ti electrodes in stirred solutions at 90°C and current density was 600 Am^{-2} for 0.5-2 h. Pulse current (pc) electrodeposition method has been applied to the preparation of manganese based oxide deposits on IrO_2/Ti substrate. A computer connected to a dc source was used to generate a rectangular pulse current T_{on} and T_{off} respectively. The T_{on} and T_{off} were varied at constant peak current density and the temperature of deposition was 90°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 Am^{-2} until the amount of charge of 300 coulombs, that is 10^6 coulombs 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 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 MnO_2 anode prepared in 0.2M Mn^{2+} electrolyte and MnMo-oxide anode prepared in 0.2M Mn^{2+} -0.003M Mo^{6+} , at 600 Am^{-2} for 1 h were compared. The MnO_2 anode shows the initial 96% OEE. Afterwards, the OEE decreases along with steep increase in the loss in weight of 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 Mn^{4+} species to soluble 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 MnO_2 anode surface after 1400 h of electrolysis revealed significant detachment of catalyst layer from the IrO_2/Ti substrate, which actively evolves chlorine. It can, therefore, be said that the decrease in OEE and significant loss in the anodic weight of MnO_2 anode is attributed to oxidative dissolution and partial detachment of deposit layers from IrO_2/Ti substrate.

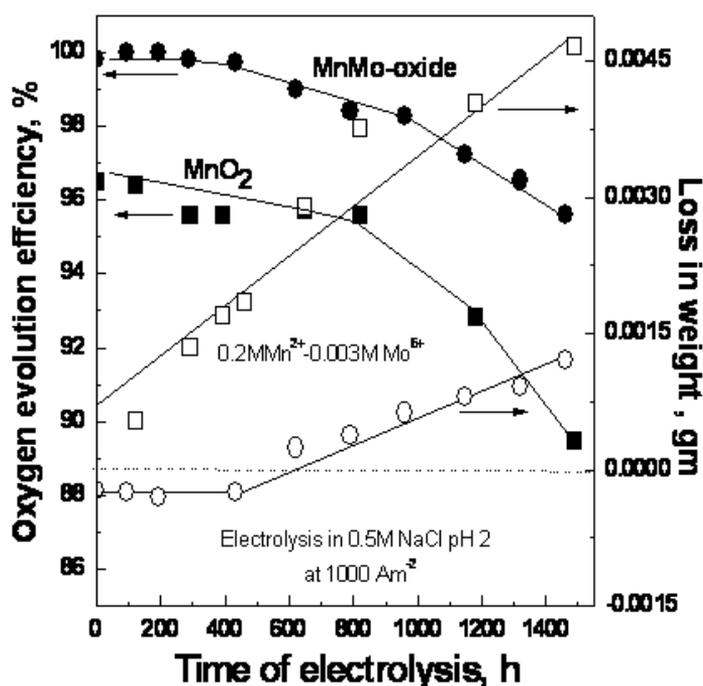


Figure 1: Variation in OEE and loss in weight with time of electrolysis for MnO_2 and MnMo -oxide anodes.

On the other hand, data of Figure 1 reveal that MnMo -oxide anode generally shows better durability (OEE and stability) than 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 I_p 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.

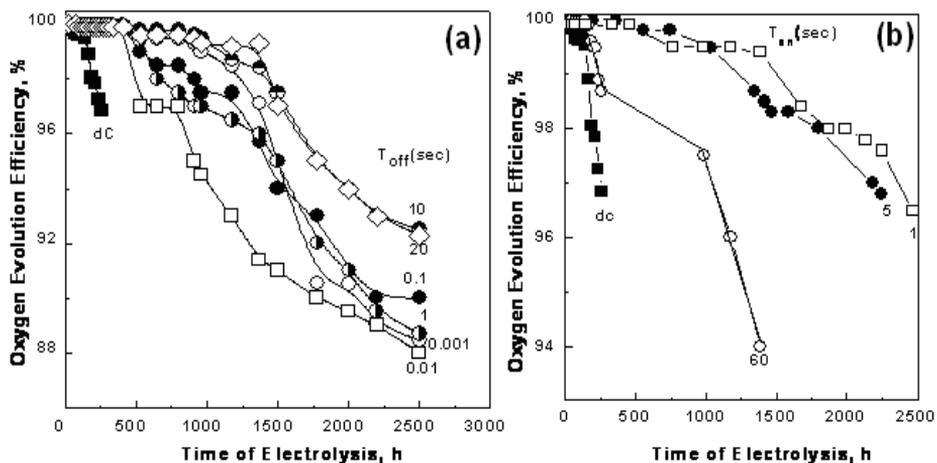


Figure 2: Variation in OEE of pc-deposited anode (a) $T_{on} = 60$ sec and different T_{off} values, (b) $T_{off} = 0.1$ sec and different T_{on} values, with the time of electrolysis, compared with dc-deposited anode.

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).

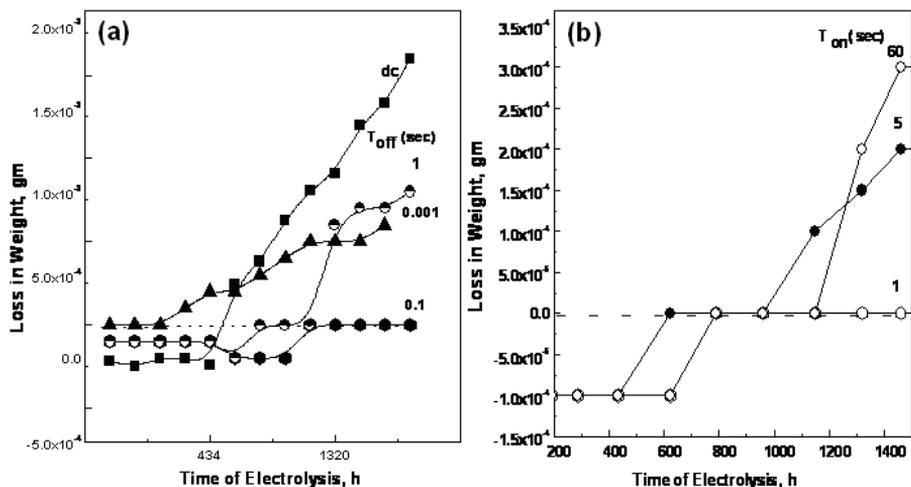


Figure 3: Loss in weight of pc -deposited anode with time of electrolysis (a) $T_{on} = 1$ sec with different T_{off} values, (b) $T_{off} = 0.1$ sec with different T_{on} values.

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)

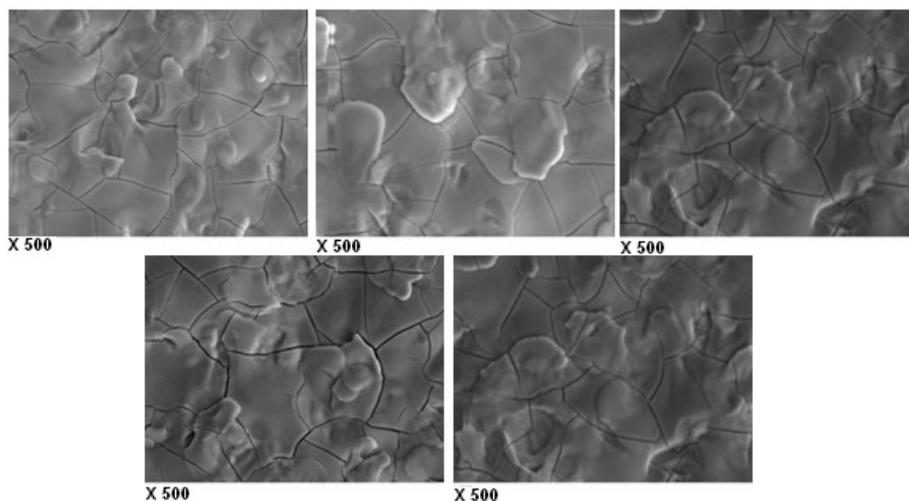


Figure 4: SEM images (a), (b), (c) and (d) for pulse deposited MnMo- oxide anodes prepared in 0.2M Mn^{2+} - 0.003M Mo^{6+} electrolyte of pH 0.0 at constant $T_{\text{on}} = 1$ sec and different T_{off} values of 0.001, 0.01, 0.1 and 1 sec, respectively compared with SEM image (e) for dc- deposited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

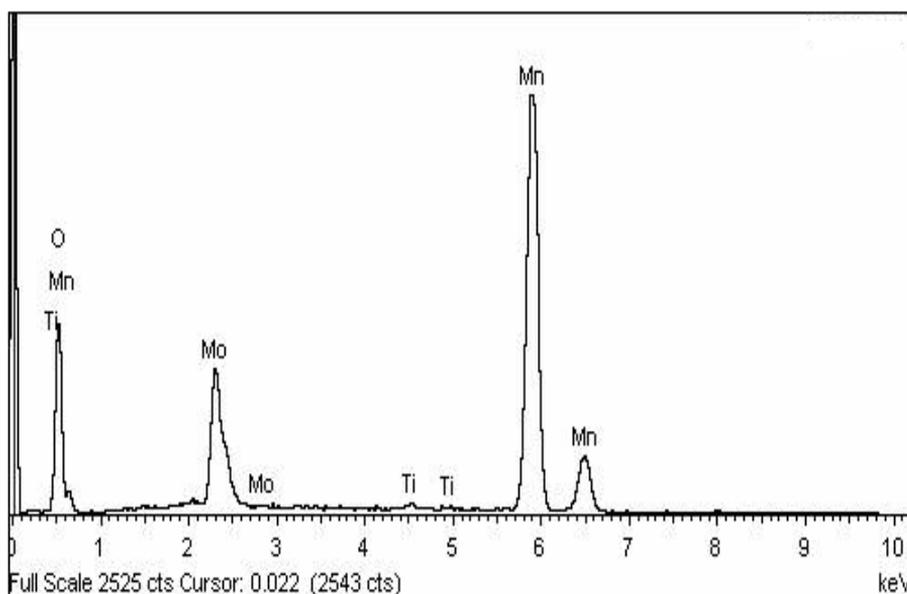


Figure 5: EDX spectrum of MnMo-oxide anode prepared in 0.2M Mn^{2+} -0.003M Mo^{6+} electrolyte of pH 0.0 for 1h at $600Am^{-2}$ at $T_{off} = 0.1$ sec and $T_{on} = 1$ sec using pulse current deposition.

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 (δ) of pc-deposited MnMo-oxide anode prepared in 0.2M Mn²⁺-0.003M Mo⁶⁺ electrolyte of pH 0.0 at T_{on} = 1 sec and different T_{off} compared with dc-deposited MnMo-oxide anode

T _{off}	O%	Ti%	Mn%	Mo%	CE %	δ μm
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 Am². The results have revealed that I_p value of 600 Am² presents the optimum deposition current density during pulse deposition for tailoring oxide anode with the best OEE.

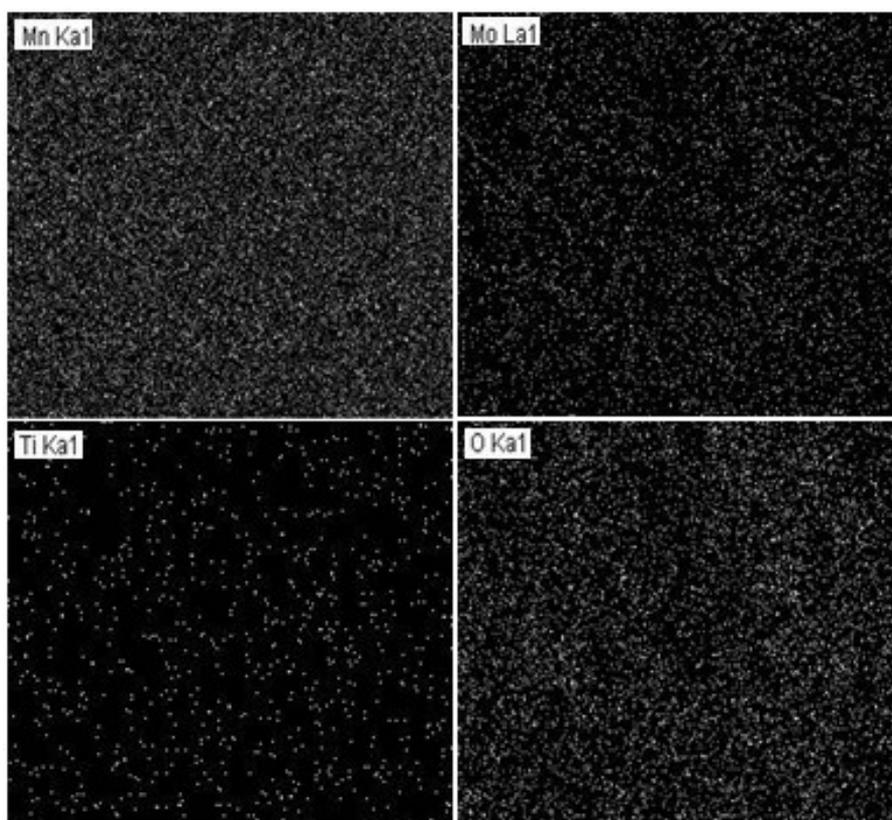


Figure 6: Mapping images of elements constituting deposited MnMoTi-oxide anode prepared by using pulse anodic current deposition.

3- Effect of addition of 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.

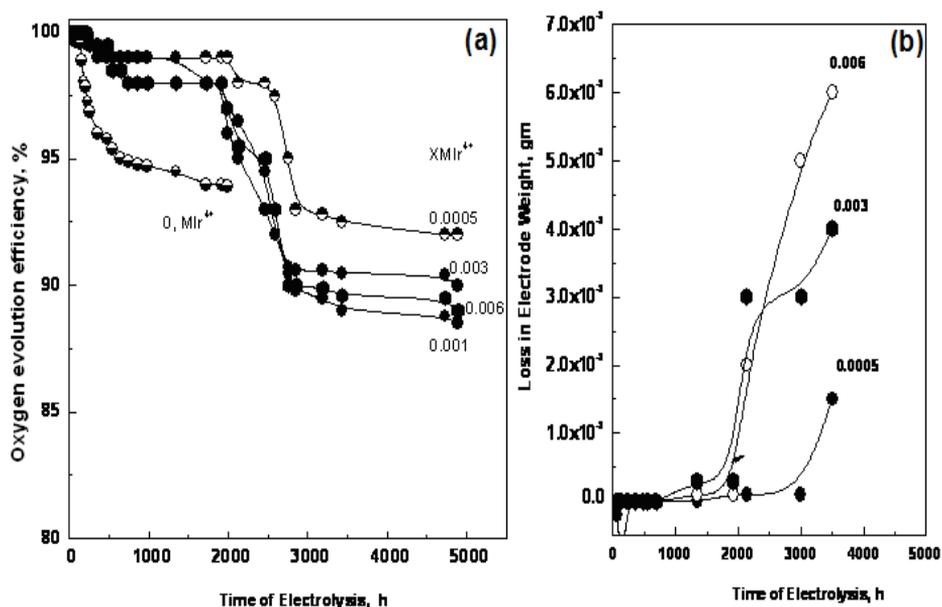


Figure 7: Variation in (a) OEE with time of electrolysis, (b) Loss in weight with time of electrolysis for MnMoIr-oxide anodes prepared in deposition electrolytes of different $[Ir^{4+}]$.

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 Am^{-2} presents the optimum deposition current density during pulse deposition for tailoring oxide anode with the best OEE.

References

1. J. O. M. Bockris, and T. N. Veziroglu; *Int. J. Hydrogen Energy* 8 (1983) 323.
2. M. G. Salameh; *Appl. Energy* 75 (2003) 33.
3. B. Suresh, S. Schlag, and Y. Inogucji; „Chemical Economics Handbook Marketing Research Report”, SRI Consulting, (2004).
4. Z. D. Wei, M. B. Ji, S. G. Ghen, Y. Liu, C. X. Sun, G. Z. Yin, P. K. Shen and S. H. Chan; *Electrochim. Acta* 52 (2007) 3323.
5. K. Kikuchi, S. Nagata, Y. Tanaka, Y. Saihara and Z. Ogumi; *J. Electroanal Chem.* 600 (2007) 303.
6. T. N. Veziroglu, and S. Sahin; *Energy Conversion and Management* 49 (2008) 1820.
7. J. E. Bennett; *Int. J. Hydrogen Energy* 5 (1980) 401.
8. K. Hashimoto; *Mater. Sci. Eng.* A179/A180 (1994) 27.
9. Cornell, B. Hakansson and G. Lindbergh; *Electrochim. Acta* 48 (2003) 473.
10. Cornell, B. Hakansson and G. Lindbergh; *J. Electrochem. Soc.* 150 (2003) 6.
11. J. Bahattarai ; *J. Nepal. chem. Soc.* 23 (2008/2009) 21.
12. N. A. AbdelGhany, N. Kumagai, S. Meguro, K. Asami and K. Hashimoto; *Electrochim. Acta* 84 (2002) 993.
13. E. Rasten; Ph.D. Thesis, Norwegian University of Science and Technology Trondheim, Norway, October (2001).

