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## STUDY ON ELECTROCHEMICAL PERFORMANCE OF DIMENSIONALLY STABLE ANODES DURING ZINC ELECTROWINNING

In zinc electrowinning, small amounts of manganese ions additives are needed in the electrolyte to reduce the corrosion of anodes and minimize the contamination of cathodic zinc by dissolved lead. However, excess manganese oxide could cover the dimensionally stable anodes (DSA) surface and decrease their service life. Additives of phosphoric acid are put in the electrolyte to complex the manganic  $Mn^{3+}$  ion and hence reduce its disproportionation to  $MnO_2$ . In the investigation, phosphoric acid was added to sulfuric acid or zinc electrolytes, and conventional and recent electrochemical measurements were carried out to examine electrochemical behaviour of DSA ( $Ti/IrO_2-Ta_2O_5$ ) anode during zinc electrolysis at  $48\text{ mA/cm}^2$  and  $39^\circ\text{C}$ . It was observed that the anodic potentials of DSA anodes were lower by 27 mV after 5 h polarization in the zinc electrolyte containing 35 g/L phosphoric acid at  $39^\circ\text{C}$ . Electrochemical impedance measurements show that the addition of 35 ml/L  $H_3PO_4$  to the zinc electrolyte can increase impedance resistances of the DSA mesh anodes. Cyclic voltammogram studies (CV) at a scan rate of 5 mV/s without agitation show that the oxidation peak in the solution with 35 ml/L phosphoric acid addition is highest, followed by that with 17 ml/L phosphoric acid addition and that without addition of phosphoric acid.

*Keywords:* Zinc electrowinning; Dimensionally stable anodes; Manganese ions; Phosphoric acid; electrochemical performance

### 1. Introduction

The traditional anodes of choice in the zinc electrowinning industry have been lead based alloys. However, these anodes display much energy consumption and high corrosion resistance during electrolysis. Also, the lead impurity will contaminate the zinc deposit [1]. To solve the problems, other anode materials such as dimensionally stable anodes (DSA), consisting of mixed metal oxide coatings on titanium or nickel substrates, have been investigated. Coating  $IrO_2-Ta_2O_5$  on the surfaces of titanium base anodes is used in the zinc sulfuric acid electrolyte. After 24 hours of anodic polarization,  $Ti/IrO_2-Ta_2O_5$  coating mesh anode has much lower oxygen evolution overpotential and better corrosion performance than Pb-0.7% Ag lead anode [2].

It was reported that good DSA anode materials should have low overpotential, insoluble protective layer in electrolyte and have enough resistance to the mechanical and chemical action of oxygen evolution on the anodic surfaces [3].  $RuO_2$ , which is a platinum group metal ruthenium oxide, has a low overpotential. However,  $RuO_4$  will be formed under the reaction of  $O_2$  and dissolved continuously, resulting in the loss of active sub-

stances, which makes the poor service life of ruthenium coating in strong electrowinning environment. For improving the stability of active oxides, it is a feasible approach to add other inert components, such as  $Ta_2O_5$  and  $SnO_2$ , into  $RuO_2$  coating, which can effectively protect the active. It was found that the  $IrO_2$  and  $RuO_2$  mixed compounds have good electrocatalytic properties due to their advanced properties of these two oxides by addition of  $IrO_2$  to  $RuO_2 + TiO_2$  coating [4].

$IrO_2-Ta_2O_5$  coating Ti based anodes containing different  $SnO_2$  were prepared by thermal decomposition method. The electrocatalytic performance of the coatings were tested by cyclic voltammetry, polarization curve study and electrochemical impedance spectroscopy. The corrosion resistance of the coating was measured by enhanced life. The results show that after doping  $SnO_2$ , the specific surface area of  $IrO_2-Ta_2O_5$  coating on Ti based anode increases, also the oxygen evolution potential and total resistance of the coating rise, but the corrosion resistance decreases. When the content of  $SnO_2$  is 7.7%, the comprehensive electrocatalytic performance is the best [3].

Zhang et al. (2017) had researched the mesh  $Ti/IrO_2$  (30%)- $Ta_2O_5$  (70%) and the mesh  $Ti/MnO_2$  DSA in a zinc electrolyte at

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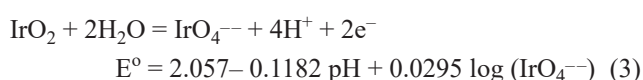
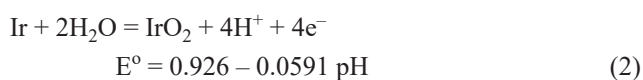
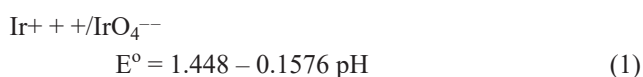
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a current density of 50 mA/cm<sup>2</sup> and 38°C, it was found that the Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> mesh DSA anode had the lower corrosion rate during the potential decay, the better performance and a higher current efficiency during polarization than the Ti/MnO<sub>2</sub> DSA anode [5].

IrO<sub>2</sub> has the widest electrocatalytic activity for oxygen evolution reaction in sulfuric acid electrolyte among the three coatings of IrO<sub>2</sub>, RuO<sub>2</sub> and Ta<sub>2</sub>O<sub>5</sub>. Also, IrO<sub>2</sub> service life is 20 times of that of RuO<sub>2</sub>. However, since IrO<sub>2</sub> is more expensive than RuO<sub>2</sub>, other components, such as Ta<sub>2</sub>O<sub>5</sub>, are added to the coating for saving cost and improving coating performance [6]. In addition, IrO<sub>2</sub> is a good catalyst for the oxygen evolution reaction of DSA anode in the electrolytic solution containing chloride ions, so Ti/IrO<sub>2</sub> is also employed to extract zinc from zinc content waste liquid containing considerable amount of chloride ions [7].

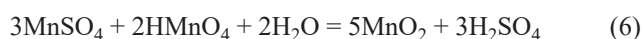
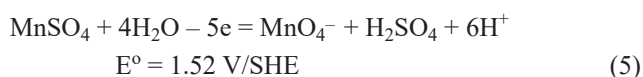
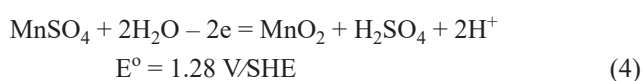
The surface electrochemical behaviour of DSA anodes is controlled by the Ir(III)/Ir(IV) redox transition as the surface properties [8]:



Manganese added into the zinc electrolyte leads to reduce the corrosion of anodes and minimizing the contamination of lead impurity in the zinc cathodes [9]. Manganese ions react in the process of surface oxidation on the DSA anode, forming soluble substance or insoluble manganese dioxide, which could passivate the DSA anode. Increase of concentrations of manganese ions during the zinc electrowinning can cause a significant decrease in current efficiency, which have to be removed or controlled when building up to a certain level. So the presence of manganese has dual effects, positive and negative, depending on its concentration in the electrolytes [10,11].

The particles of MnO<sub>2</sub>, which are produced on the anodes, passivate the anode surface and lead to an increase in anode potential. Manganese oxide deposition blocks the catalytic sites on the DSA anodes [12]. Mn<sup>2+</sup> ions in the electrolyte could be oxidized to MnO<sub>4</sub><sup>-</sup> which was proposed to react immediately with Mn<sup>2+</sup> to form Mn<sup>3+</sup> and finally MnO<sub>2</sub>. Manganese ions can be present as Mn(II), Mn(III), Mn(VII) and possibly also Mn(IV) in strongly acidic solutions [13]. It is apparent that a number of manganese species can be oxidized to form deposits on the surface of an electrode, with MnO<sub>2</sub> as the predominant product.

The reactions of Mn<sup>2+</sup> on the anode are as follows [14]:



The oxidation of Mn<sup>2+</sup> to Mn<sup>3+</sup> and Mn<sup>2+</sup> to MnO<sub>4</sub><sup>-</sup> both have similar standard potentials of about 1.51 V.



The effect of certain compounds on the inhibition of MnO<sub>2</sub> formation has been studied using additives such as soluble phosphorous (V) and arsenic (III) [15]. For the neutralized zinc solution at pH 5, oxidative precipitation using a strong oxidant such as Caro's acid and SO<sub>2</sub>/O<sub>2</sub> can selectively precipitate manganese as insoluble MnO<sub>2</sub> or Mn(OOH), leaving other impurities, e.g., Mg<sup>2+</sup>, Cl<sup>-</sup>, F<sup>-</sup>, etc. in the circuit. Solvent extraction of zinc using D2EHPA (di-2-ethylhexyl phosphoric acid) can selectively recover zinc from the solution and leave other impurities including manganese in the electrolytes [16].

Velayutham et al (1993) found that phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) can be used to complex the Mn<sup>3+</sup> ion and hence reduce its disproportionation of MnO<sub>2</sub>. Also, it can stabilize the Mn<sup>3+</sup> ion in the electrolyte, and the anodic peak current decreased as compared to that in the electrolyte with H<sub>2</sub>SO<sub>4</sub> only [17]. Few additions of H<sub>3</sub>PO<sub>4</sub> to the sulfuric acid may diminish the deposition of MnO<sub>2</sub> on the anodic surface during oxygen evolution reaction [18]. In addition, the inhibition of MnO<sub>2</sub> formation by arsenic and phosphorous compounds can be explained on the basis of preferential adsorption of such compounds on the electrode surface [16].

Ramachandran et al. (1985) studied the addition of phosphoric acid compounds as a deterrent for MnO<sub>2</sub> deposition using galvanostatic technique because of the probable role of these compounds in the inhibition of anodic formation of MnO<sub>2</sub> [19]. The presence of manganese in solution is deterrent for the operation of catalytic anodes since a coating of MnO<sub>2</sub> is formed on the anode surface, which results in reducing catalytic activity.

In this manuscript, to overcome the shortcoming of the DSA anodes, the electrochemical performance of the Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> mesh and plate anodes was studied in the zinc electrolyte containing different Mn<sup>2+</sup> by recent electrochemical measurements such as electrochemical impedance tests and electrochemical noise measurements. 17 g/L and 35 g/L phosphoric acid was added to the zinc electrolyte to complex the manganic Mn<sup>3+</sup> ion and hence reduce its disproportionation to MnO<sub>2</sub>. This can result in increase of their service life, electrochemical performance and then replace of the traditional lead silver anodes. Also, the DSA can improve the quality of zinc deposit for the zinc electrowinning industry.

## 2. Experimental

### 2.1. Materials and sample preparation

The Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> mesh and plate anodes are mainly fabricated from Ti/ (30%)IrO<sub>2</sub>-(70%)Ta<sub>2</sub>O<sub>5</sub>, which are provided by Hydro-Québec research institute. One plate of platinum and one

plate of Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> mesh and plate were used as cathode, and anode respectively. All plates were casted in polyester resin in order to obtain an exposed surface area of 1 cm<sup>2</sup>. Ag, AgCl/KCl<sub>(sat)</sub> (0.199 V/SHE) was used as reference electrode. The electrodes are mounted in three-cell electrode with inter distance of 2 cm. Before electrolysis, the cathode was manually polished by several grits SiC papers then washed by distilled water & ethanol and dried before the immersion in the electrolyte. While the anode was only washed by distilled water & ethanol and dried before the immersion in the electrolyte [5].

The zinc sulphate electrolytes used in this study were prepared from ZnSO<sub>4</sub>·7H<sub>2</sub>O, and pure H<sub>2</sub>SO<sub>4</sub> (Conc. 98%) and 6, 9, and 12 g/L Mn<sup>2+</sup>, respectively. The cations of Mn<sup>2+</sup> was added as the form of MnSO<sub>4</sub>·2H<sub>2</sub>O. The blank electrolytic solution was always prepared from 60 g L<sup>-1</sup> of Zn<sup>2+</sup> and 170 g L<sup>-1</sup> of H<sub>2</sub>SO<sub>4</sub>. The standard zinc electrolyte was based on electrolytic solution with 6, 9, and 12 g L<sup>-1</sup> Mn<sup>2+</sup>. Reagents were supplied from Lab mat and VWR Canada. Small-scale galvanostatic electrolysis was performed in 1000 ml solution in double-glazed beaker. The solution was heated by the flow of thermostated water in order to maintain a constant working temperature. The electrolyte was stirred at 412 rpm by a magnetical stirrer (4 cm long and 1 cm in diameter) during the electrochemical measurements except for the CV and the ENM studies.

## 2.2. Experimental setup

Electrochemical studies were based on the analysis of cyclic voltammetric measurements and potentiodynamic polarization tests without agitation in atmospheric conditions by using potentiostat Gamry reference 3000. Cyclic voltammetry experiments were employed to measure the electrochemical performance of the Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> mesh and plate alloy electrodes. The potential was scanned from from -300 to 1800 mV vs OCP for the cathodic potentiodynamic polarization with a constant scan rate of 5 mV s<sup>-1</sup> [20].

After 24 h of polarization, the anode was held for 2 h of decay at open circuit potential (OCP). This is followed by linear polarization (LP) and electrochemical impedance spectroscopy (EIS) tests. LP measurements were carried out at ±20 mV with respect to corrosion potential (E<sub>corr</sub>) at constant scan rate of 0.166 mV/s [21]. EIS tests were carried out at frequency range from 100 kHz to 0.01 Hz with an amplitude of 5 mV. The EIS data were examined using Gamry EchemAnalyst based on the appropriate equivalent electrical circuit [22]. After 24 h of electrolysis, two identical anodes were connected to zero resistance ammeter (ZRA) mode for 2 h controlled by Gamry model PC4/750 – USA. Also, after galvanostatic polarization, the anode was scanned employing scanning reference electrode technique (SRET) using EG&G Instruments model SVP100 – UK. The surface of specimen was adjusted and leveled in parallel with the surface of the Persoex tripod. The probe was lowered using the Z-axis control to negative direction to a distance of z50e100 mm from the specimen surface. The specimen was connected to the

negative input of the apparatus while the probe was connected to the positive one for free corrosion measurement mode. The signal was adjusted at 20 mV of sensitivity and vibrating amplitude of 20 mm. Each scan lasted 15 min for a total period of 2 h. All corrosion tests were performed at least in duplicates to assure a good reproducibility.

## 2.3. Consecutive series of electrochemical testing

The experimental were carried out by the following procedures: (a) Cyclic voltammetry, (b) Chronopotentiometry (galvanostatic), (c) Open circuit potential, (d) Electrochemical noise, (e) Electrochemical impedance measurements, (f) Scanning reference electrode technique.

## 3. Results and discussion

### 3.1. Cyclic voltammetry study for DSA anode

Fig. 1 shows cyclic voltammograms of the fresh surfaces of the DSA-mesh electrodes in 0.5 M/L H<sub>2</sub>SO<sub>4</sub> with and without 9 g/L Mn<sup>2+</sup> addition at a scan rate of 5 mV/s at 39°C without agitation. It was found that addition of 9 g/L Mn<sup>2+</sup> into the sulfuric acid solution decreased the values of oxidation peaks in the sulfuric acid solution. The reason is that addition of Mn<sup>2+</sup> into sulfuric acid solution promoted a formation of MnO<sub>2</sub> layer on the surface of DSA anode and decreased the value of current density.

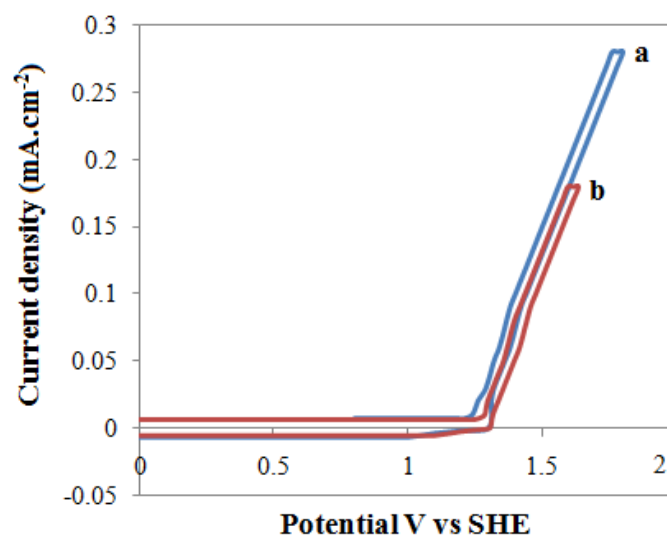


Fig. 1. Cyclic Voltammograms before electrolysis for DSA-mesh electrodes in 0.5 M/L H<sub>2</sub>SO<sub>4</sub> containing different contents of Mn<sup>2+</sup> with addition of (a) 0, (b) 9 g/L at a scan rate of 5 mV/s and 39°C without agitation

The effect of phosphoric acid on the inhibition of MnO<sub>2</sub> formation has been studied using cyclic voltammetric technique. Fig. 2 shows cyclic voltammograms of the fresh surfaces of the DSA-mesh electrodes in 0.5 M/L H<sub>2</sub>SO<sub>4</sub> containing 9 g/L Mn<sup>2+</sup>

in absence and in presence of 17 and 35 ml/L phosphoric acid addition at a scan rate of 5 mV/s at 39°C without agitation. It can be observed the three oxidation peaks at around 1.5 V were corresponding to:  $2\text{H}_2\text{O} - 4\text{e} \rightarrow \text{O}_2 + 4\text{H}^+$  (9) [23]. The oxidation peak in the solution with 35 ml/L phosphoric acid addition is highest, followed by that with 17 ml/L phosphoric acid addition and that without addition of phosphoric acid. It means that addition of 17 and 35 ml/L phosphoric acid to the solution can complex the manganic ion and increase oxidation peak height. Also, the cathodic peak at 1.2 to 1.3 V due to reduction of  $\text{MnO}_2$  is observed only in the electrolyte without phosphoric acid. The reduction reaction is corresponding to:  $\text{MnO}_2 + \text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e} = \text{MnSO}_4 + 2\text{H}_2\text{O}$  (10) since the potential of reduction reaction of  $\text{MnO}_2$  is 1.28 V/SHE. In addition, some  $\text{MnO}_2$  particles were also observed to suspend in the electrolyte.

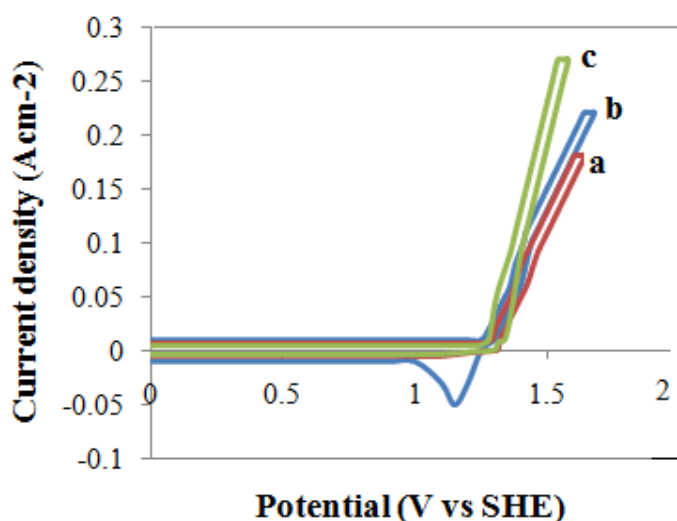


Fig. 2. Cyclic Voltammograms before electrolysis for DSA-mesh electrodes in 0.5 M  $\text{H}_2\text{SO}_4$  containing 9 g/L  $\text{Mn}^{2+}$  with addition phosphoric acid of (a) 0; (b) 17 g/L; (c) 35 g/L at a scan rate of 5 mV/s and 39°C without agitation

### 3.2. Anodic potential for the oxygen evolution reaction (ORE) on the DSA anode in acid zinc sulphate electrolyte with different contents of $\text{Mn}^{2+}$

The anodic potentials of anodic galvanostatic polarization at 48 mA/cm<sup>2</sup> and 39°C for the DSA-mesh anode in acid zinc sulphate electrolyte containing 6, 9 and 12 g/L  $\text{Mn}^{2+}$  with time have been investigated in Fig. 3. After five hours of electrolysis, the solution became purple red because of the formation of permanganate ions.

At the end of the electrolysis, the potentials of the DSA-mesh anode in standard electrolyte with addition of 6 g/L  $\text{Mn}^{2+}$ , 9 g/L  $\text{Mn}^{2+}$  and 12 g/L  $\text{Mn}^{2+}$  were 1638, 1653, and 1686 mV/SHE, respectively. The anodic potentials increased from 1653 to 1686 mV when manganese ion was added from 9 to 12 g/L. The reason is that more manganese ion added in the zinc electrolyte resulted in more manganese oxides layer on the surfaces of the DSA-mesh anodes. This leads to higher overpotential on

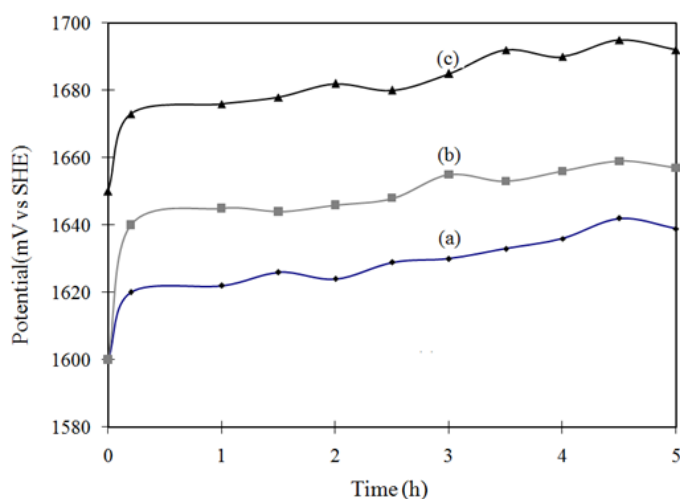


Fig. 3. 5 h galvanostatic test of DSA-mesh anode at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing (a) 6 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$ ; (c) 12 g/L  $\text{Mn}^{2+}$

the DSA-mesh anodes with more anodic potential. It was found that the anodic potential was increased from 1638 to 1653 mV when addition of manganese ion increased from 6 to 9 g/L, the range of potential increased for addition manganese ion from 6 to 9 g/L is much less than that of addition manganese ion from 9 to 12 g/L, it is possible that the manganese ion added to the zinc electrolyte has a function of depolarization [13].

To complex the manganic  $\text{Mn}^{3+}$  ion and hence reduce its disproportionation of  $\text{MnO}_2$ , the anodic potentials of the DSA-mesh anodes were measured at a current density of 48 mA/cm<sup>2</sup> and 39°C in acid zinc sulphate electrolyte containing 9 g/L  $\text{Mn}^{2+}$ , or 9 g/L  $\text{Mn}^{2+}$  with addition of 17 and 35 ml/L  $\text{H}_3\text{PO}_4$  on DSA-mesh anodes for five hours. The anodic potentials vs time curves are shown in Fig. 4.

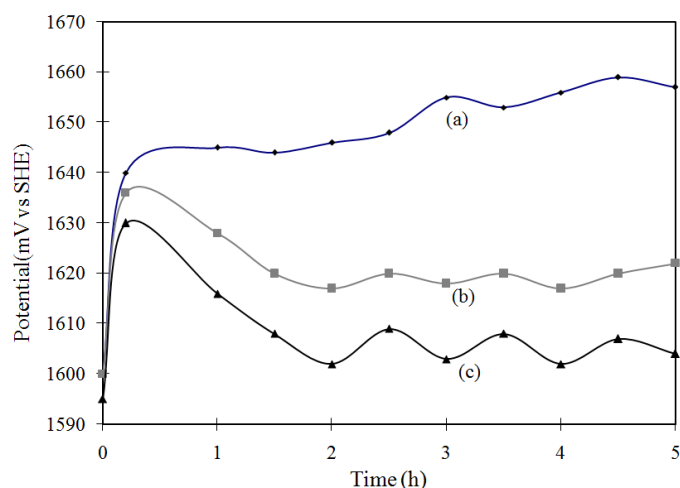
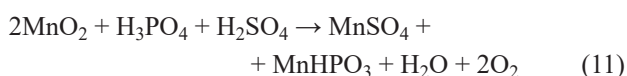


Fig. 4. 5 h galvanostatic test of DSA-mesh anode at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing (a) 9 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$ ; (c) 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$

Fig. 4 shows that there is a cell voltage relating to the standard electrolyte with addition of different concentrations of

phosphoric acid. When the different concentrations of phosphoric acid were added to the electrolyte, it results in the decrease of the anodic potentials. At the end of 5 h galvanostatic test, the anodic potentials for the DSA anode with 9 g/L  $\text{Mn}^{2+}$  alone (a), 9 g/L  $\text{Mn}^{2+}$  with addition of 17 ml/L  $\text{H}_3\text{PO}_4$  (b) and 9 g/L  $\text{Mn}^{2+}$  with 35 ml/L  $\text{H}_3\text{PO}_4$  (c) were 1653, 1624 and 1607 mV/SHE, respectively. It has been shown that the lower potential can be maintained for longer periods when there is sufficient phosphoric acid to complex the manganic ion [16]. The presence of phosphoric acid confirms the reduction of  $\text{MnO}_2$  on the surface of the DSA anode. Few additions of  $\text{H}_3\text{PO}_4$  to the sulphuric acid can diminish the deposition of  $\text{MnO}_2$  on the surface of anode during oxygen evolution reaction. The reaction should be as follows [16].



### 3.3. Potential decay of DSA mesh anode after 5 h galvanostatic polarization in acid zinc sulphate electrolyte with 6, 9 and 12 g/L $\text{Mn}^{2+}$

After 5 h galvanostatic polarization, the corrosion potential decay of one hour was recorded, then potentiodynamic measurements were performed to measure the corrosion potential ( $E_{\text{corr}}$ ) and corrosion current ( $i_{\text{corr}}$ ). The tests were followed by second hour potential decay and another potentiodynamic measurement. The curves of potential decay of the DSA-mesh anode following 5 h polarization in acid zinc sulphate electrolyte containing 6, 9 and 12 g/L  $\text{Mn}^{2+}$  respectively are shown in Fig. 5. The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current ( $i_{\text{corr}}$ ) of the DSA anode after the first hour and the second hour potential decay following 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> in the zinc electrolyte containing 6, 9 and 12 g/L  $\text{Mn}^{2+}$ , respectively, are shown in TABLE 1.

Fig. 5 shows that the potential of the DSA-mesh anode in the zinc electrolyte containing 12 g/L  $\text{Mn}^{2+}$  drop slowly, and

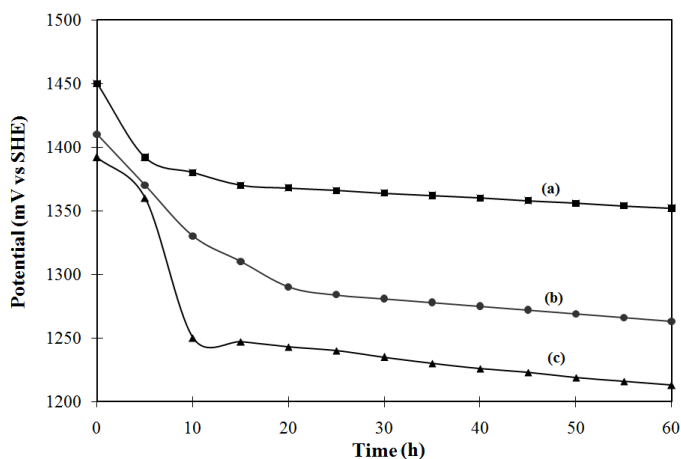


Fig. 5. Potential decay of the first hour for the DSA-mesh anode after 5 hours of galvanostatic polarization at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing (a) 12 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$ ; (c) 6 g/L  $\text{Mn}^{2+}$

had a longest potential plateaus among the DSA anode in the zinc electrolyte containing different contents of manganese ion around 1370 mV/SHE corresponding to the theoretical potential value of the  $\text{MnO}_2/\text{Mn}^{2+}$  equilibrium. This shows a spontaneous transformation of manganese dioxide into manganese sulphate because thermodynamically manganese dioxide is unstable on the surface of manganese in the sulphuric acid solution [24]. The potentials at the end of 1 hour for the DSA-mesh anode in acid zinc sulphate electrolyte containing 6 g/L  $\text{Mn}^{2+}$ , 9 g/L  $\text{Mn}^{2+}$ , 12 g/L  $\text{Mn}^{2+}$  were 1212, 1233, and 1352 mV vs. SHE respectively. After the galvanostatic polarization, it was observed that the less potential leads to the less corrosion rate for the DSA-mesh anode in a bath with  $\text{MnSO}_4$  addition.

TABLE 1

Corrosion potentials, corrosion currents of the DSA-mesh anodes after one hour and two hour potential decay in the zinc electrolyte containing 6 g/L  $\text{Mn}^{2+}$ , 9 g/L  $\text{Mn}^{2+}$  and 12 g/L  $\text{Mn}^{2+}$  with agitation

Anodes $\text{Mn}^{2+}$ contents	$E_{\text{corr}}$ (mV vs SHE)		$i_{\text{corr}}$ ( $\mu\text{Acm}^{-2}$ )	
	One hour decay	Two hour decay	One hour decay	Two hour decay
6	1212	714	65.3	46.7
9	1263	743	51.6	40.6
12	1352	894	51.4	38.8

TABLE 1 shows that after one and two hour potential decay following 5 hours of galvanostatic polarization at 48 mA/cm<sup>2</sup> in acid zinc sulphate electrolyte containing 6 g/L  $\text{Mn}^{2+}$ , 9 g/L  $\text{Mn}^{2+}$  and 12 g/L  $\text{Mn}^{2+}$  respectively with agitation at 39°C, it was seen that addition of more manganese into the zinc electrolyte results in the more decrease of the corrosion rate of the DSA-mesh anode. The corrosion of the DSA-mesh anode after the second decay was lower than that after the first decay.

Fig. 6 shows that the potential decay of the DSA anode in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$ , or 9 g/L  $\text{Mn}^{2+}$  with addition of 17 and 35 ml/L  $\text{H}_3\text{PO}_4$  on DSA-mesh anode, respec-

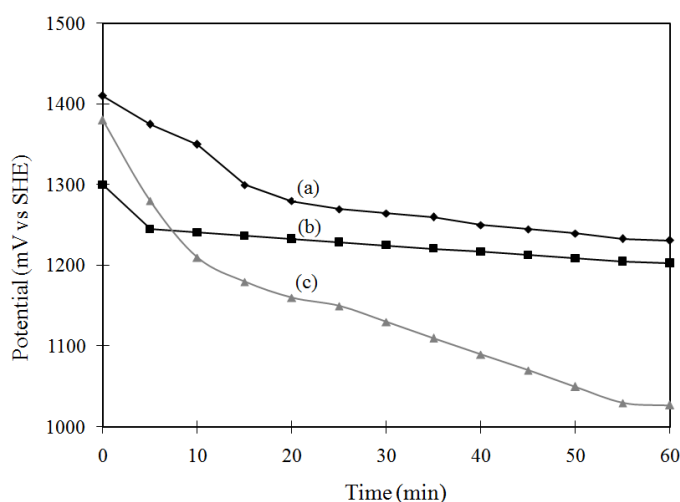


Fig. 6. Potential decay of the DSA-mesh anode after 5 hours of galvanostatic polarization at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing (a) 9 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$ ; (c) 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$

tively. The potentials at the end of 1 hour for the DSA-mesh anode in acid zinc sulphate electrolyte containing 9 g/L  $\text{Mn}^{2+}$ , or 9 g/L  $\text{Mn}^{2+}$  with addition of 17 and 35 ml/L  $\text{H}_3\text{PO}_4$  on DSA-mesh anodes were 1263, 1235, and 1048 mV vs. SHE respectively. The corrosion potential ( $E_{\text{corr}}$ ) and corrosion current ( $i_{\text{corr}}$ ) of the DSA-mesh anode after the first hour and the second hour potential decay following 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$ , or 9 g/L  $\text{Mn}^{2+}$  with addition of 17 and 35 ml/L  $\text{H}_3\text{PO}_4$  additions were shown in TABLE 2.

As shown in Fig. 6, the open circuit potential was lower when phosphoric acid was added to the electrolyte. The lower potential can be maintained for longer periods when there is sufficient phosphoric acid to complex the manganic ion. Also, it was found that addition of 35 ml/L  $\text{H}_3\text{PO}_4$  to the zinc electrolyte decreased more potential value than that of 17 ml/L  $\text{H}_3\text{PO}_4$ . It means that addition of 35 ml/L  $\text{H}_3\text{PO}_4$  into the zinc electrolyte can reduce more  $\text{MnO}_2$  to  $\text{MnSO}_4$  than that of 17 ml/L  $\text{H}_3\text{PO}_4$ .

TABLE 2

Corrosion potentials, corrosion currents of the DSA-mesh anode after one hour and two hour potential decay in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  with addition of 0, 17 and 35 ml/L  $\text{H}_3\text{PO}_4$  with agitation, respectively

$\text{H}_3\text{PO}_4$ contents	$E_{\text{corr}}$ (mV vs SHE)		$i_{\text{corr}}$ ( $\mu\text{Acm}^{-2}$ )	
	One hour decay	Two hour decay	One hour decay	Two hour decay
0	1263	743	51.6	40.6
17	1235	718	59.2	48.4
35	1048	549	54.7	43.5

TABLE 2 shows that addition of 17 ml/L  $\text{H}_3\text{PO}_4$  into the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  results in an increase (~12.7%) the corrosion rate of the DSA-mesh anode. It implies that addition 17 ml/L  $\text{H}_3\text{PO}_4$  to the electrolyte reduced the  $\text{MnO}_2$  layer and increased the corrosion rates of DSA-mesh anodes. However, the addition of 35 ml/L  $\text{H}_3\text{PO}_4$  into the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  results in a decrease (~7.6%) of the corrosion rate of the DSA anode compared to that of 17 ml/L  $\text{H}_3\text{PO}_4$ , it is very possible that the  $\text{H}_3\text{PO}_4$  forms a phosphoric oxide layer on the surface of DSA anode and protects it from the corrosion. Also, the corrosion rates and potential values of the DSA anode after the second decay were lower than that after the first decay.

### 3.4. Electrochemical noise measurements after galvanostatic polarization

Zero resistance ammeters in electrochemical noise measurements were employed to monitor the corrosion of DSA-mesh anode during electrolysis in situ. For the measurements, the most important parameters of the statistical analysis in the time domain, is the noise resistance ( $R_n$ ), defined as the proportion of a standard deviation of the potential noise to that of a current

noise which is related to the polarization resistance ( $R_p$ ). The opposite  $R_n$  is admittance, unit of Siemens (S), which is ratio to the corrosion rate [25,26]. It was found that electrochemical noise is a good technique to investigate the influence of silver on the corrosion rate of lead anodes. After 5 h of polarization in the zinc sulphate acidic solutions with different  $\text{Mn}^{2+}$  contents, it was carried out for the evolution of admittance “ $1/R_n$ ” (mS) during 16 h of decaying of the DSA-mesh anodes (Fig. 7). In situ measurements in a continuous way were summarized every 1 h period in one point by statistics.

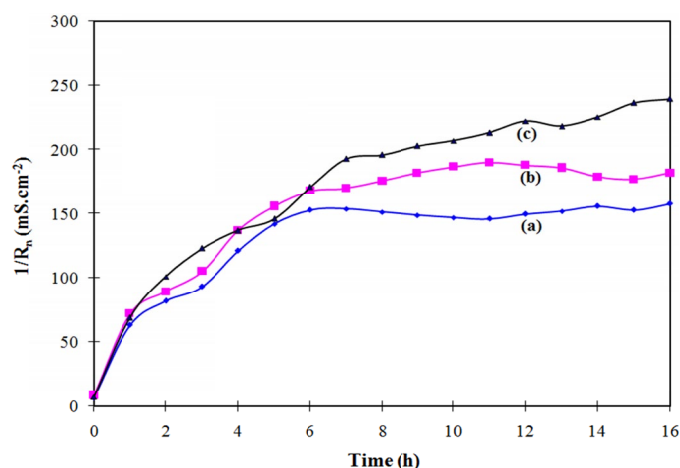


Fig. 7. Evolution of admittance “ $1/R_n$ ” (mS/cm<sup>2</sup>) of the DSA-mesh anodes following 5 h galvanostatic polarization during 16 h immersion period in the zinc electrolyte containing (a) 12 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$  and (c) 6 g/L  $\text{Mn}^{2+}$

Seen from Fig. 7, it was found that the DSA mesh anode in the zinc electrolyte containing 12 g/L  $\text{Mn}^{2+}$  (149 mS/cm<sup>2</sup>) had the lowest corrosion rate among the three test results, followed by 9 g/L  $\text{Mn}^{2+}$  (176) and 6 g/L  $\text{Mn}^{2+}$  (231) after the 16 h decaying following 5 h polarization at 48 mA/cm<sup>2</sup>. It means that the DSA mesh anode in the zinc electrolyte containing higher manganese ion content had better corrosion behaviour during the current interrupt.

Evolution of admittance “ $1/R_n$ ” (mS/cm<sup>2</sup>) of the DSA mesh anodes following 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  without and with 17 ml/L  $\text{H}_3\text{PO}_4$  or 35 ml/L  $\text{H}_3\text{PO}_4$  is shown in Fig. 8.

Seen from Fig. 8, it was found that the DSA mesh anode in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  with addition of 17 ml/L  $\text{H}_3\text{PO}_4$  (198 mS/cm<sup>2</sup>) had the highest corrosion rate among the test results, followed by that without addition (176) and with addition of 35 ml/L  $\text{H}_3\text{PO}_4$  (141) and, respectively. It means that addition of 17 ml/L  $\text{H}_3\text{PO}_4$  to the zinc electrolyte can decrease the  $\text{MnO}_2$  layer and increase the corrosion rate of the DSA-mesh anode. However, the addition of 35 ml/L  $\text{H}_3\text{PO}_4$  to the zinc electrolyte can decrease the corrosion rate of the DSA mesh anode, since addition of 35 ml/L  $\text{H}_3\text{PO}_4$  to the solution resulted in the decrease the  $\text{MnO}_2$  layer and the formation of phosphoric oxide layer in the zinc electrolyte during the current interrupt.

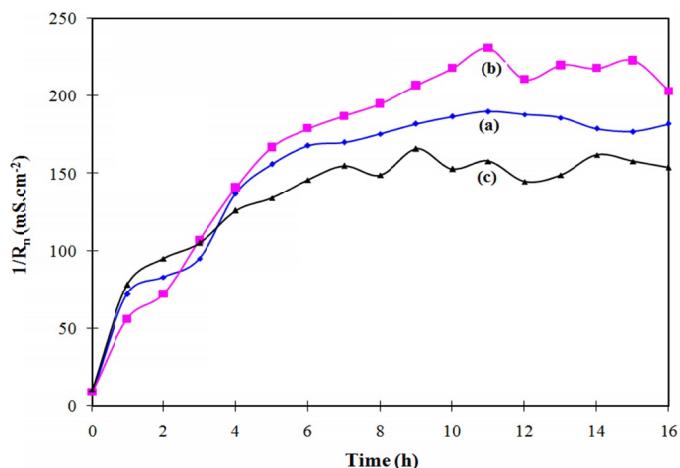


Fig. 8. Evolution of admittance “ $1/R_n$ ” (mS/cm<sup>2</sup>) of the DSA mesh anodes following 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> and 39°C in the zinc electrolyte containing (a) 9 g/L Mn<sup>2+</sup>; (b) 9 g/L Mn<sup>2+</sup> and 17 ml/L H<sub>3</sub>PO<sub>4</sub>; (c) 9 g/L Mn<sup>2+</sup> and 35 ml/L H<sub>3</sub>PO<sub>4</sub>

### 3.5. Electrochemical impedance measurements of polarization resistance after 5 hours galvanostatic polarization

In this test, the DSA working electrode was introduced into the cell and 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> was started immediately in the zinc electrolyte containing 6, 9, and 12 g/L Mn<sup>2+</sup>, respectively. Then the measurements of electrochemical impedance at open circuit potential were carried out and the polarization resistance corresponding to corrosion resistance was calculated.

Fig. 9 displays the Nyquist plots of electrochemical impedance measurement after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> for the DSA mesh anode in the zinc electrolyte containing 6, 9, 12 g/L Mn<sup>2+</sup>.

The data of the DSA mesh anode after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> in the zinc electrolyte with different

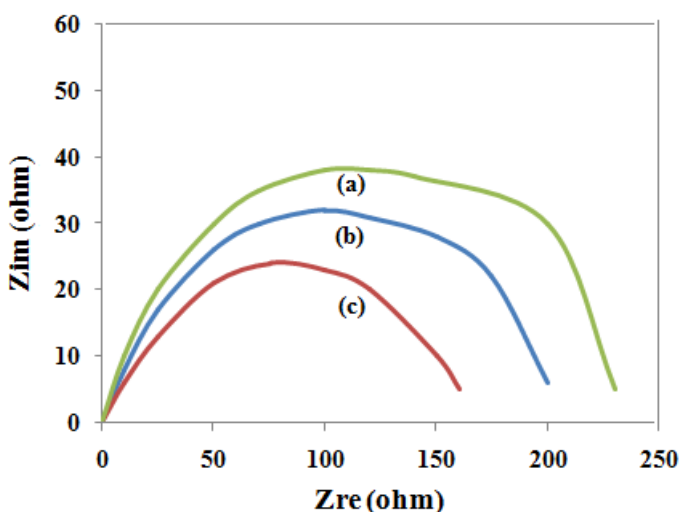


Fig. 9. Nyquist plots of the DSA mesh anode after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> at 39°C in the zinc electrolyte containing (a) 12 g/L Mn<sup>2+</sup>; (b) 9 g/L Mn<sup>2+</sup>; (c) 6 g/L Mn<sup>2+</sup>

contents of Mn<sup>2+</sup> at 39°C obtained by fit circle of “PowerSINE” software are 137, 186 and 223 ohm for addition of 6, 9, 12 g/L Mn<sup>2+</sup>, respectively. The DSA mesh anode in the zinc electrolyte containing 12 g/L Mn<sup>2+</sup> had the highest corrosion resistance among the three corrosion resistances in the zinc electrolyte from that containing 9, 6 g/L Mn<sup>2+</sup>, respectively. It means that the impedance resistance of the DSA mesh anode increased with addition of Mn<sup>2+</sup>.

Fig. 10 displays the Nyquist plots of electrochemical impedance measurement after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> for the DSA mesh anode in the zinc electrolyte containing 9 g/L Mn<sup>2+</sup>; 9 g/L Mn<sup>2+</sup> with additions of 17 and 35 ml/L H<sub>3</sub>PO<sub>4</sub>, respectively.

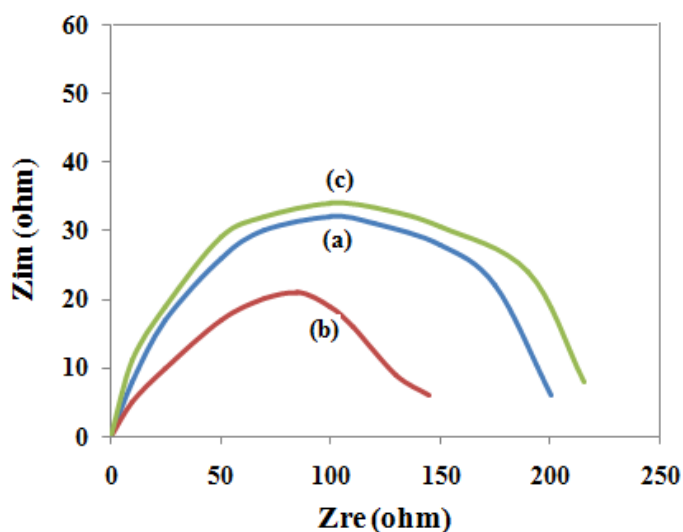


Fig. 10. Nyquist plots of DSA-mesh anode after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> in the zinc electrolyte containing (a) 9 g/L Mn<sup>2+</sup>; (b) 9 g/L Mn<sup>2+</sup> and 17 ml/L H<sub>3</sub>PO<sub>4</sub>; (c) 9 g/L Mn<sup>2+</sup> and 35 ml/L H<sub>3</sub>PO<sub>4</sub>

The data of the DSA mesh anode after 5 h galvanostatic polarization at 48 mA/cm<sup>2</sup> in the zinc electrolyte with different contents of Mn<sup>2+</sup> at 39°C obtained by fit circle of “PowerSINE” software are 186, 167 and 205 ohm for addition of 9 g/L Mn<sup>2+</sup>, or 9 g/L Mn<sup>2+</sup> with 17 and 35 ml/L H<sub>3</sub>PO<sub>4</sub>, respectively. The DSA mesh anode in the zinc electrolyte containing 9 g/L Mn<sup>2+</sup> with 35 ml/L H<sub>3</sub>PO<sub>4</sub> addition had the highest impedance resistance among the three impedance resistances in the zinc electrolyte containing 9 g/L Mn<sup>2+</sup> with different contents of H<sub>3</sub>PO<sub>4</sub>. It means that the addition of 35 ml/L H<sub>3</sub>PO<sub>4</sub> to the zinc electrolyte can increase impedance resistance of the DSA mesh anode.

### 3.6. Scanning reference electrode technique for the corrosion of the DSA anodes

Scanning reference electrode technique (SRET) is a useful technique in determining the form of corrosion especially for the localized one. Two additives of Mn<sup>2+</sup> and H<sub>3</sub>PO<sub>4</sub> were chosen to be compared to blank electrolyte in order to examine the effect of the anionic part on the corrosion form of the DSA plate anode.

After galvanostatic polarization, the anode was scanned employing SRET in acidic zinc sulfate electrolyte for 2 h. The specimen surface was scanned for surface area of 8 mm (X-axis) and 6 mm (Y-axis). Each scan lasted approximately 15 min and a rest of 1 min after each one in order to enable the probe to relocate to the first scanning point. After each scan (every 15 min), the measured potential was plotted against time and 2D maps for the cathodic and anodic zones on the surface are given (Fig. 11). Seen from the Fig. 11, it can be observed that the potential differences were distributed into different zones corresponding to neutral, lower intense cathodic and higher anodic activities. The deep blue area corresponds to the higher anodic zone (corrosion zone), green area represents neutral zone and the red area means the higher cathodic zone [27]. Fig. 11 displays 2-D corrosion activity map of the DSA plate electrodes in the zinc sulfuric acid solution containing  $\text{Mn}^{2+}$  and  $\text{H}_3\text{PO}_4$  additives after 2 hours immersion at  $25^\circ\text{C}$ . Moreover, the observed form of corrosion from 2D maps was quasi uniform on the center surface of the DSA plate anode. It is very possibly due to the formed protective oxide

film on the center of the anodic surface. However, the corrosion products on the corners and edges of the DSA plate anodes were observed during the scanning period, the blue color represents the potentials of localized corrosion. It means that localized corrosion appears on the corners and edges of the DSA anodes.

The term “quasi electromotive force” (QEMF) is used to express the potential difference between the most active cathode and the most active anode on the surfaces of the DSA plate electrodes in the zinc sulfuric acid solution. It is reported that higher QEMF corresponds to higher corrosion rate of the active electrodes [28]. Fig. 12 shows the QEMF of corrosion cell on the surface as a function of immersion time.

Fig. 12 shows that during 2 h polarization, the DSA plate anode in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$  had the highest QEMF, followed by that containing 9 g/L  $\text{Mn}^{2+}$ ; and that containing 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$ . It means that the DSA plate anode in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$  had the best corrosion resistance.

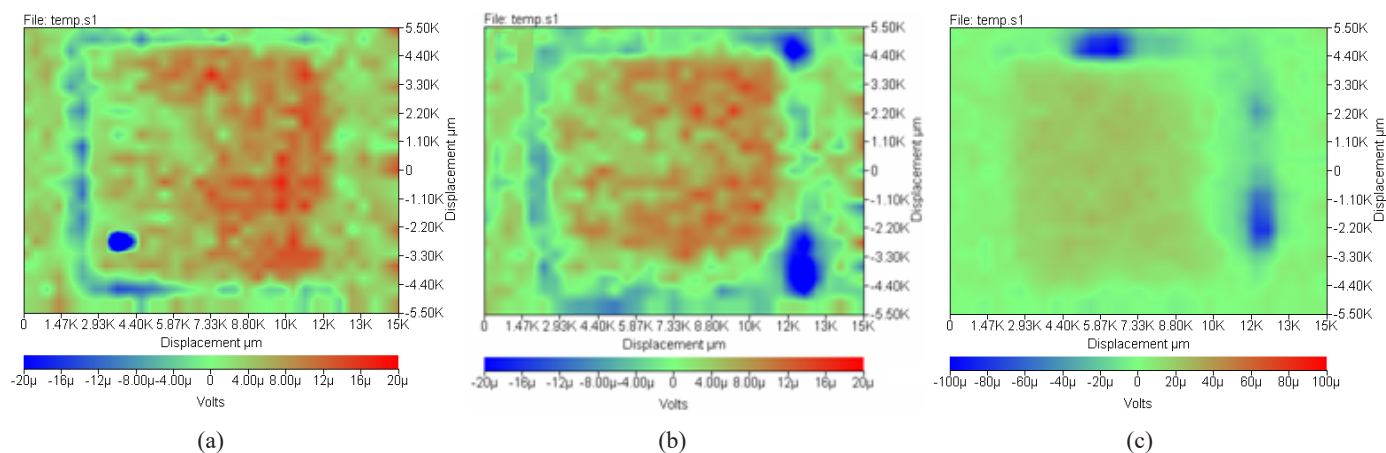


Fig. 11. Potential distribution on the DSA plate anode in the zinc electrolyte containing (a) 9 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$ ; (c) 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$  at the end of one hour of polarization at  $48 \text{ mA/cm}^2$  in the zinc sulfuric acid solution

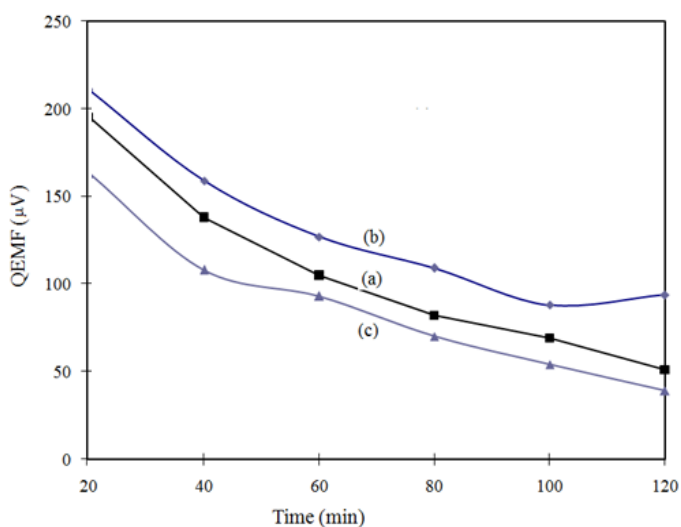


Fig. 12. QEMF evolution of the DSA plate anode in the zinc electrolyte containing (a) 9 g/L  $\text{Mn}^{2+}$ ; (b) 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$ ; (c) 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$

#### 4. Conclusions

To overcome the shortcoming of the DSA anodes, the electrochemical performance of the  $\text{Ti/IrO}_2\text{-Ta}_2\text{O}_5$  mesh and plate anodes was studied in the zinc electrolyte containing different  $\text{Mn}^{2+}$  by recent electrochemical measurements such as electrochemical impedance tests and electrochemical noise measurements. 17 g/L and 35 g/L phosphoric acid was added to the zinc electrolyte to complex the manganic ion. It has then been found that the anode potentials were lower when phosphoric acid was added to the electrolyte and the lower potential can be maintained for longer periods when there is sufficient phosphoric acid to complex the manganic ion. The presence of phosphoric acid confirmed the reduced formation of  $\text{MnO}_2$  on the anode DSA-mesh for both concentrations.



After consecutive series of electrochemical testing, the following conclusions can be obtained:

- (a) cyclic voltammetry study before polarization shows that the oxidation peak in the solution with 35 ml/L phosphoric acid addition is highest, followed by that with 17 ml/L phosphoric acid addition and that without addition of phosphoric acid.
- (b) Addition of  $\text{H}_3\text{PO}_4$  to the zinc electrolyte led to the decrease of potential value of DSA anode. The anodic potential of DSA anode in zinc electrolyte with 35 ml/L  $\text{H}_3\text{PO}_4$  was lower (17 mV) than that in zinc electrolyte with 17 ml/L  $\text{H}_3\text{PO}_4$ . Also, the potentials of the DSA-mesh anode in the zinc electrolyte with the addition of 6, 9, and 12 g/L  $\text{Mn}^{2+}$  were 1638, 1653, and 1686 mV/SHE, respectively.
- (c) After 16 h decay following 5 h polarization at  $48 \text{ mA/cm}^2$ , the DSA mesh anode in the zinc electrolyte containing 12 g/L  $\text{Mn}^{2+}$  ( $149 \text{ mScm}^{-2}$ ) had the lowest corrosion rate among the test results, followed by 9 g/L  $\text{Mn}^{2+}$  ( $176 \text{ mScm}^{-2}$ ) and 6 g/L  $\text{Mn}^{2+}$  ( $231 \text{ mScm}^{-2}$ ).
- (d) Addition of 35 ml/L  $\text{H}_3\text{PO}_4$  to the zinc electrolyte can decrease the corrosion rate ( $4.5 \mu\text{A/cm}^2$ ) of the DSA mesh anode compared to that of 17 ml/L  $\text{H}_3\text{PO}_4$  in the zinc electrolyte during the current interrupt
- (e) The impedance resistance of the DSA mesh anode increased from 137 to 223 ohm with increase of  $\text{Mn}^{2+}$  addition from 6 to 12 g/L.
- (f) Addition of 35 ml/L  $\text{H}_3\text{PO}_4$  to the zinc electrolyte can form a phosphate oxide layer on the surface of DSA anode and increase impedance resistance.
- (g) The positive effect of phosphoric acid can be used to complex the manganic  $\text{Mn}^{3+}$  ion and hence reduce its disproportionation to  $\text{MnO}_2$ . Various concentrations of phosphoric acid (17 and 35 g/L) were added to the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$ , more addition of phosphoric acid to the solution results in more complex the manganic  $\text{Mn}^{3+}$  ion.
- (h) Scanning reference electrode technique shows that the DSA plate anode in the zinc electrolyte containing 9 g/L  $\text{Mn}^{2+}$  and 17 ml/L  $\text{H}_3\text{PO}_4$  had the highest QEMF, followed by that containing 9 g/L  $\text{Mn}^{2+}$ ; and that containing 9 g/L  $\text{Mn}^{2+}$  and 35 ml/L  $\text{H}_3\text{PO}_4$ .

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