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Fabrication and corrosion behaviour of platinum-coated titanium electrodes from low temperature molten salt electrolytes

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Abstract

The development of corrosion-resistant platinum coated titanium (Pt/Ti) electrodes for seawater electrolysis in the production of sodium hypochlorite is an important requirement. In this study a new ternary low temperature molten salt (LTMS) LiCl–NaCl–KCl system was chosen as the electrolyte. The direct current method of four Pt electrodes combined with a computer program was employed to measure the relationship between conductivity and temperature of the chosen electrolyte at various $PtCl_2$ concentrations. The pulse current technique was used for fabrication of Pt/Ti electrodes from the chosen LTMS electrolyte at the temperature and $PtCl_2$ concentration where the conductivity of the LTMS system was highest by changing the duty-cycle and plating current density. The morphology and composition of the Pt-coated layer was examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Tafel plots, anodic polarization curves and electrochemical impedance spectroscopy (EIS) were employed to evaluate the corrosion behaviour of the Pt/Ti electrodes. The best quality Pt-coated electrodes were obtained from the pulse plating condition of T_{on}:T_{off} = 3:1 with a current density (i_{plat}) of 127.5 mA cm^{-2}. These had a higher Pt content, nobler corrosion potential (E_{corr}), lower corrosion current density (i_{corr}), lower passive current density (i_{pass}) and higher impedance. Furthermore, AFM demonstrated that the best quality Pt/Ti electrode had the lowest surface roughness (R_a) with the finest grain size.

1. Introduction

In many cases, seawater is utilized as cooling water in heat exchangers in large coastal factories. The materials used for cooling water pipes are corrosion resistant metals such as brass and titanium. Marine microorganisms attach themselves to the pipe walls of heat exchangers, which results in reduced heat exchanger efficiency, and increased flow resistance and corrosion. Therefore, reducing or removing microorganisms in seawater pipes is an important consideration. Methods for diminishing microorganisms include (i) the liquid chlorine process (i.e., vaporizing liquid chlorine and adding chlorine vapour to seawater), (ii) the sodium hypochlorite process (i.e., adding sodium hypochlorite to seawater directly), (iii) the calcium hypochlorite process (i.e., adding bleaching power to seawater directly), and (iv) the electrolysis process (i.e., electrolysing seawater to produce sodium hypochlorite). Process (i) has the problem of chlorine leakage and corrosion and processes (ii) and (iii) have higher material costs. However, process (iv) has the following advantages: it is safer (only 0.2% chlorine vapour is produced), more stable, more economical (lower operating cost) and less polluting. Therefore, the electrolysis process is preferable in practical application [1–5].

In the electrolytic industries, the development of higher quality electrodes for increasing electrolysis efficiency in the production of sodium hypochlorite is a very important task. A dimensionally stable electrode for seawater electrolysis to produce sodium hypochlorite must have characteristics such as low impedance, large catalytic energy of reaction, and better electrochemical stability. Platinum metals such as Rh, Pt, Ir and Ru have the necessary characteristics. For example, a pure Pt electrode is a good electrocatalyst with better electrochemical stability, but is more expensive. Therefore, developing an alternative electrode material by electrodeposition is important. The base electrolyte for the fabrication of Pt/Ti electrodes is usually based on cyanide compounds, which are both expensive and toxic. Therefore, inexpensive and non-toxic processes have been considered to replace cyanide [6–11]. Among the Pt plating baths, a molten salt electrolyte has the advantages of high conductivity, high density and high surface tension. Moreover, a low temperature molten salt (LTMS) electrolyte is especially favoured for energy saving. In this study, a ternary LTMS, LiC–NaCl–KCl, system was chosen to prepare Pt/Ti electrodes.

The Pt/Ti electrodes fabricated in this study had previously been tested for the electrogeneration of sodium hypochlorite from a NaCl solution. The current efficiency of these electrodes was within the range 83.4–90.2%, which was similar to the results reported by Yanagase et al. [12]. The detailed performance of the electrodes has been reported elsewhere [13]. In this paper, we focus on the corrosion behaviour of the Pt/Ti electrodes [14–16]. The durability of the Pt/Ti electrodes is very important from the viewpoint of practical applications. In order to evaluate their corrosion resistance, a potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) were employed. AFM of the surface topography before and after anodic polarization tests is also discussed.

2. Experimental methods

2.1. *Chemical purification and substrate pretreatment*

Since ternary alkali chloride LiCl–NaCl–KCl can absorb moisture, it was dried by heating under vacuum before use. $PtCl_2$ (Showa, Japan) was used without purification. Different substrate pretreatment methods may affect the electrodeposition layers. The Ti substrates can be treated by mechanical polishing and chemical acid washes.

In mechanical polishing the substrate was abraded with coarse, and then fine, SiC papers, then rinsed ultrasonically with distilled water and acetone for 3 min. It was then rinsed with distilled water alone and dried. For the chemical acid wash the substrate was etched in 50% (v/v) aqueous H_2SO_4 and 4% (v/v) aqueous HF for 15 min each and then rinsed ultrasonically with distilled water for 3 min.

2.2. *Conductivity measurement*

The characteristic of the alkali chloride electrolyte is high conductivity, leading to it being chosen as the electrolyte medium for the thermal reaction process. In this experiment, the direct current method of four Pt electrodes combined with a computer program was employed to measure the conductivity of the molten salt electrolyte. The ternary molten salt with composition 53.5 mol % LiCl–8.5 mol % NaCl–38 mol % KCl has a low co-melting temperature (621 K) and high LiCl composition (53.5 mol %) [17], and was chosen as the electrolyte. Furthermore, addition of $PtCl_2$ increases the electrolyte activity. Therefore, the relationship between conductivity and temperature of the chosen ternary molten salt at different $PtCl_2$ concentrations (0.00, 0.04, 0.09, 0.15 mol %: highest $PtCl_2$ dissolution) could be obtained.

2.3. *Fabrication and characterization of the Pt/Ti electrodes*

The pretreated Ti substrates were coated by painting with a 0.1 M $Pt(NH_3)_2(NO_2)_2$ solution and then heated in air at 623 K for 30 min. In this way, the active bases were produced on the Ti substrates facilitating easy fabrication of the Pt/Ti electrodes. The chosen ternary low temperature molten salt at the $PtCl_2$ concentration where the conductivity of the LTMS system was highest was put in a quartz crucible, inert gas, N_2, was introduced into the electrodeposition apparatus (Figure 1) and the salt was heated until molten. Finally, the current densities (i_{plat}) and pulse plating conditions (T_{on}:T_{off}) were adjusted for Pt coating of the Ti substrates (cathode) from the Pt anode at the temperature where the conductivity of the LTMS system was highest.

Examination of the surface morphology and the determination of the chemical composition of the Pt-coated layer was conducted by SEM (Hitachi S3000N, Japan) combined with EDS (Horiba, England). The SEM was operated in the range 20–25 keV. Additional information on the grain size and surface roughness of the Pt/Ti electrodes was obtained by AFM (Digital Instrument, Nanoscope III, USA) operating in the tapping mode.

2.4. *Corrosion behaviour of Pt/Ti electrodes*

Tafel plots and anodic polarization curves were obtained through an EG&G M352 corrosion measurement system. EIS measurement was carried out via an EG&G M398 a.c. impedance measurement system operated at 10 mV a.c. amplitude with a frequency range between 100 kHz and 10 mHz. The electrolyte was a 3.5% NaCl

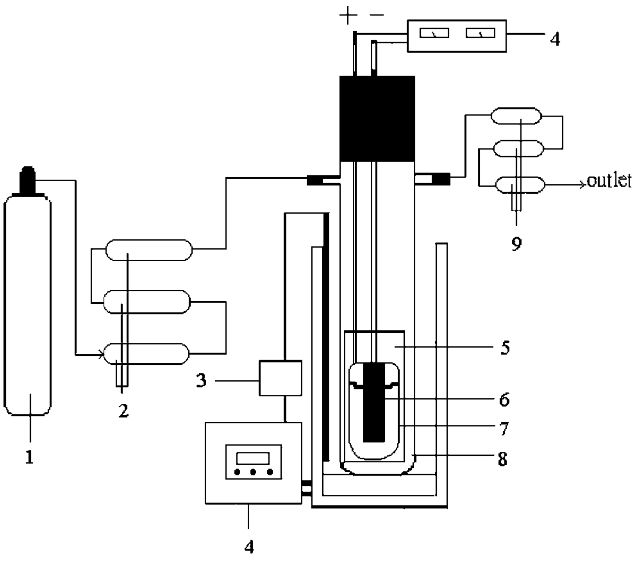

Fig. 1. Schematic diagram and apparatus of electrodeposition experiment. Key: (1) N_2, (2) H_2SO_4 + drier + molecular seizure, (3) temperature controller, (4) power supplier, (5) quartz crucible, (6) cathode–Ti, (7) anode–Pt, (8) molten salt, (9) NaOH + drier + molecular seizure.

solution prepared from reagent grade chemicals and distilled water. A three-electrode corrosion cell consisted of Ag/AgCl as the reference electrode, Pt as the counter electrode and our Pt/Ti as the working electrode. All the corrosion experiments were conducted at room temperature and the potentials reported are against the Ag/AgCl reference electrode except where stated.

3. Results and discussion

3.1. *Molten salt electrolyte conductivity measurement*

Figure 2 shows that the conductivity of the ternary molten salt (53.5 mol % LiCl–8.5 mol % NaCl–38 mol % KCl) at different $PtCl_2$ concentrations increased as temperature increased, and the higher the Pt dissolution, the higher the conductivity. This observation is consistent with larger ionic separation and lower coulombic forces between cations and anions in the LiCl–NaCl–KCl system at higher temperatures – the resulting increase in conductivity. Moreover, with higher Pt dissolution, lower coulombic forces between Pt ions and anions, lead to higher salt conductivity [18]. So a concentration of 0.15 mol % $PtCl_2$ in the molten salt of composition 53.5 mol % LiCl–8.5 mol % NaCl–38 mol % KCl mol %, and an operating temperature of 673 K would be favourable for the fabrication of Pt/Ti electrodes.

3.2. *Activation pretreatment of Ti substrates*

$Pt(NH_3)_2(NO_2)_2$ was coated on the pretreated Ti substrates as described above: 10, 20, 30, 40 and 50 times, respectively. The thickness of the coated Pt layer increased from 13.1 μm to 20.45 μm as the number of coats increased from 10 to 50 (Table 1). EDS analysis showed that the Pt content on the Ti substrates also increased from 27.5% to 99.1% (Table 1). Because the Pt content reached 90.73% after only 30 coats, this number was chosen to activate substrates for further experiments.

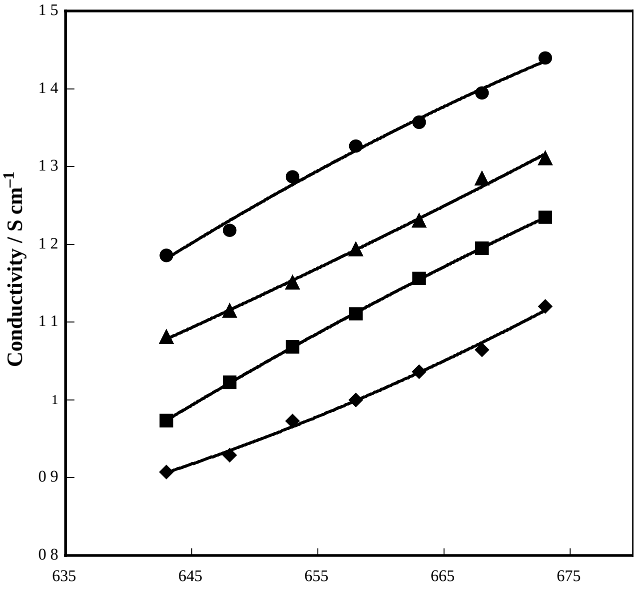

Fig. 2. Relationship between conductivity and temperature of the ternary molten salt LiCl–NaCl–KCl system at various $PtCl_2$ concentrations: (A ◆) 0.00, (B ■) 0.04, (C ▲) 0.09 and (D ●) 0.15 mol %.

3.3. *Fabrication of Pt/Ti electrodes by pulse current techniques*

With a pulse plating condition of T_{on}:T_{off} = 1:3, four different plating current densities (i_{plat}) were used in the fabrication of the Pt/Ti electrodes. From the SEM photographs, it is seen that a coarser grain is obtained with the smaller i_{plat} and a finer grain is observed at the larger i_{plat} (Figure 3). From Table 2, with a pulse plating condition of T_{on}:T_{off} = 1:3, a higher Pt content was achieved by using a larger plating current density.

The four different plating current densities were repeated with a pulse plating condition of T_{on}:T_{off} = 3:1. Under these conditions, SEM shows that needle-like crystalline Pt grains are obtained with the smaller i_{plat} and a denser, finer grain is obtained at larger plating current densities (Figure 4). Table 2 shows how grain size, as measured with the AFM, varied with plating

Table 1. Results of coatings $Pt(NH_3)_2(NO_2)_2$ on Ti substrates (Temperature: 623 K)

No. of coats	Thickness* /μm	Pt content† /%
10	13.10	27.52
20	16.36	86.02
30	16.16	90.73
40	20.00	95.10
50	20.45	99.06

* Thickness measured by SEM.
† Pt content measured by EDS.

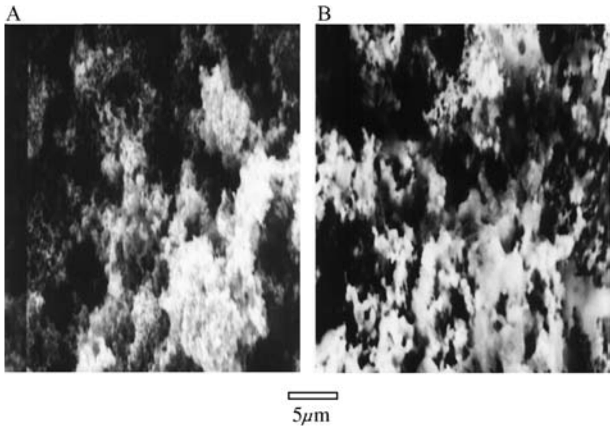

Fig. 3. Scanning electron micrograph of Pt-coated layers in ternary molten salt on Ti substrates at 673 K, using the pulse plating condition of T_{on}:T_{off} = 1:3, 3000 °C. (A) i_{plat} = 37.5 mA cm^{-2}, (B) i_{plat} = 127.5 mA cm^{-2}.

Table 2. Experimental conditions (Temperature 673 K) and results of Pt electrodeposition on Ti substrates

Plating conditions		Thickness* /μm	Pt content† /%	Grain size‡ /μm
T_{on}:T_{off}	I_{plat} /mA cm^{-2}			
1:3	37.5	2.50	56.98	1.151
1:3	82.5	6.25	70.68	1.009
1:3	105.0	6.50	86.15	0.899
1:3	127.5	13.10	90.35	0.817
3:1	37.5	1.82	57.31	1.683
3:1	82.5	13.64	65.41	1.405
3:1	105.0	18.18	82.53	1.288
3:1	127.5	45.45	94.53	0.958

* Thickness measured by SEM.
† Pt content measured by EDS.
‡ Grain size measured by AFM.

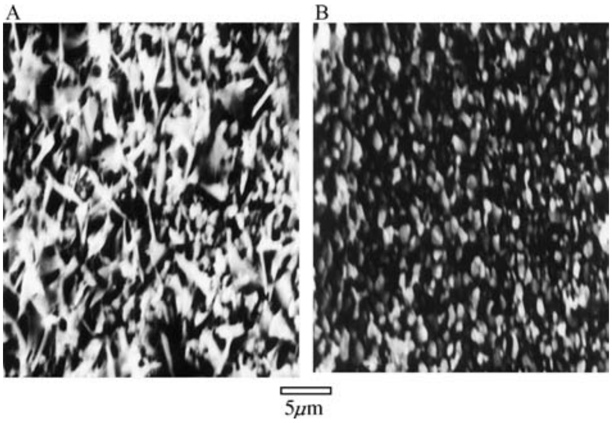

Fig. 4. Scanning electron micrograph of Pt-coated layers in ternary molten salt on Ti substrates at 673 K, using the pulse plating condition of T_{on}:T_{off} = 3:1, 3000 °C. (A) i_{plat} = 37.5 mA cm^{-2}, (B) i_{plat} = 127.5 mA cm^{-2}.

conditions (the larger the i_{plat}, the finer the grain). Table 2 also shows that a thicker Pt-coated layer was produced at the larger current density. Moreover, the larger the i_{plat}, the higher the Pt content (Table 2). Figure 5 and Table 2 show that, in general, a pulse plating condition of T_{on}:T_{off} = 3:1 produced a thicker Pt-coated layer and a higher Pt content than the pulse plating condition of T_{on}:T_{off} = 1:3 at the same plating current density.

3.4. *Corrosion behaviour of Pt/Ti electrodes in 3.5% NaCl solution*

Figure 6 shows Tafel curves of Pt/Ti electrodes fabricated from the pulse plating condition of T_{on}:T_{off} = 1:3. Corrosion data obtained from these curves are shown in Table 3. The dynamic corrosion potential (E_{corr}) of the Pt/Ti electrodes tended towards a more noble value as the current density (i_{plat}) increased, while the corrosion current density (i_{corr}) varied inversely as the current density. The Pt/Ti electrodes fabricated from the plating condition of T_{on}:T_{off} = 3:1 showed similar corrosion behaviour, and data for those are presented in Figure 7 and Table 3.

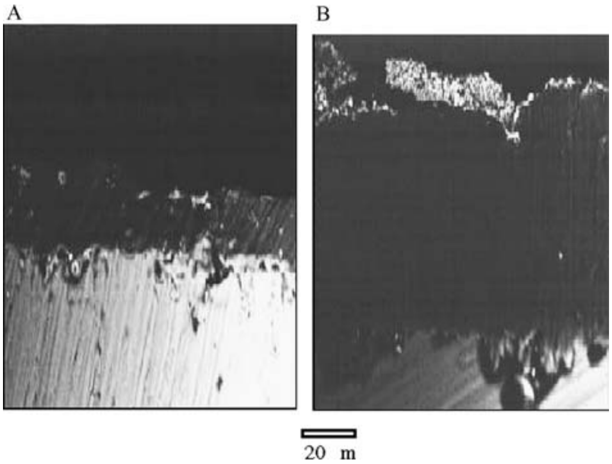

Fig. 5. SEM micrograph of polished cross section of Pt-coated layers in ternary molten salt on Ti substrates at 673 K, using the pulse plating current density, i_{plat} = 127.5 mA cm^{-2}, 3000 C. (A) T_{on}:T_{off} = 1:3, (B) T_{on}:T_{off} = 3:1.

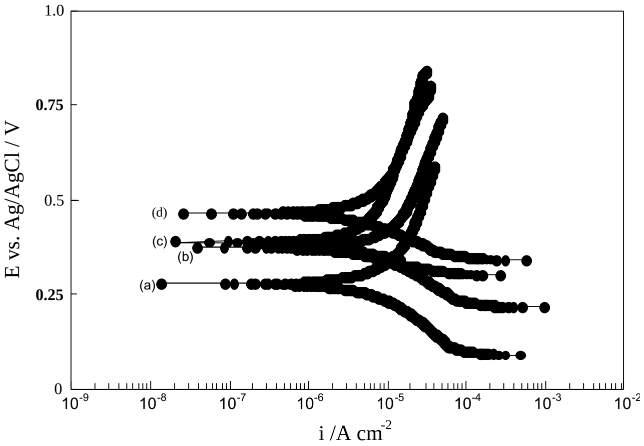

Fig. 6. Tafel curves of Pt/Ti electrodes in a 3.5% NaCl solution. Plating conditions: T_{on}:T_{off} = 1:3, 3000 °C and i_{plat} for (a) 37.5, (b) 82.5, (c) 105 and (d) 127.5 mA cm^{-2}.

Table 3. Corrosion data of the Pt/Ti electrodes fabricated from different plating conditions

Plating conditions		Tafel plots		EIS, R_p /ohm	
T_{on}:T_{off}	i_{plat} /mA cm^{-2}	E_{corr} /mV	I_{corr} /mA cm^{-2}	E = 0.9 V	E = 1.2 V
1:3	37.5	272	18.7	26700	24400
1:3	82.5	364	13.3	35000	54300
1:3	105.0	391	6.5	49100	71000
1:3	127.5	465	6.1	89900	71500
3:1	37.5	281	19.3	40400	35800
3:1	82.5	352	15.6	58700	61300
3:1	105.0	427	7.0	100600	79100
3:1	127.5	494	5.0	112800	94700

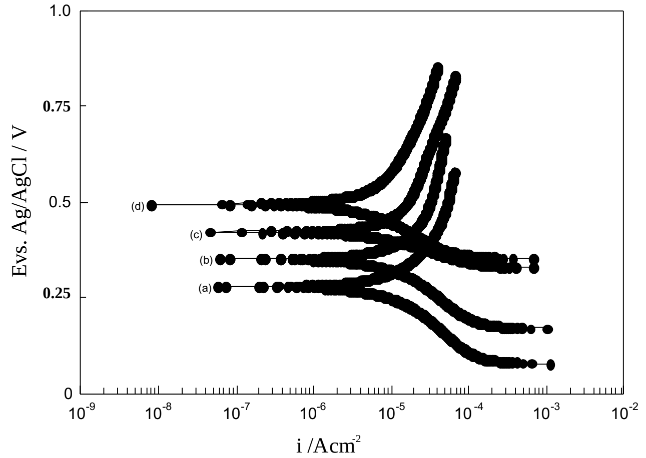

Fig. 7. Tafel curves of Pt/Ti electrodes in a 3.5% NaCl solution. Plating conditions: T_{on}:T_{off} = 3:1, 3000 °C and i_{plat} for (a) 37.5, (b) 82.5, (c) 105 and (d) 127.5 mA cm^{-2}.

Since the Pt/Ti electrodes used for the electrogeneration of sodium hyperchlorite are always polarized in the anodic direction, the anodic behaviour of these electrodes is worthy of further study. Figure 8 shows the potentiodynamic polarization curves of the Pt/Ti electrodes. The range from 0.15 to 1.00 V was associated with the passive region. Between 1.00 and 1.20 V represented the breakdown potential and above the breakdown potential the transpassive region was entered. To further understand the effects of anodic polarization on the corrosion behaviour, data deduced from the curves in Figure 8 are given in Table 4. The passive current density (i_{pass}) of the Pt/Ti electrode was strongly affected by the fabrication conditions as seen in Table 4. For the pulse plating condition of T_{on}:T_{off} = 1:3, the i_{pass} of the i_{plat} = 37.5 mA cm^{-2} was about three times greater than that of the i_{plat} = 127.5 mA cm^{-2}. Similar results were obtained for the Pt/Ti electrodes fabricated from the pulse plating condition of T_{on}:T_{off} = 3:1. Moreover, it is also demonstrated that the i_{pass} of the pulse plating condition of T_{on}:T_{off} = 1:3 was about 1.5 times greater than that of the plating condition of T_{on}:T_{off} = 3:1 at the same plating current density (i_{plat}). From the data presented above, it is evident that the corrosion resistance of Pt/Ti electrodes fabricated from the plating condition of T_{on}:T_{off} = 3:1 is better than those for plating condition of T_{on}:T_{off} = 1:3 because of the higher Pt content and finer grain size achieved in the deposited layer.

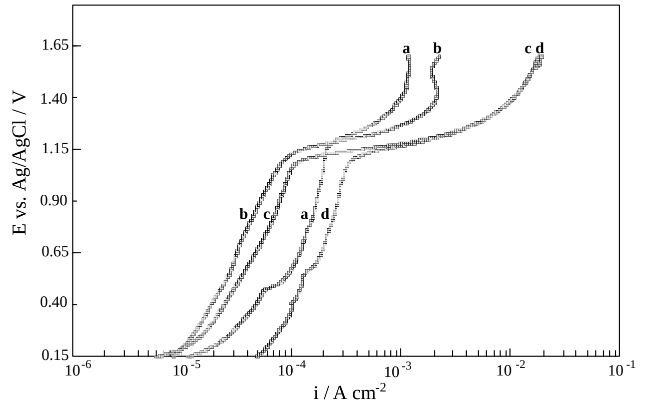

Fig. 8. Anodic polarization curves of Pt/Ti electrodes in a 3.5% NaCl solution. Plating conditions: (a)T_{on}:T_{off} = 3:1, i_{plat} = 37.5 mA cm^{-2}; (b)T_{on}:T_{off} = 3:1, i_{plat} = 127.5 mA cm^{-2}; (c)T_{on}:T_{off} = 1:3, i_{plat} = 127.5 mA cm^{-2}; (d)T_{on}:T_{off} = 1:3, i_{plat} = 37.5 mA cm^{-2}.

Furthermore, the mean roughness (R_a) of the Pt/Ti electrodes measured by AFM before and after anodic polarization tests (Table 4) shows that the lowest R_a value was obtained from the plating condition of T_{on}:T_{off} = 3:1, and with the largest value of i_{plat} (127.5 mA cm^{-2}). Therefore, we conclude that the higher Pt content, lower surface roughness and finer grain size give greater corrosion resistance.

In addition, EIS was measured at anodic potentials of 0.9 and 1.2 V vs Ag/AgCl as shown in Figures 9–11, respectively. At 0.9 V (i.e., in the passive region), the mechanism was under diffusion control, as indicated by the slope (Figure 9) of the diffusion tail lines in the Nyquist plots (also named Warburg impedance). At 1.20 V (i.e., in the transpassive region), the Nyquist plots in Figures 10 and 11 clearly show that the mechanism was dominated by activation control [19, 20]. Moreover, in general, lower impedances were obtained for 1.2 V, as compared to 0.9 V, because Cl$^-$ penetrates to the Pt/Ti electrode interface in the transpassive region. According to double layer theory, when the potential difference between the solid phase and the liquid phase is low, the ions in the diffusion layer are far from the electrode/solution interface and the rate-determining step is diffusion. Conversely, when the

Table 4. Corrosion data and surface roughness of the Pt/Ti electrodes fabricated from different plating conditions

Plating conditions		Polarization data	Mean roughness	
T_{on}:T_{off}	i_{plat} /mA cm^{-2}	i_{pass} /mA cm^{-2}	R_{a1}* /nm	R_{a2}* /nm
1:3	37.5	266.1	198.6	255.5
1:3	127.5	79.4	138.3	150.3
3:1	37.5	167.6	161.2	188.1
3:1	127.5	53.1	101.9	117.8

* $R_{a1}$and R_{a2} is mean roughness of Pt/Ti electrodes measured by AFM before (R_{a1}) and after (R_{a2}) anodic polarization tests, respectively.

potential difference between the solid phase and the liquid phase is high, the ions rapidly penetrate the compact layer of the electrode–solution interface and proceed to transfer electric charge [21–25].

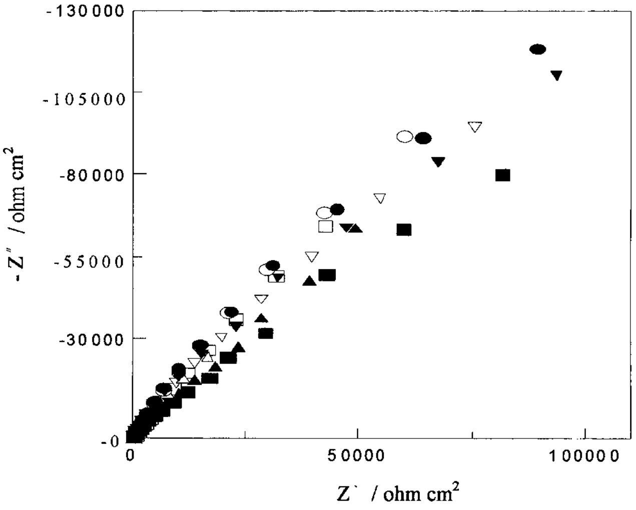

Fig. 9. Nyquist diagrams of Pt/Ti electrodes measured at $E = 0.9$ V in a 3.5% NaCl solution. Plating conditions: T_{on}:T_{off} = 1:3 (open plots) and T_{on}:T_{off} = 3:1 (closed plots), 3000° C and i_{plat} for (△, ▲) 37.5, (□, ■) 82.5, (▽, ▼) 105 and (○, ●) 127.5 mA cm^{-2}.

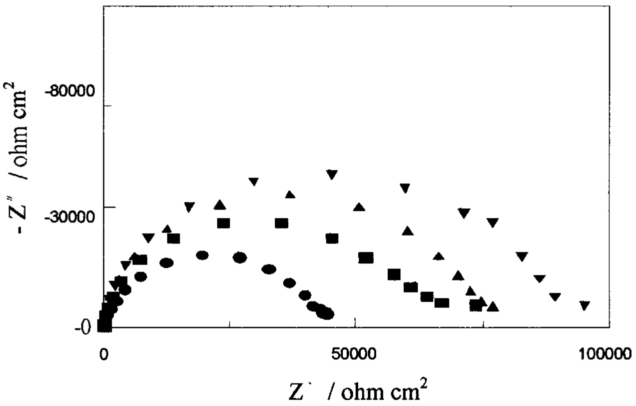

Fig. 10. Nyquist diagrams of Pt/Ti electrodes measured at $E = 1.2$ V in a 3.5% NaCl solution. Plating conditions: T_{on}:T_{off} = 1:3, 3000° C and i_{plat} for (●) 37.5, (■) 82.5, (▲) 105 and (▼) 127.5 mA cm^{-2}.

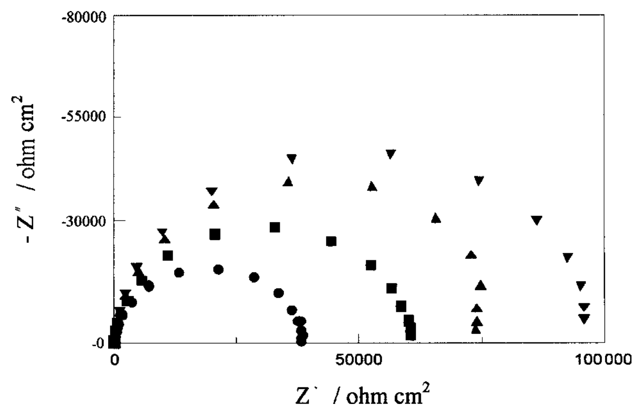

Fig. 11. Nyquist diagrams of Pt/Ti electrodes measured at $E = 1.2$ V in a 3.5% NaCl solution. Plating conditions: T_{on}:T_{off} = 3:1, 3000° C and i_{plat} for (●) 37.5, (■) 82.5, (▲) 105 and (▼) 127.5 mA cm^{-2}.

4. Conclusion

The pretreated Ti substrates were most effectively activated by coating with a 0.1 M $Pt(NH_3)_2(NO_2)_2$ solution and thermally treating at 623 K for 30 min before electrodeposition of the Pt layer. The 53.5 LiCl–8.5 NaCl–38.0 KCl (mol %) melt containing 0.15 mol % $PtCl_2$ and operating at 673 K gave best conditions for the fabrication of Pt/Ti electrodes according to the conductivity measurement of the LTMS system. In addition, by using a larger current density (i.e., i_{plat} = 127.5 mA cm^{-2}), a finer grain size in the Pt-coated layer was achieved. Furthermore, a thicker deposited layer with a higher Pt content was obtained with this current density and a plating condition with higher pulse ratio (T_{on}:T_{off} = 3:1). The polarization curves, EIS and AFM demonstrate that these fabrication parameters leading to a thicker layer, higher Pt content and finer grain size of the electrodeposited layer also improved the corrosion resistance of the electrodes. In summary, the conductivity of the ternary LTMS electrolyte and adjustment of electrodeposition operation parameters are important factors in fabrication of corrosion resistant Pt/Ti electrodes.

Acknowledgments

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