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ORIGINAL PAPER

Platinization of Ti for the fabrication of a Sn-modified Pt/Ti electrode for reduction of nitrate

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Abstract This work investigated the fabrication characteristics of platinized-Ti for use in the preparation of a Sn-modified platinized-Ti electrode to reduce nitrate. A Pt electro-plating method to form special open clearances within a Pt coating layer on an etched Ti substrate was important to effectively remove the residual contaminate due to the plating solution at the fabricated electrode surface and to maximize the electrode's actual surface area. The electro-cleaning caused a morphologic change of the platinized-Ti electrode surface through a place-exchange process of Pt atoms, with many of the downy hair-like polyps formed on the surface disappearing, resulting in a decrease in the electrode area. The platinized-Ti electrode itself had some electro-activity to the reduction of nitrate even though its surface was not Sn-modified. The Sn-modified platinized-Ti electrode significantly increased electro-activity to the reduction of nitrate compared with the Pt metal electrode.

Keywords Nitrate reduction · Sn-adatom · Pt electro-deposition · Platinization

1 Introduction

Electrochemical methods have attracted considerable attention for the advanced treatment of wastewater. Numerous studies on the modification of a Pt electrode surface through its adsorption of catalytic metal atoms such as Sn, Cu, and Ge, the so called "metal adatom-Pt electrodes," have been recently carried out to enhance the electroactivity of Pt electrodes in reducing nitrate ions in solutions [1–5]. A Sn-modified Pt electrode was reported to be outstanding for this purpose [6]. The use of massive Pt as a base electrode is not practical from a commercial point of view because of its high cost. Therefore, the platinization of a suitable substrate should be considered for the fabrication of such an improved Pt electrode. Ti is considered to be suitable as a substrate for a platinization because of its electric conductivity, mechanical strength, corrosion resistance, environmental harmlessness, and cost, among others. However, Ti is known to be a difficult metal on which to electro-deposit a metal coating because of the formation of a passivation oxide film on its surface due to an exposure to air or other oxidizing conditions.

Studies on platinized-Ti electrode are scarce compared with studies on platinized-Pt electrode [7, 8]. Moreover, in our preliminary work, the surface of the platinized-Ti electrode was observed to be changeable even after washing with water and electro-cleaning, which are enough for an ordinary metal Pt electrode. Accordingly, the cyclic voltammogram measured to evaluate the Sn coverage on the Sn-modified platinized-Ti, or the linear voltammogram measured to observe the electroactivity in nitrate solutions, continuously changed when measured at the same electrode. Contamination of the platinized-Ti electrode by the anions of a plating solution remaining within the Pt coating layer, which can readily occur according to the surface structure formed during a platinization, and change of the surface morphology, which is caused by the electro-cleaning carried out to remove the contaminant on the electrode surface, severely hinders the evaluation of a

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Sn-modified platinized-Ti electrode. By observing the electro-deposition characteristics of Pt on a Ti substrate, this work studied a method aimed at obtaining a stable platinized-Ti electrode necessary to prepare a Sn-modified platinized-Ti electrode. Moreover, the electrochemical characteristics of the Sn-adatom platinized-Ti electrode in a nitrate solution were evaluated.

2 Experimental

All the reagents used in this work were reagent grade, and were dissolved, as received, in 18.2 MΩ demineralized water prepared through double distillation and one ion-exchange (Milli-Q plus).

A Ti wire with an area of 1 cm^2 and a diameter of 1.5 mm was used as a substrate for Pt electroplating. The Ti wire was etched in 20 wt.% oxalic acid at 90 °C for 40 min to rid it of contaminants and to create a certain level of roughness on its surface. Next, it was thoroughly washed in a sonicator for 10 min and then boiled in water. The etched Ti was electroplated at −0.05 V (vs. Ag/AgCl in 3 M NaCl) in a platinum solution of 0.075 M H_2PtCl_6 in 1.0 M HCl at 70 °C with different plating times. At this condition, the current efficiency of the platinization was about 62%, taking into account the four-electron reaction for the platinization. This agreed well with other results [9, 10].

The surface of the prepared platinized-Ti samples was analyzed through Scanning Electron Microscopy (SEM: JSM-5200) and Scanning Probe Microscopy (SPM: NanoScope V) to provide an Atomic Force Measurement (AFM) image. This aided observation of morphological changes of the surface. The platinized-Ti sample was boiled in water for a specified time to remove the chloride ions from the plating solution, which remained at the electrode surface after platinization; it was then electro-cleaned in a potential range −0.22 to 1.3 V_{SSE} at 300 mV s^{-1}. After every 50-cycle electro-cleaning, cyclic voltammograms were measured in the range between the onset potentials of the hydrogen and oxygen evolutions at a scan rate of 40 mV s^{-1}.

To modify the surface of the platinized-Ti electrode by Sn-adatoms, the prepared electrode was dipped into a Sn solution of 0.5 mM $SnCl_2$ in 0.1 M $HClO_4$ for 10 min [1, 2, 6, 11]. Cyclic voltammograms before and after the Sn-modification of the platinized-Ti electrode were measured in the potential region of the hydrogen adsorption-desorption to evaluate the Sn coverage at the electrode. Linear sweep voltammograms of the final prepared electrodes were then measured in a nitrate solution of 0.05 M $NaNO_3$ in 0.1 M $HClO_4$ to compare the relative electroactivities of the electrodes to nitrate ions. In all the voltammograms of this work, the third of three measurements was taken as the first characteristic voltammogram, as the first two measurements were unreliable because of the initial charging current [12]. The reason why we used a $HClO_4$ solution as a supporting electrolyte in the nitrate solution is that ClO_4^- ions are known to be less competitive with nitrate ions during adsorption at a cathode when compared with the anions Cl^-, SO_4^{-2}, and PO_4^{-3}. This allows us to obtain a more accurate electro-activity of nitrate ions at the electrode [13, 14].

3 Results and discussion

Figure 1 shows SEM photographs of the oxalic acid-etched Ti substrate (a) and the platinized-Ti electrodes with plating times of 15, 30, and 60 min (b, c, and d, respectively). Platinization at the etched Ti surface did not occur uniformly over the whole surface. It started at sharp-point parts on the reentrant surface generated by the etching, forming cauliflower-like clusters about 7−8 μm in diameter, which are considered to be agglomerates of Pt crystals. As the plating time progressed, the clusters gradually grew to cover the whole Ti surface, finally giving an embossed surface pattern, as seen in Fig. 1d. The Pt clusters were observed to have many downy polyps on their surfaces. These polyps were more developed in the case of longer platinization (compare Fig. 1e, f). Based on the figures, the cohesion of the Pt coating layer to the Ti surface is considered to be accomplished through a mechanical locking between the rough Ti surface and the Pt clusters which grow during the plating process.

The fabricated platinized-Ti electrode must be checked to see if it behaves like a polycrystalline Pt metal electrode before its use. In other words, the platinized-Ti electrode has to show distinct adsorption-desorption peaks of hydrogen and oxygen, which can be obtained only at a very little or non-contaminated Pt surface. In such a condition, the adsorption of catalytic metal atoms such as Sn can be maximized and the surface coverage accurately evaluated. The Pt metal electrode usually reveals a stable voltammogram only by electro-cleaning for a few minutes in the potential region between hydrogen and oxygen evolution. Figure 2 shows the voltammogram changes of the platinized-Ti electrodes with different plating times of 15, 30, 60 min according to the number of electro-cleaning cycles. Each voltammogram was measured after 50 cycles of electro-cleaning in a range between the onset potentials of hydrogen and oxygen evolution at 300 mV s^{-1}. The overall voltammetric current heights at the electrodes were nearly linear with the applied plating time. It was observed that plating time can influence the voltammogram pattern change along with the electro-cleaning cycle at the electrodes. In the case of a 15-min plating, clear adsorption and

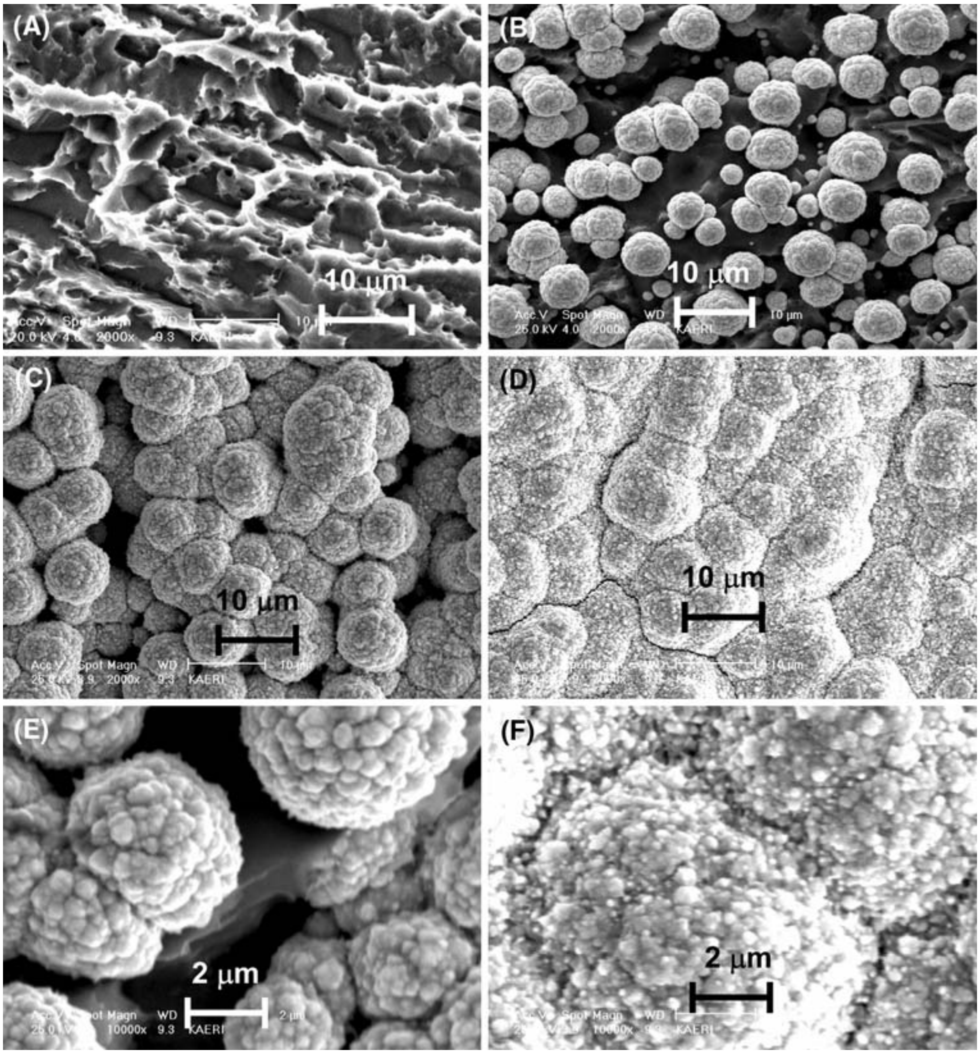


Fig. 1 SEM photographs of the oxalic acid-etched Ti substrate and the platinized-Ti electrode with the plating times of 15, 30, and 60 min at -0.05 V_{SSE} in a 0.075 M H_2PtCl_6 solution. (**a**) Oxalic acid etching Ti, (**b**) 15 min plating, (**c**) 30 min plating, (**d**) 60 min plating, (**e**) 15 min plating, (**f**) 60 min plating

desorption peaks of hydrogen and oxygen were obtained with only one electro-cleaning of 50 cycles, similar to those at a polycrystalline Pt metal electrode. This means that the electrode surface can be easily cleaned by washing it with water and carrying out a short electro-cleaning process. However, peak currents of the voltammogram progressively decreased with further electro-cleaning, while maintaining the ratio of the peak heights constant. Change in the voltammogram almost stopped after a long electro-cleaning of about 500 cycles. In contrast, in the case of the platinized-Ti electrodes with a longer plating time of 30 and 60 min, the voltammogram peaks became unclear and skewed. Moreover, the non-faradic current in the electric double layer region became abnormally large. Even an unusual peak was observed between the oxide reduction and hydrogen adsorption peaks. In the case of a 30-min plating, the typical adsorption and desorption peaks of hydrogen, each of which should be divided into two peaks, were gradually developed with increase in the number of electro-cleaning cycles. However, the peaks were not as clear as those in the case of a 15-min plating for the same number of electro-cleaning cycles. Moreover, the relative ratio of the oxide reduction peak height to the hydrogen adsorption peak height was smaller. For the 60-min plating, each adsorption and desorption peak of hydrogen was skewed; these were not split into two peaks even after a longer electro-cleaning of 700 cycles.

Based on the results, the instability of the platinized-Ti electrode was characterized as a skewness of the adsorption-desorption peaks of hydrogen and oxygen and as a progressive change of voltammetric current through electro-cleaning. These can be attributed to the chloride ions trapped within the rough reentrant electrode surface and the many unstable fine polyps formed during the plating. First, to confirm that the chloride ions at the electrode surface were responsible for the skewness of the voltammograms in Fig. 2b and c, we carried out an experiment in which the voltammograms of a pure polycrystalline Pt wire with no

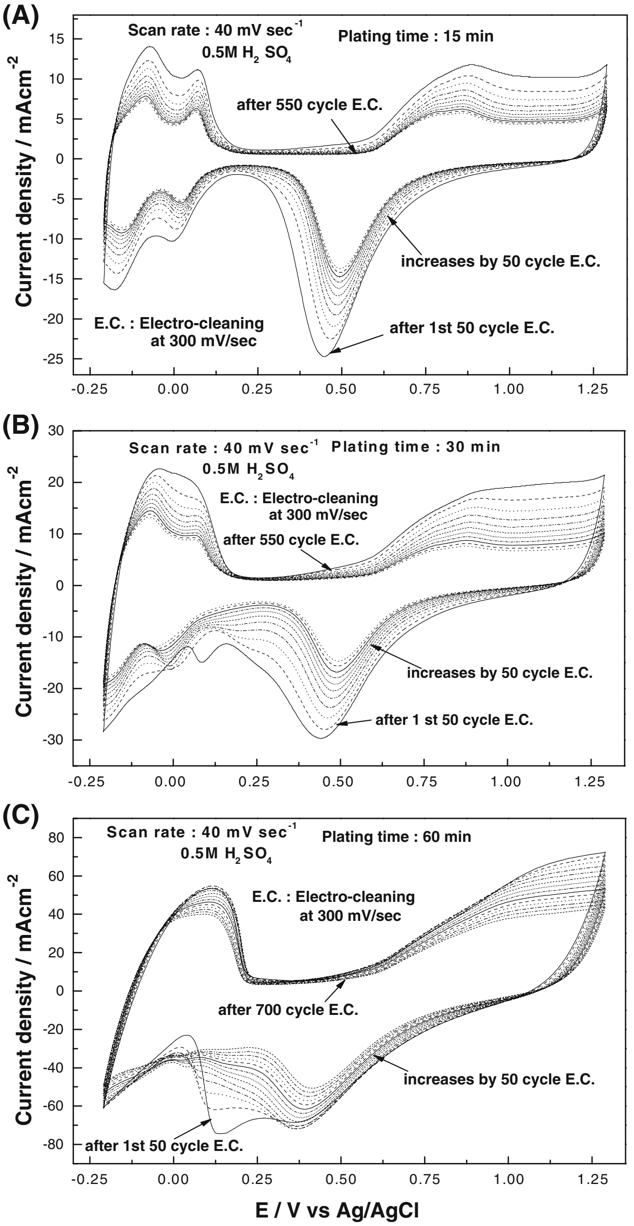


Fig. 2 Changes of the cyclic voltammograms of the platinized titanium electrodes with different plating times with electro-cleaning cycles

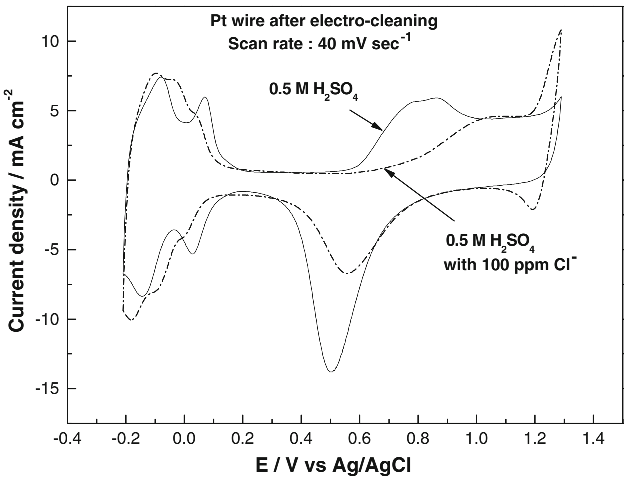


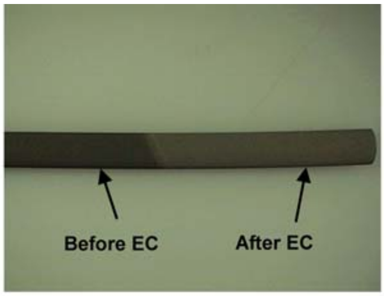
Fig. 3 Cyclic voltammograms of the Pt electrode in 0.5 M H_2SO_4 solutions with and without chloride ions

surface contamination were measured in 0.5 M H_2SO_4 solutions with and without 100 ppm chloride ions, the results of which are shown in Fig. 3. The redox peaks due to chloride ions were observed at around 1.2 V. The two separated peaks for respective adsorption and desorption of hydrogen were merged, and subsequently appeared as one peak. The oxide formation peak almost disappeared, and the oxide reduction peak decreased considerably and shifted slightly in the positive direction. Chloride ions, strongly adsorbed at the Pt electrode, are known to hinder the adsorption and desorption of hydrogen and oxygen [12, 13]. The electrodes of the 30- and 60-min platings, which showed unusual peaks between the oxide reduction peak and the hydrogen adsorption peak in their early voltammograms with short electro-cleaning cycles, as seen in Fig. 2b and c, have many fine polyps on their surface (Fig. 1). Such peaks after the platinization are attributable to the reduction of Pt hydrous oxide formed by oxidation of the Pt adatoms with a lower coordination number. The Pt adatoms are considered to be in a transient state before a stable deposition of Pt. When an electrode is platinized, its surface is known to be covered with several Pt species of Pt-adatom, Pt combined with hydroxide (whose valence is Pt^{d+} ($0 < d < 2$), e.g., $PtOH_{ads}$, $Pt(OH)_2$), as well as Pt bulk metal. In addition, these Pt-adatoms are known to be easily oxidized to hydrous oxides in the less positive potential region. Other researchers have discovered the presence of Pt hydrous oxide through X-ray Photoelectron Spectroscopy (XPS) [15–18]. Accordingly, the small polyps on the electrodes are considered to have something to do with the distortion of the voltammogram of the platinized-Ti electrode. The gradual decrease in voltammetric current is attributed to a morphological change of the electrode surface due to a place-exchange process caused by the electro-cleaning.

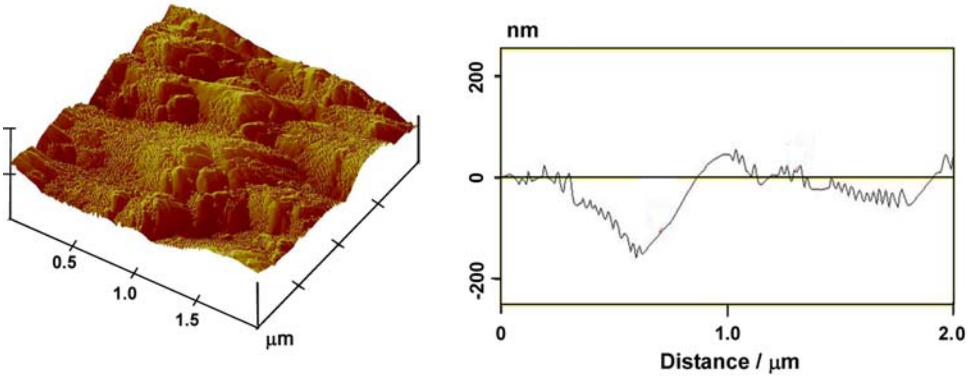
Pt adatoms in a meta stable state are known to be rearranged into a more stable state structure by a surface movement whose activation energy is supplied from a repetitive formation-reduction of surface oxide during electro-cleaning cycles [15, 16, 18–21]. To confirm the morphological surface change of a platinized-Ti electrode by electro-cleaning, which was not clearly observed in SEM, AFM images and their cross sections at certain parts of the Ti electrode platinized for 60 min before and after an electro-cleaning of about 500 cycles were measured, together with a photograph of a platinized-Ti electrode with and without an electro-cleaning. The results are shown in Fig. 4. The surface color of the platinized-Ti electrode was observed to have changed from dark gray to light gray after electro-cleaning in Fig. 4a. The AFM image showed many tiny polyps about 20 nm long on the electrode surface before the electro-cleaning in Fig. 4b. On the other hand, the polyps disappear from the electrode surface after electro-cleaning in Fig. 4c. The reason why the platinized-Ti electrode surface before the electro-cleaning was darker could be ascribed to unknown impurities simultaneously deposited during the Pt plating. To confirm this, a platinized electrode surface before electro-cleaning was analyzed by Electron Probe Micro Analysis (EPMA), but no metal impurity was detected. Accordingly, based on the result of the AFM image change, the color change of the platinized-Ti electrode surface after electro-cleaning is believed to be caused by the surface being smoothed through a place exchange action of Pt atoms caused by electro-cleaning, such that the diffused light reflection on the surface is decreased. Accordingly, the decrease in voltammetric current according to electro-cleaning cycles is attributable to the decrease in actual electrode surface area due to the place exchange action of unstable Pt species formed during the platinization.

Based on the change in the morphological structure with plating time (as seen in Fig. 1), we considered that the Pt plating solution was likely to be trapped during plating between the cavities or clearances formed between the spherical Pt clusters deposited on the etched Ti substrate. This therefore causes a severe skewness of the

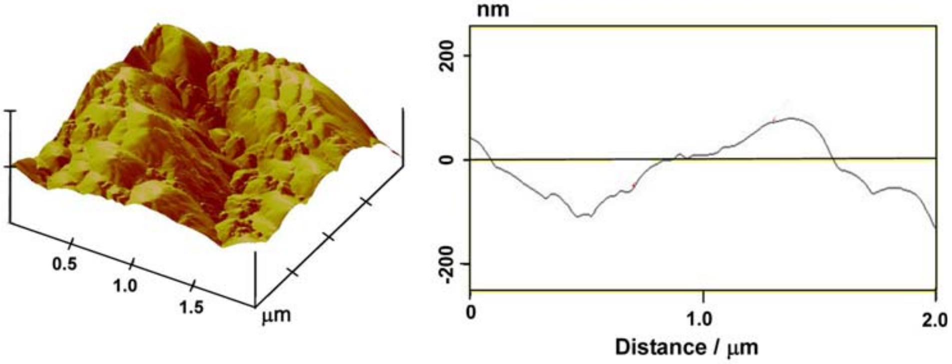
Fig. 4 Photograph (**a**), and AFM image and its cross section of a Ti electrode platinized for 60 min before (**b**) and after (**c**) an electro-cleaning



(A) Photograph of platinized-Ti electrode with and without electro-cleaning



(B) AFM image and cross section before electro-cleaning



(C) AFM image and cross section after electro-cleaning voltammetric curve even after washing with water and electro-cleaning of the electrode. Actually, many small crevices and cavities within the Pt coating layers of the platinized-Ti electrodes of 30- and 60-min platings were observed in SEM images of the electrode cross-sections. However, these are not presented in this paper. These small crevices and cavities caused difficulty in removing residual plating solution with chloride ions from the electrode surface by washing with water. However, in the case of short plating time where the Pt clusters were only grown at different sharp-point parts on the reentrant surface without interconnecting with each other (see Fig. 1b), there is less chance for the plating solution to be trapped under the coating layer. It is thus necessary to confirm that chloride ions exist within the internal structure of the Pt coating layer and to elucidate the time required for an electrode to be sufficiently washed by boiling it in water. Just prepared platinized-Ti electrodes with different plating times were boiled in water, and the concentration of chloride ions in the water was monitored with time. The results are shown in Fig. 5. In the case of the 15-min plating, the chloride ion concentration became constant at 5 ppm from the outset of boiling. However, the concentrations in the cases of 30- and 60-min platings increased to 13 and 24 ppm after about 3 and 6 h, respectively, which shows that the residual chloride ions trapped inside the Pt coating layer deposited at an etched Ti substrate are difficult to remove, as it takes a long time for the trapped plating solution to come out from the inside of the Pt coating layer through the crevices and cavities by diffusion.

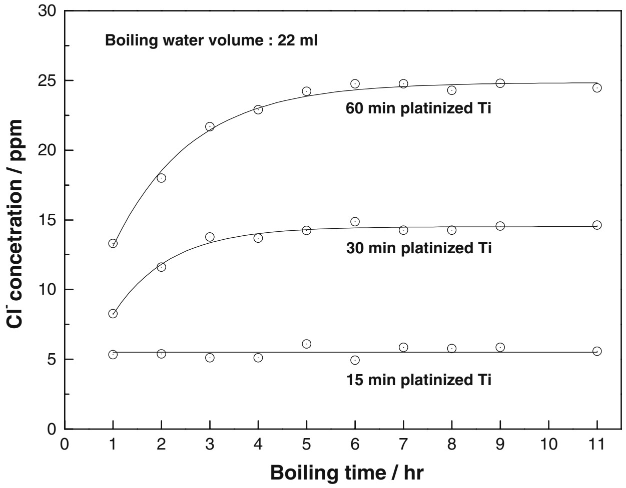


Fig. 5 Concentration changes of the chloride ions in solution during boiling the platinized-Ti electrodes in water

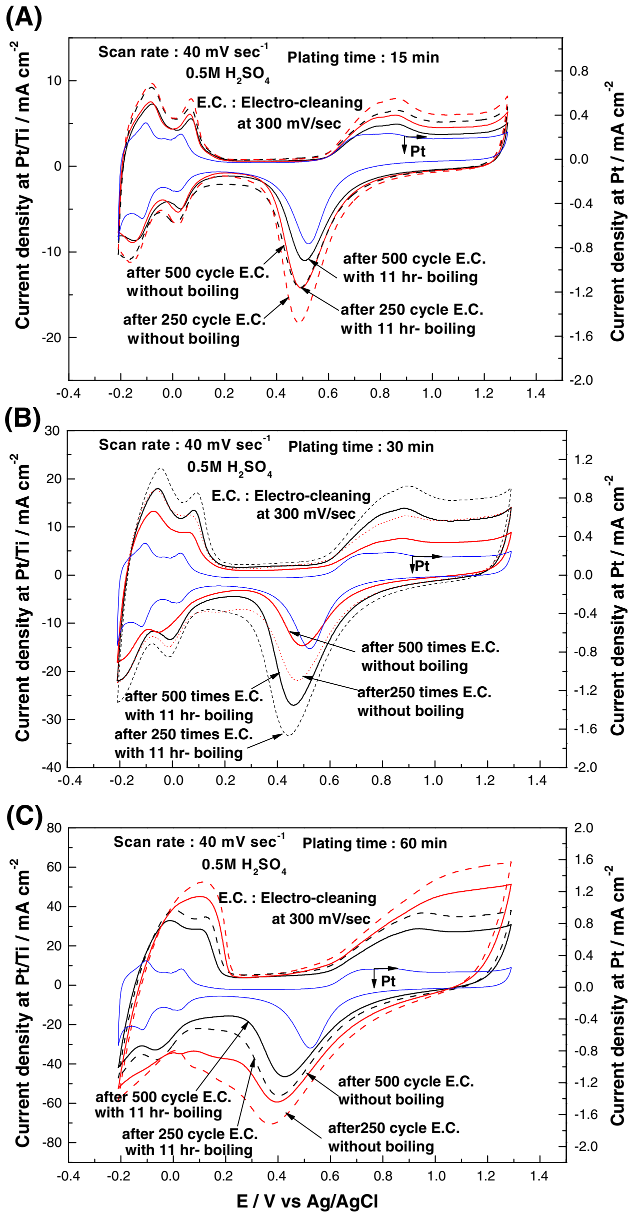


Fig. 6 Changes of the cyclic voltammograms of the platinized-Ti and Pt electrodes with different pretreatments

Figure 6 shows the voltammogram changes of the platinized-Ti electrodes prepared with and without a boiling step after simple washing of the plated electrodes with a change in the number of electro-cleaning cycles. The figure also shows the voltammogram of the polycrystalline Pt metal electrode as a reference. In this experiment, because the platinized-Ti electrodes with and without the boiling step were prepared independently, observing the skewness changes of the adsorption-desorption peaks of hydrogen and oxygen is necessary, rather than directly comparing the voltammetric current heights themselves. For the 15-min plating, a clear and typical Pt voltammogram were obtained regardless of the boiling procedure because the chloride ions that remained after the plating were easily removed from the surface even by simple washing of the electrode with water due to its Pt deposited structure, as seen in Fig. 1b. With the plating time increasing, in the case without a previous boiling step before electro-cleaning, the development of clear adsorption-desorption peaks of hydrogen and oxygen was retarded. In addition, compared to those of a polycrystalline Pt metal electrode, the peaks of oxygen-desorption and oxide formation shifted positively and became unclear. The 60-min plating did not show clear peaks for hydrogen adsorption-desorption even after long electro-cleaning followed by a long boiling process, which means that a platinization of Ti, where a thick Pt coating layer completely covers the whole electrode surface as seen in Fig. 1d, is not effective. From the above results, it can be summarized that there are two kinds of voltammogram changes at a platinized-Pt electrode due to electro-cleaning. One is that the adsorption and desorption peaks of hydrogen and oxygen become clearer, approaching the typical peaks at a pure polycrystalline Pt electrode with increased electro-cleaning cycles. This is ascribed to the contaminant anions remaining at the electrode surface after platinization. The other change refers to the decrease in voltammogram current, attributed to the decrease in surface area due to a place-exchange process at the electrode.

In this work, a Sn-modification of polycrystalline metal Pt or platinized-Ti electrodes was carried out by dipping a Pt electrode into a solution of 0.5 mM Sn for 10 min. The Pt electrode in this case underwent sufficient pretreatment through boiling and electro-cleaning steps to obtain a stable voltammetric behavior. The prepared electrode was used without further treatment after washing with water. Figure 7 shows the cyclic voltammograms of the platinized-Ti electrode and a polycrystalline metal Pt electrode in the hydrogen adsorption-desorption region before and after Sn-modification of the electrode surfaces. Differences in the peak potentials at the platinized-Ti electrode and the Pt electrode were observed. The peak potential shift at the platinized-Ti electrode was not due to ohmic drop between Pt coating layer and Ti substrate by passivation of Ti. It was due instead to the equilibrium potential change of the electro-adsorption/desorption of hydrogen resulting from a pH change in the solution adjacent to the Pt-platinized electrode because of an enhanced adsorption/desorption of hydrogen at the platinized-Ti electrode of much larger actual surface area [8, 22]. The differences in the peak potentials could be thought to be caused by ohmic drop due to the passivation of Ti. However, this is not true because a similar peak shift was confirmed to at a platinized-Pt electrode in which there was no contact resistance between the Pt deposit and the Pt substrate. The Sn-coverage was calculated from a change in charge capacity of the electrodes in the potential region (i.e., a change in the number of sites for the adsorption-desorption of hydrogen at the electrode) [1–4, 8, 14]. The values of the Pt metal and the 15-min-platinized-Ti electrodes were 46% and 17%, respectively. Those of the platinized-Ti electrodes with 30- and 60-min plating times were 9% and 2%, respectively.

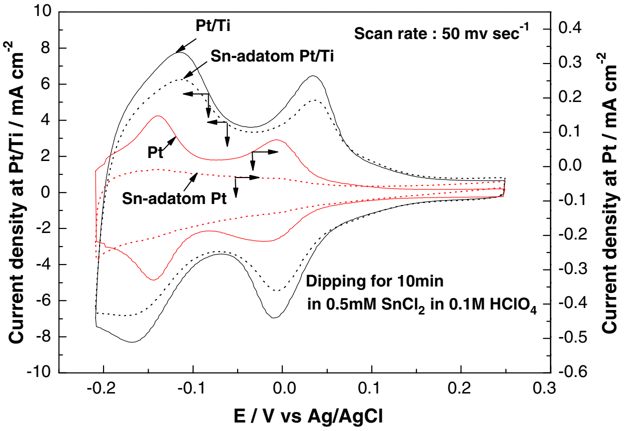


Fig. 7 Cyclic voltammograms of the Pt wire and 15 min platinized-Pt electrodes before and after Sn-adsorption on the electrodes

Figure 8 shows the linear voltammograms of a Pt polycrystalline metal electrode and platinized-Ti electrodes

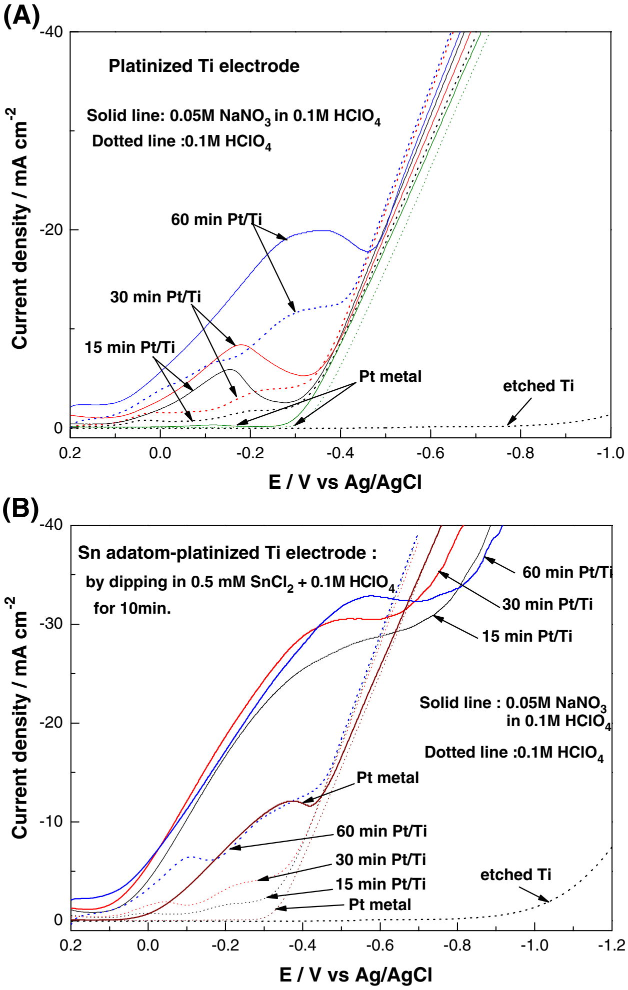


Fig. 8 Linear voltammograms of the platinized-Ti electrode (**a**) and Sn-modified platinized-Ti electrode (**b**) in a 0.1 M $HClO_4$ solution with and without 0.05 M $NaNO_3$

with different plating times of 15, 30, and 60 min with (A) and without (B) a Sn-modification of their surfaces in a nitrate solution of 0.05 M $NaNO_3$ with 0.1 M $HClO_4$. The reductive currents in the nitrate solution at the Sn-modified Pt and platinized-Ti electrodes are much larger than those for electrodes without Sn-modification. This is because the Sn atoms adsorbed at the Pt surface act as a catalyst for the reduction of nitrate ions. Perchlorate ions, used as a supporting electrolyte in this work, may be reduced at the electrode [23]. However, in our preliminary experiments, the Sn-modified Pt electrode used in this work had a negligible electro-activity to perchlorate ions when compared to its electro-activity to nitrate ions. In Fig. 8a, the Pt metal electrode without Sn-modification had almost no electro-activity to nitrate. However, surprisingly, the platinized-Ti electrodes without Sn-modification were observed to have some electro-activity to nitrate, even increasing with plating time. This increase was not expected, even if their background currents increased with the plating time because of a contaminant that remained within the Pt coating layer. The reason is considered to be because of the metastable Pt adatoms forming during the platinization, as described above, which acted as a catalyst for reducing nitrate on the electrode. In Fig. 8b with Sn-modification, the platinized-Ti electrode showed a much larger current than the Pt metal electrode of the same geometric surface area. This was caused by a large surface roughness formed during Pt plating of the etched Ti substrate. In the background solution, the set-in potential of the hydrogen evolution was not affected by Sn-modification of the electrode surface. However, in the nitrate solution, the overpotential of hydrogen evolution shifted toward negatively. The reason is thought to be because the affinity of nitrate ions to the electrode increases by a cooperative action of Sn and Pt atoms rather than by the Pt atoms alone [14], which hinders hydrogen adsorption at the electrode. Thus, a more negative potential is necessary for hydrogen evolution. In the case of the Sn-modified platinized-Ti electrodes, the order of the apparent reduction currents in the nitrate solution was $i_{60\ \mathrm{min}}(\sim 32\ \mathrm{mA\ cm^{-2}}) > i_{30\ \mathrm{min}}(\sim 30\ \mathrm{mA\ cm^{-2}}) > i_{15\ \mathrm{min}}(\sim 27\ \mathrm{mA\ cm^{-2}})$, showing a larger current according to the plating time. However, the current did not change linearly with plating time. Considering their background currents (shown as dotted lines in the figure), the order of the net reduction currents in the nitrate solution was $i_{30\ \mathrm{min}}\ (\sim 27\ \mathrm{mA\ cm^{-2}}) \geq i_{15\ \mathrm{min}}\ (\sim 26\ \mathrm{mA\ cm^{-2}}) > i_{60\ \mathrm{min}}\ (\sim 22\ \mathrm{mA\ cm^{-2}})$. The reason why the platinized-Ti electrode of the 30-min plating showed the largest electro-activity in the nitrate solution among the three electrodes could be explained by the differences in surface areas. As seen in Fig. 1d, in the case of the sufficiently developed Pt clusters covering the whole Ti substrate similar to that of the 60-min plating, its exposed surface was approximately two-dimensional. In contrast, for the special open clearances remaining between the Pt clusters like those of the 15- and 30-min platings, the exposed surface of the Pt coating was three-dimensional. Thus it had a larger electrode surface area. Compared to the 30-min plating, the platinized-Ti electrode of the 15-min plating had insufficiently developed Pt clusters on the Ti substrate; therefore, the electrode of the 30-min plating could develop the largest surface area among the three plating times. In conclusion, given all aspects such as electrode surface area, amount of Pt consumed for a platinization, simplicity of cleaning and stabilization of a plated electrode, a suitable plating time should be chosen for the platinization of Ti. In our work, this was determined to be approximately 30 min.

4 Conclusions

A platinization of Ti with some special open clearances between Pt clusters produced during the plating was effective in removing the residual contaminant after plating, rather than platinization with Pt clusters completely covering the whole substrate area, thus causing the contaminant to be trapped under the Pt coating layer. Such a platinization method could maximize actual electrode surface as well. The electro-cleaning caused a morphological change of the platinized-Ti electrode surface through a place-exchange process of Pt atoms, while many of the downy hair-like polyps formed on the surface disappeared. The time required to remove the residual contaminant from the plating solution at the electrode by boiling the platinized-Ti electrode in water changed depending on the Pt coating layer structure affected by the plating time. The platinized-Ti electrode itself had some electro-activity to the reduction of nitrate, even though its surface was not Sn-modified. The Sn-modified platinized-Ti electrode had a much more enhanced electro-activity to the reduction of nitrate than did the Pt metal electrode because of its Pt deposition shape.

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