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Electrochemical and structural investigations of oxide films anodically formed on ruthenium-plated titanium electrodes in sulfuric acid

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Abstract The electrochemical characteristics of ruthenium oxides, formed on Ru-plated Ti electrodes in 0.5 M H₂SO₄ by potential cycling with different CV upper potential limits (E_{SU}), were systematically compared. The repeated potential cycling between 0.2 and 0.75 V activated the formation/reduction of surface Ru oxides with hysteretic behavior. This application of repeated CVs also modified the ability of Ru deposits for hydrogen adsorption/desorption. An irreducible Ru oxide accumulated on the electrode at potentials more positive than ca. 0.95 V, whose capacitive characteristics are applicable for electrochemical supercapacitors. This irreducible oxide was composed of an aggregate consisting of Ru in various oxidation states, bridged oxygen, OH and water in a 3D-like structure with a relatively ordered and compact nature, from the X-ray photoelectron spectroscopic and voltammetric results. The surface reconstruction of the Ru deposits induced by the repeated potential cycling with $E_{SU} \geq 0.75$ V was clearly observed from the SEM photographs. From the X-ray diffraction patterns, all the anodically formed Ru oxides showed an amorphous nature.

Keywords Cyclic voltammetry · Hydrogen adsorption/desorption · Irreducible ruthenium oxide · Pseudocapacitance · Ruthenium deposit

Introduction

Owing to the existence of several oxidation states [i.e., Ru(0), Ru(II), Ru(III), Ru(IV), Ru(V), Ru(VI), Ru(VII)

and Ru(VIII)], ruthenium gives rise to many compounds having interesting and unique properties, especially the electrochemical properties of ruthenium oxides [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. The electrochemistry of ruthenium oxides, particularly crystalline RuO₂ prepared by thermal decomposition, has been extensively investigated in the past 30 years because of the great contribution of dimensionally stable anodes (DSA) in the chlor-alkali industry and the possibility of oxygen evolution in acidic media [4, 5, 6, 7, 8, 9, 11, 12, 13, 14, 15]. The formation/reduction as well as the accumulation of hydrous ruthenium oxides formed by potential cycling on bulk Ru and Ru-plated Pt electrodes were systematically investigated by Conway et al. [1, 2, 3]. Moreover, the complicated redox transitions of various ruthenium oxides, including the formal potentials and the super-Nernstian responses, have been widely investigated by Burke et al. [4, 5, 6]. All the above studies reveal that the redox transitions of ruthenium oxides are electrochemically reversible but too complicated to identify separately.

Owing to the highly electrochemical reversibility of Ru oxides in different oxidation states, hydrous oxides, especially formed by the sol-gel or the electrochemical processes [16, 17, 18, 19, 20], have been recognized as promising electrode materials for electrochemical supercapacitors [1, 16, 17, 18, 19, 20, 21]. Since the voltammetric responses of these hydrous Ru oxides were significantly different from those formed by thermal decomposition of the chloride precursor [4, 5, 6, 7, 8, 9, 11, 12, 13, 14, 15] or by the potential cycling method from Ru metal [1, 2, 3, 8], the capacitive properties of the redox couples on/within the oxide matrix should be a strong function of the preparation conditions. Accordingly, the effects of the preparation variables on the formation/reduction and capacitive characteristics of hydrous ruthenium oxide are worthy of being studied.

Since hydrous ruthenium oxide is a promising electrode material for supercapacitors, this material can be easily formed by the anodic polarization of Ru metal. On the other hand, bulk metal is considered to be

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unsuitable for practical applications [7, 22]. Hence, ruthenium oxide coatings appear to be more desirable and suitable for such applications. In this work, the possibility that hydrous ruthenium oxides can be formed on Ru-plated titanium electrodes by means of potential cycling for application as supercapacitors was systematically studied. The electrochemical characteristics of these oxides formed under different conditions were carefully compared. Moreover, variations in the crystalline structure, morphology and oxidation state of the Ru deposits before and after the potential cycling pretreatments were also compared to gain a further understanding for the capacitive properties of Ru oxides, which is very important in the supercapacitor application.

Experimental

Prior to the electrolytic deposition, the commercial 99% titanium substrates (10×10×2 mm) were first mechanically polished by emery paper, which was blown by a high-pressure air compressor. These substrates were degreased with soap and water, and etched for 1.5 h in a 6 M HCl solution at ca. 90 °C. They were then rinsed with water again and pickled for 10 min in a solution consisting of *N,N*-dimethylformamide (DMF, Wako E.P., Japan), water and HF (Wako E.P., Japan) in the volume ratio 40:7.5:2.5. After the pickling pretreatment, the substrates were rinsed with acetone and water, coated with PTFE films with an exposed surface area of 1 cm², and then placed in the plating solution. The plating solution, consisting of 20 g dm⁻³ RuCl₃·xH₂O and 0.01 M HCl, was stirred on a hot plate during the plating process. Ruthenium deposits were electroplated onto these pretreated substrates at a constant current density of 20 mA cm⁻². The electroplating was stopped when the passed charge was equal to 30 C cm⁻². After deposition, the PTFE films were removed from the electrodes. These electrodes were then rinsed with water and dried in a vacuum oven at room temperature. The loading of every deposit was the weight difference of the electrode without the PTFE coating before and after the application of the electroplating. For the electrochemical studies, the electrode areas without the Ru coating were doubly coated with epoxy resin and PTFE films. For textural analysis, the epoxy resin and PTFE films were removed after the electrochemical tests. Finally, these electrodes were rinsed in an ultrasonic bath containing pure water and then were dried and kept in a vacuum chamber at room temperature before textural analysis.

Surface morphologies of the Ru deposits before and after electrochemical pretreatments were examined by a scanning electron microscope (SEM, JEOL JSM 35). X-ray diffraction analysis (XRD, Rigaku X-ray diffractometer using a Cu target) was used to obtain crystalline information of the deposits before and after the electrochemical pretreatments. X-ray photoelectron spectra (XPS) were measured by an ESCA 210 (VG Scientific) spectrometer. XPS spectra employed Mg K α ($h\nu=1253.6$ eV) irradiation as the photosource with a primary voltage of 12 kV and an emission current 17 mA. The analysis chamber pressure during scans was approximately 10⁻¹⁰ mbar. The samples were cleaned with an Ar-ion gun for 25 min before measuring the XPS spectra in order to avoid interference by adventitious carbon.

Electrochemical techniques for the oxide formation and characterization were performed by an electrochemical analyzer system (CHI 633A, CH Instruments, USA). All experiments were carried out in a three-compartment cell. An Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs. SHE at 25 °C) was used as the reference, and a piece of platinum gauze with an exposed area of 4 cm² was employed as the counter electrode. A Luggin capillary, whose tip was set at a distance of 1–2 mm from the surface of the working electrode, was used to minimize errors due to the *iR* drop in the electrolytes.

All solutions used in this work were prepared with 18 M Ω cm water produced by a reagent water system (Milli-Q SP, Japan). All reagents not otherwise specified in this work were from Merck. The electrolyte, containing 0.5 M H₂SO₄, used to study the electrochemical behavior of ruthenium oxides was degassed with purified nitrogen gas before the voltammetric measurements and nitrogen was passed over the solution during the measurements. The solution temperature was maintained at 25 °C by means of a water thermostat (Haake DC3 and K20).

Results and discussion

Formation and capacitive behavior of Ru oxides on Ru-plated Ti electrodes with different pretreatments

The voltammetric curves of a freshly electroplated Ru/Ti electrode and a Ru/Ti electrode after an application of repeated potential cycling with E_{SU} varying from 1.15 to 0 V (–50 mV for every E_{SU} shift), measured in 0.5 M H₂SO₄ between 0.2 and 1.15 V, is shown as curves 1 and 2 in Fig. 1, respectively. Typical *iE* responses measured in 0.5 M H₂SO₄ between 0.2 and 1.15 V and between 0.2 and 0.75 V for another Ru/Ti electrode after an application of repeated potential cycling with E_{SU} varying from 1.15 to 0.75 V (–50 mV for every E_{SU} shift), in the same medium, are shown as curves 3 and 4 in Fig. 1, respectively. For curve 1, a broad peak between 0.75 and 1.15 V on the positive sweep and relatively high background currents on both positive and negative sweeps at potentials more positive than 0.1 V are clearly found. For curve 2, an anodic peak with a shoulder in the potential range of UPD hydrogen oxidation is clearly found on the positive sweep. In addition, voltammetric currents of the broad anodic peak between 0.75 and 1.15 V and the background currents on the positive sweep are clearly increased. However, the voltammetric currents on the negative sweep of curve 2 approximately follow the same trace of the negative sweep of curve 1. Since the voltammetric charge on the positive sweep is much larger than that on the negative sweep, there should exist an irreversible oxidation (e.g., the formation of irreducible ruthenium oxide) on this Ru/Ti electrode.

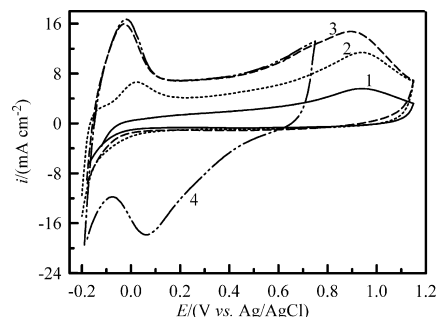


Fig. 1 Cyclic voltammograms of (1) a freshly prepared Ru/Ti electrode and a Ru/Ti electrode after the application of CVs with the negative shift in E_{SU} from 1.15 to (2) 0 and (3, 4) 0.75 V measured at 25 mV s⁻¹ in 0.5 M H₂SO₄. The upper potential limits of the CV for curves 3 and 4 are equal to 1.15 and 0.75 V, respectively

The above comparison reveals two facts. First, the adsorption/desorption of UPD hydrogen on the freshly deposited Ru metal is inhibited, probably due to the formation of surface oxyruthenium species resulting from the high oxygen affinity of Ru adatoms, since adatoms can be easily formed on the deposit surface during the electroplating [22]. This inhibition can be reactivated by the application of repeated CVs, although the inhibition phenomenon is not visible for bulk Ru metal or a Ru/Pt electrode [2, 3]. Second, the application of CVs with a negative shift in E_{SU} can reactivate and roughen the surface of this deposit. For curve 4, a broad anodic peak between 0.15 and 0.1 V and a gradual increase in currents commencing at ca. 0.45 V are found. In addition, the voltammetric currents on the whole positive sweep are obviously higher than those on curves 1 and 2. The former result supports the statement that the application of CVs with a negative shift in E_{SU} can reactivate the surface of the Ru deposit for the responses of UPD hydrogen. The latter result indicates the fact that the repeated oxidation/reduction of surface ruthenium oxide roughens the deposit due to the place-exchange mechanism [8] and enhances the hydrogen responses and oxide formation on the following positive sweep. Note a very broad reduction peak commencing at about 0.6 V on the negative sweep of curve 4 corresponding to the reduction of Ru oxide, whose peak potential (E_p) is found to positively shift with the negative movement of E_{SU} when it is between 1.0 and 0.8 V (not shown here).

The above hysteretic response of oxide formation and reduction are attributable to the formation of an ordered and irreducible ruthenium oxide on the Ru surface [3]. From a comparison of curves 3 and 4, the voltammetric behavior of this Ru/Ti electrode between 0.2 and 0.75 V on the positive sweep is the same, indicating that the electrochemistry of this Ru deposit is not significantly affected by the application of one CV cycle between 0.2 and 0.75 V. On the other hand, the voltammetric behavior of this Ru deposit on the negative sweep (curve 3) is very similar to that of curve 2 in the whole potential region. The difference in iE responses on the negative sweeps between curves 3 and 4 is undoubtedly due to the reaction occurring between 0.75 and 1.15 V. Owing to the absence of an oxide reduction peak on the negative sweep of curve 3, the process occurring between 0.75 and 1.15 V is believed to render the formation and accumulation of irreducible Ru oxides. Thus, a lower reduction charge on the negative sweep is obtained in comparison with that on the positive sweep. In fact, anodic currents of Ru oxidation on the following positive sweep (i.e., after the application of curve 3) decrease significantly (not shown here), further supporting the above statement.

The Ru/Ti electrode was subjected to potential cycling with different upper potential limits to illustrate the effect of the potential region on the electrochemical characteristics of the surface Ru oxide. Typical results of a freshly plated Ru deposit measured in 0.5 M H_2SO_4

for the 2nd, 4th, 7th, 10th, 15th, 30th and 100th cycles of CV between 0.2 and 0.75 V are shown in Fig. 2 as curves 1–7, respectively. For curve 1, the voltammetric behavior of the oxide formation/reduction and hydrogen adsorption/desorption is unclear, while relatively large background currents, not attributable to the double-layer charge/discharge, are visible on both positive and negative sweeps. When the cycle number is increased, the voltammetric currents corresponding to the formation/reduction of Ru oxides and the adsorption/desorption of UPD hydrogen are significantly increased, indicating that these reactions can be promoted by potential cycling between 0.2 and 0.75 V. Since the voltammetric charges on the positive sweeps are approximately equal to those on their corresponding negative sweeps for all curves, the formation/reduction of Ru oxide as well as the adsorption/desorption of UPD hydrogen are electrochemically reversible, although hysteretic behavior of the oxide formation/reduction, unsuitable for supercapacitor application, is very obvious. Note that the anodic peak in the potential region of UPD hydrogen desorption becomes wider on increasing the cycle number of the CV and shows a peak with a shoulder when the cycle number is ≥ 30 . Therefore, there should exist two reactions in this potential region, which are reasonably attributed to the desorption of UPD hydrogen and the oxidation of Ru adatoms formed in the preceding negative sweep.

The effect of the repeated formation/reduction of reducible Ru oxides on the formation and reduction of ruthenium oxides at a freshly plated Ru/Ti electrode was investigated and the results with E_{SU} varying from 1.15 to 0 V are shown in Fig. 3. The voltammetric currents on the positive sweeps gradually decrease with the negative shift in E_{SU} , reach the minimum at E_{SU} equal to 1.05 V, then gradually increase with the further negative movement of E_{SU} from 1.05 to 0.75 V and finally overlap in the following cycles. The decrease in voltammetric currents at E_{SU} more positive than or equal to 1.05 V is not attributable to the dissolution of ruthenium species in the highly positive potential region, because all iE curves on the positive sweeps approximately

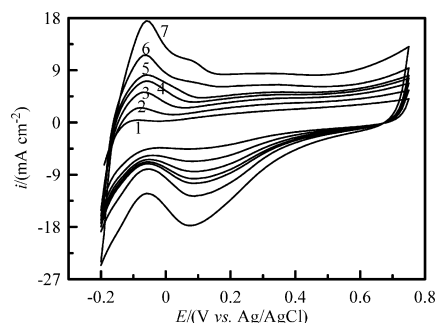


Fig. 2 Cyclic voltammograms of a freshly plated Ru deposit measured at 25 mV s^{-1} in 0.5 M H_2SO_4 for the (1) 2nd, (2) 4th, (3) 7th, (4) 10th, (5) 15th, (6) 30th and (7) 100th cycles of CV between 0.2 and 0.75 V

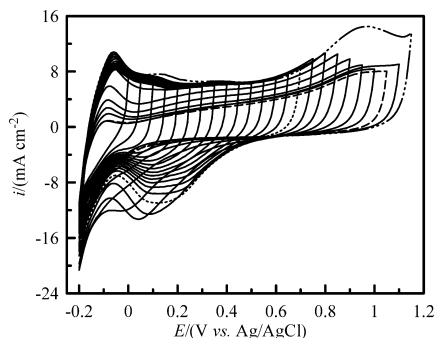


Fig. 3 Voltammetric behavior of a Ru deposit with 100 cycles of CV between 0.2 and 0.75 V. Cyclic voltammograms were measured at 25 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ with the negative shift in E_{SU} from 1.15 to 0 V

follow the same trace of the CV curve with E_{SU} at 1.15 V (i.e., dash-dot-dot-dot line) when E_{SU} is less positive than 0.75 V. Thus, the oxidation reaction that occurs between 0.75 and 1.15 V on the positive sweeps should be mainly due to the formation and accumulation of a more ordered and irreducible Ru oxide. The proposal that a more ordered oxide is formed between 0.75 and 1.15 V is supported by the fact that E_{P} of the oxide reduction on the negative sweep is negatively shifted with the positive increase of E_{SU} in Fig. 3, since a negative shift in E_{P} for oxide reduction indicates a more hysteretic character for the formation/reduction of oxides [23]. Note that when E_{SU} is less positive than 0.7 V (dotted line), less hysteretic behavior for oxide redox transitions is found. Similar behavior is also found for a freshly prepared Ru/Ti electrode, while lower voltammetric currents on both positive and negative sweeps are clearly found. Hence, the potential cycling employed in Fig. 2 is considered as a method activating and roughening the surface of a freshly plated Ru deposit.

Based on the above results and discussion, irreducible Ru oxides can form and be accumulated on the Ru/Ti electrode when E_{SU} is above 1.05 V. Accordingly, the Ru/Ti electrode was subjected to potential cycling between 0.2 and 1.15 V to form the Ru oxide in different oxidation states and/or structures with different electrochemical characteristics. Typical results with E_{SU} varying from 1.15 to 0 V are shown in Fig. 4. In this figure there is no obvious redox peak corresponding to the redox transitions of oxides and UPD hydrogen on this Ru/Ti electrode, while relatively high background currents are clearly observed in the whole potential range of investigation. This indicates that the irreducible Ru oxide accumulated on the deposit surface exhibits capacitive characteristics. Moreover, the electrochemical reversibility of redox transitions for this oxide is good enough for supercapacitor applications since all CV curves show the capacitive-like responses. Similar results have been found on the Ru/Pt electrode [3], attributed to the intrinsic features of hydrous ruthenium oxide, although the negative movement in E_{SU} (see Fig. 4) gradually increases the voltammetric currents on the

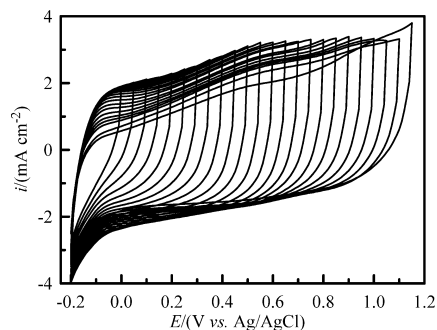


Fig. 4 Voltammetric behavior of a Ru deposit with 100 cycles of CV between 0.2 and 1.15 V. Cyclic voltammograms were measured at 25 mV s^{-1} in $0.5 \text{ M H}_2\text{SO}_4$ with the negative shift in E_{SU} from 1.15 to 0 V

positive sweeps. On the other hand, the electrochemical characteristics of this hydrous ruthenium oxide, including hydrogen adsorption/desorption as well as the redox transitions of ruthenium oxide, are different from that deposited by cyclic voltammetry from the chloride precursor [18, 19, 24, 25]. In addition, hydrogen adsorption/desorption is clearly found for an anhydrous Ru oxide prepared by thermal decomposition [4, 5, 6, 7, 8, 9, 11, 12, 13, 14, 15], revealing that the electrochemistry of Ru oxide also strongly depends on the history of the oxide preparation.

The electrochemical reversibility of hydrous ruthenium oxides formed on the Ru/Ti electrodes with different pretreatments can be compared with the dependence of the anodic and cathodic charge ratio on E_{SU} , where anodic and cathodic charges are respectively integrated from the positive and negative sweeps. Typical results integrated from the CV curves of a freshly plated Ru/Ti electrode and those shown in Figs. 4 and 3 are represented in Fig. 5 as curves 1–3, respectively. From these three curves, the charge ratio is close to 1.0 when E_{SU} is negative to ca. 0.9 V, indicating that most oxides formed during the positive sweep can be reduced in the following negative sweep. On the other hand, a rapid rise in the $q_{\text{a}}/q_{\text{c}}$ ratios is found when E_{SU} is more

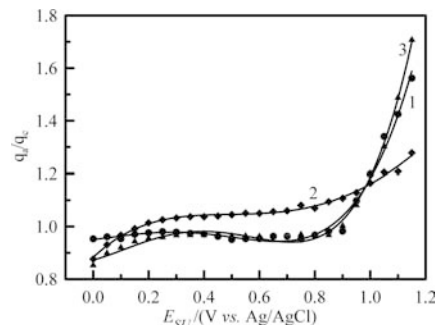


Fig. 5 Dependence of the $q_{\text{a}}/q_{\text{c}}$ ratio on E_{SU} , where q_{a} and q_{c} are respectively integrated from the positive and negative sweeps of the CVs. Data of the voltammetric charges were integrated from the CV curves of (1) a freshly plated Ru/Ti electrode and those shown in (2) Fig. 4 and (3) Fig. 3

positive than 0.9 V, especially for curves 1 and 3, revealing that surface Ru oxides are gradually transformed from a reducible state to an irreducible structure. This transformation should commence at ca. 0.75 V, since a negative shift in E_P for the oxide reduction is found with a positive shift in E_{SU} ; meanwhile the oxide becomes irreducible when electrode potentials were swept above 0.95 V.

Typical charge-discharge responses of a freshly plated Ru deposit and another two freshly plated Ru deposits with 100 cycles of CV between 0.2 and 1.15 V and between 0.2 and 0.75 V, measured at $100 \mu\text{A cm}^{-2}$, are shown as curves 1–3 in Fig. 6. For curve 1, a rapid rise in potentials is found at potentials negative to ca. 0.2 V, indicating that no obvious redox transition occurs in this potential region. At potentials above 0.4 V, the electrode potential is linearly dependent on the charge time, exhibiting a capacitive-like behavior. This capacitive-like response is also found in the discharge test, while the absolute value of the slope for the discharge line is larger than that for the charge curve. Moreover, the charge-discharge efficiency is only 50% and 77% when the potential region of chronopotentiometry ranges from 0.4 to 1.15 V and from 0 to 1.15 V, respectively, indicating the irreversibility for the formation of surface Ru oxides on this freshly plated Ru deposit.

For curve 2, the discharge curve shows the typical mirror responses of the charge line with the charge-discharge efficiency close to 100%, indicating the good reversibility of the redox transitions for Ru oxides between different oxidation states, which is suitable for supercapacitor application. However, the electrode potential is kept constant at ca. 1.1 V during the charge test (not shown here), indicating that an irreversible reaction, oxygen evolution, occurs at this potential since the onset potential of this reaction on a RuO_2 -coated electrode was proposed to be equal to 1.387 V (vs. SHE) [26], which is very close to 1.1 V (vs. Ag/AgCl). Accordingly, the upper limit of the potential window for the charge-discharge test on various Ru/Ti deposits in H_2SO_4 should be less positive than 1.1 V (vs. Ag/AgCl).

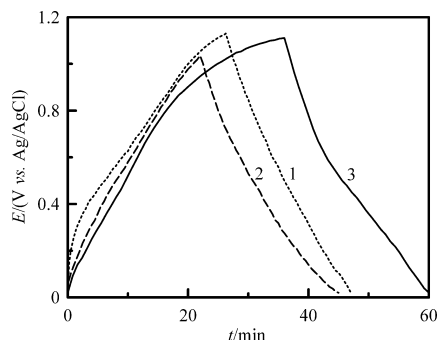


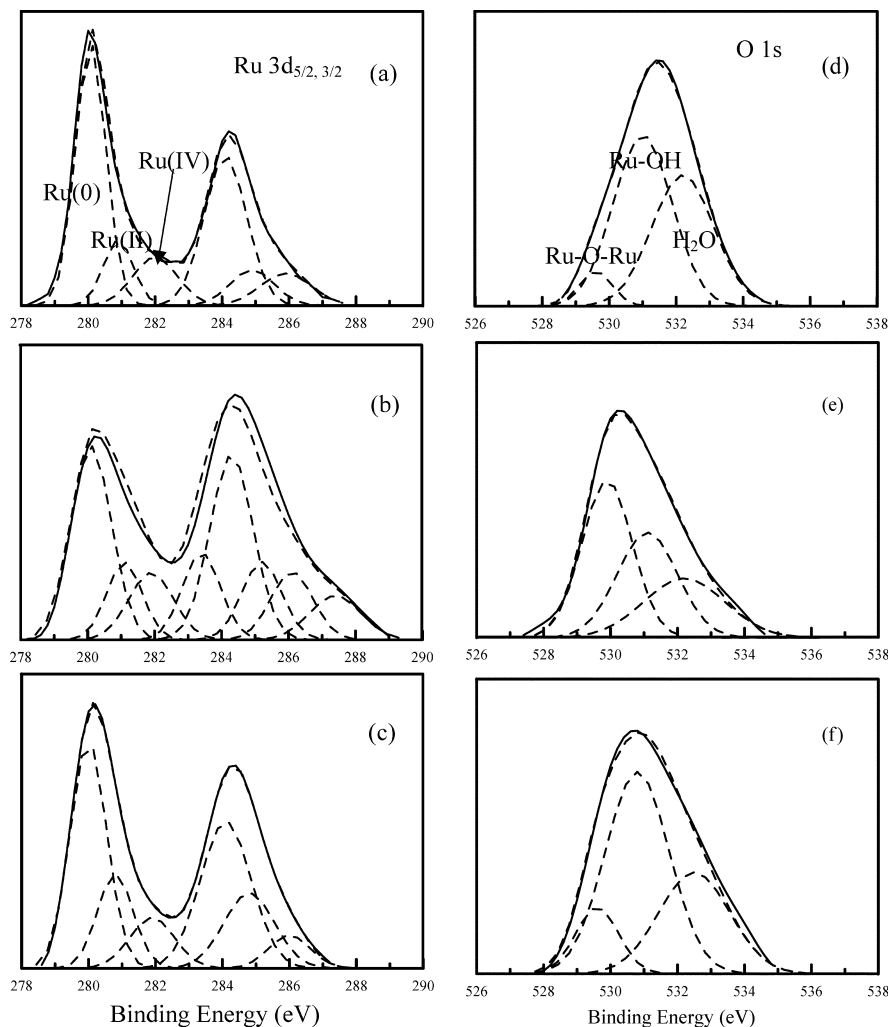
Fig. 6 Chronopotentiograms measured in a 0.5 M H_2SO_4 solution at $100 \mu\text{A cm}^{-2}$ for (1) a freshly electroplated Ru deposit and the Ru deposits with 100 cycles of CV (2) between 0.2 and 1.15 V and (3) between 0.2 and 0.75 V in 0.5 M H_2SO_4

Based on the above results and discussion, the formation of the irreducible Ru oxides on the Ru/Ti electrode should catalyze the oxygen evolution reaction. For curve 3, the charge capacity of this electrode is the highest but its charge-discharge efficiency is low (ca. 67%). This low efficiency is due to irreversible oxidation occurring at potentials positive to ca. 0.8 V on the charge curve (i.e., the formation of irreversible oxides). Moreover, from its discharge curve, the mean capacitance obtained at potentials negative to ca. 0.5 V is not equal to that in the more positive potential range, indicating poor capacitive performance.

Textural examination of Ru oxides on Ru/Ti electrodes with different pretreatments

From the above results and discussion, the voltammetric and capacitive performances of Ru/Ti electrodes with various pretreatments should be linked to the intrinsic structures of ruthenium oxides formed under different conditions. These expectations can be quantitatively illustrated by examining their XPS core level spectra. Typical XPS core level spectra of Ru $3d_{3/2,5/2}$ and O 1s for a freshly plated Ru deposit and the Ru deposits with 100 cycles of CV from 0.2 to 1.15 V and from 0.2 to 0.75 V are shown in Fig. 7. In Fig. 7a–c, the Ru $3d_{3/2,5/2}$ peaks are relatively broad, indicating the existence of several oxidation states. Thus, the XPS peaks of Ru $3d_{3/2,5/2}$ in Fig. 7a–c are reasonably decomposed into three pairs of Gaussian peaks with their Ru $3d_{5/2}$ binding energy equal to 280.0, 280.7 and 281.8 eV, respectively. These three pairs of peaks are attributed to the Ru(0), Ru(II) and Ru(IV) species, respectively [27, 28, 29]. Moreover, there is an additional pair of peaks with a binding energy for Ru $3d_{5/2}$ equal to 283.3 eV for the oxides formed by 100 cycles of CV between 0.2 and 1.15 V (see Fig. 7b), which was ascribed to the formation of RuO_3 [28]. From a comparison of the spectra in Fig. 7a–c, three features have to be mentioned. First, all the ruthenium species formed on the Ru/Ti electrode are composed of a mixture of Ru oxides with different oxidation states, while the relative amount of these species is a function of the pretreatment. The presence of Ru oxides on the freshly plated Ru deposit is due to the oxidation of surface Ru atoms by oxygen molecules in the air. This is likely to happen since there should exist several Ru adatoms on the deposit surface, especially for the deposit plated under a relatively high current density [22, 30]. Accordingly, inhibition of the UPD hydrogen adsorption/desorption on the freshly plated Ru deposit found for curve 1 in Fig. 1 is a reasonable result from the formation of these surface oxides. Second, the amount of metallic Ru atoms is decreased by the pretreatment of 100 CV cycles, which also decreases with the positive shift in E_{SU} of the CV from 0.75 to 1.15 V. The above results indicate the formation and accumulation of various Ru oxides on Ru/Ti electrodes by the repeated potential cycling. Note that all oxides on

Fig. 7 XPS spectra in the (a–c) Ru $3d_{3/2,5/2}$ and (d–f) O 1s regions for a freshly electroplated Ru deposit (a, d) and for Ru deposits with 100 cycles of CV (b, e) between 0.2 and 1.15 V and (c, f) between 0.2 and 0.75 V



different Ru/Ti electrodes show the thin-film nature since the information from the XPS data is superficial (ca. 5–8 nm) and metallic Ru atoms are clearly found on all spectra shown in Fig. 7. Third, there is an additional pair of peaks in Fig. 7b, which is absent on the other two deposits. This Ru species is probably due to the formation and accumulation of the irreducible Ru oxide formed at potentials more positive than ca. 0.95 V, whose capacitive performance is good enough for the application of supercapacitors. Although this Ru oxide was ascribed to RuO_3 formation [28], RuO_3 is expected to be relatively unstable in the very high vacuum chamber. Accordingly, this irreducible Ru oxide is considered to be an aggregate consisting of Ru atoms in various valence states, bridged oxygen, OH and water molecules. Moreover, the bridged oxygen Ru species should exist in a structure similar to a three-dimensional network having a relatively ordered and compact nature [23], resulting in the accumulation of irreducible Ru oxides and the hysteretic responses of the oxide formation/reduction.

The above speculation is supported by the XPS core level spectra of O 1s shown in Fig. 7d–f. From a

comparison of the spectra in Fig. 7d–f, the O 1s peak is negatively shifted with the application of the 100-cycle CVs, especially for the case with E_{SU} equal to 1.15 V, revealing the gradual conversion from a hydrous property (i.e., Ru-O-H) into a structure with the bridged-oxygen oxide (i.e., Ru-O-Ru). In addition, these O 1s spectra can be decomposed into three constituents (i.e., 529.8, 531.1 and 532.2 eV [27, 28, 31, 32]), corresponding to Ru-O-Ru, Ru-O-H and H-O-H, respectively. Note that the amount of Ru-O-Ru, based on the relative surface area of the O 1s spectra, is increased from ca. 5.9 to 12.4 at% when the freshly plated Ru deposit has been potential cycled between 0.2 and 0.75 V for 100 cycles. Moreover, there is a sharp increase in Ru-O-Ru species from 12.4 to 41.5 at% as E_{SU} is positively moved from 0.75 to 1.15 V. The above results support that the irreducible Ru oxides are composed of an aggregate of Ru atoms with various oxidation states, bridged oxygen, OH and water, probably in a nonstoichiometric structure. This nonstoichiometric nature also explains the absence of redox peaks but high background currents for the CV curves in Fig. 4 (i.e., redox reactions with undefined formal potentials). On the other hand, oxides

formed on the freshly plated Ru deposit (probably due to the oxidation of Ru adatoms in air), or by CV between 0.2 and 0.75 V for 100 cycles, should mainly consist of hydrous ruthenium oxides, based on the relatively large areas of the Ru-O-H peak in Fig. 7d and Fig. 7f (52.0% and 56.2%, respectively). These oxides are reducible in the investigated potential region, although hysteretic responses in the oxide formation/reduction are clearly found on the CV curves when E_{SU} is positive to ca. 0.75 V.

Typical SEM photographs for a freshly plated Ru/Ti electrode, the Ru/Ti electrodes post-100 cycles of CV from 0.2 to 1.15 V and from 0.2 to 0.75 V are shown in Fig. 8a and Fig. 8b, Fig. 8c and Fig. 8d, and Fig. 8e and Fig. 8f, respectively. In general, a freshly plated Ru deposit shows a spherical outward appearance with a rough morphology. This porous deposit becomes relatively smooth and compact by the repeated CV treatments. Based on these results, the application of repeated CVs with E_{SU} equal to 0.75 V can render the surface reconstruction of Ru deposits, which also modifies its reaction activity for the adsorption/desorption of UPD hydrogen. This process is believed to pass through the place-exchange mechanism for the oxide formation/reduction, which is applicable for the formation and

accumulation of the irreducible Ru oxides when E_{SU} is equal to 1.15 V. In fact, similar phenomena for the surface reconstruction of Pt adatoms on a Pt/Ti electrode by means of cyclic voltammetry have also been found [30]. In addition, the place-exchange process is proposed to provide the energy overcoming the barrier for the movement of surface Pt adatoms from a metastable state (e.g., at the adatom site) to a more stable state (e.g., at the kink and edge sites) during the repeated formation/reduction of oxides.

XRD analysis was employed to obtain structural information for the Ru/Ti electrodes with different pretreatments. The XRD patterns for a freshly plated Ru deposit and other two freshly plated Ru deposits post 100 CV cycles between 0.2 and 1.15 V and between 0.2 and 0.75 V are shown in Fig. 9 as curves a–c, respectively. For all XRD patterns, diffraction peaks corresponding to Ru and Ti metals are clearly found. The diffraction peaks for Ru are very broad, indicating a poor crystalline structure for the Ru deposit, although it should be of a polycrystalline structure. The presence of Ti diffraction peaks indicates that the Ru deposit should be thinner than 10 μm . Note the absence of any diffraction peaks corresponding to crystalline oxides (e.g., RuO_2), indicating an amorphous nature of the ruthenium oxides formed on the Ru deposits. From a comparison of the XRD patterns in Fig. 9, the diffraction intensities of the Ru and Ti peaks are respectively decreased and increased by the application of repeated CV cycling. The latter result is attributable to the minor dissolution of Ru deposits during the CV treatments. The former result is reasonably due to the formation of amorphous ruthenium oxides during the potential cycling.

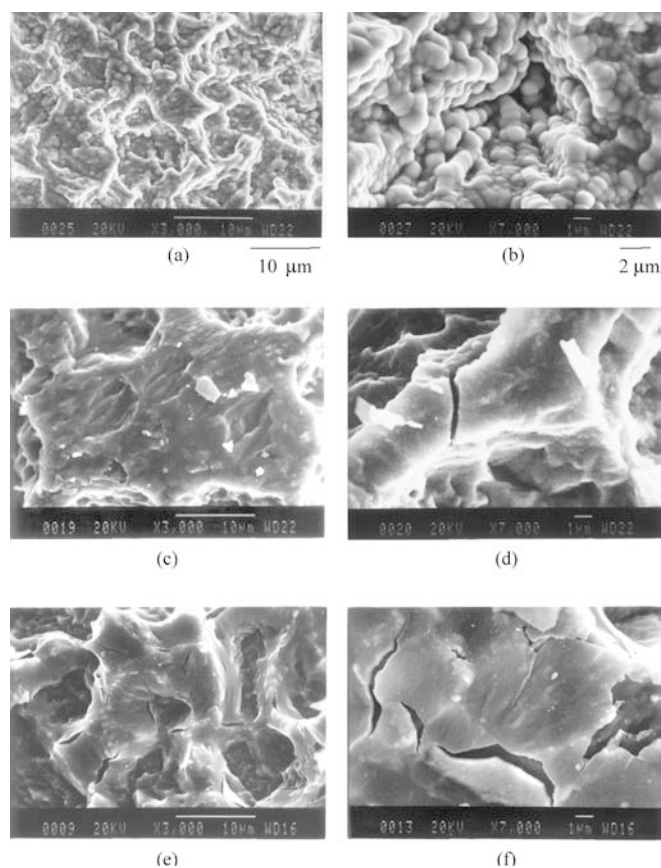


Fig. 8 SEM photographs of (a, b) a freshly electroplated Ru deposit, and for Ru deposits with 100 cycles of CV (c, d) between 0.2 and 1.15 V and (e, f) between 0.2 and 0.75 V

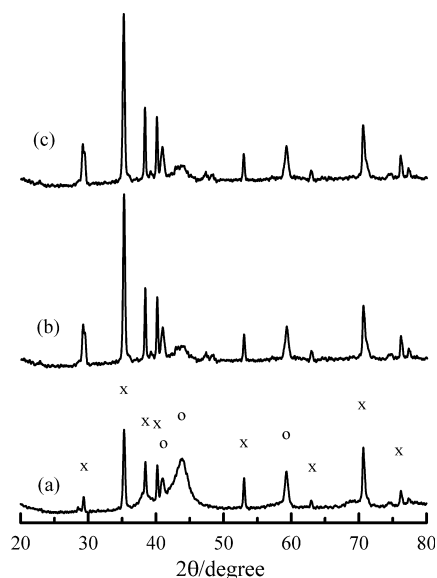


Fig. 9 XRD patterns of (a) a freshly electroplated Ru deposit, and for Ru deposits with 100 cycles of CV (b) between 0.2 and 1.15 V and (c) between 0.2 and 0.75 V, where crosses and circles indicate the diffraction peaks for Ti and Ru, respectively

Conclusions

There should exist at least two kinds and/or structures of Ru oxides with different reduction properties. The irreversible process occurring at potentials more positive than ca. 0.95 V resulted in the formation and accumulation of irreducible ruthenium oxides, whose capacitive characteristics are applicable for supercapacitors. From the XPS results, the irreducible ruthenium oxide should be composed of an aggregate consisting of Ru atoms in various oxidation states, bridged oxygen, OH and water in a 3D-like structure with a relatively ordered and compact nature. All oxides formed by potential cycling exhibited an amorphous structure with a nonstoichiometric property, while the distribution of Ru in different oxidation states could be controlled by changing the upper potential limit of the CV. The application of repeated CVs with different E_{SU} renders the surface reconstruction of Ru deposits and activates the formation/reduction of Ru oxides, and also modifies their reactivity for the adsorption/desorption of UPD hydrogen.

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