

# Influences of Coating Cycles and Composition on the Properties of Dimensionally Stable Anode for Cathodic Protection

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Properties of the anode for cathodic protection need low overvoltage for oxygen evolution and high corrosion resistance. It is well known that DSA (Dimensionally Stable Anode) has been the best anode ever since. DSA is mainly composed of RuO<sub>2</sub>, IrO<sub>2</sub>, ZrO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, and also Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, MnO<sub>2</sub> are added to DSA for better corrosion resistance. The lifetime of DSA for cathodic protection is also one of the very important factors. RuO<sub>2</sub>, IrO<sub>2</sub>, RhO<sub>2</sub>, ZrO<sub>2</sub> are well used for life extension, and many researches are focused on life extension by lowering oxygen evolution potential and minimizing dissolution of oxide coatings. This work aims to evaluate the influence of constituents of MMO and coating cycles and ZrO<sub>2</sub> coating on the electrochemical properties and lifetime of DSA electrodes. From the results of lifetime assessment in the anodes coated with single component, RuO<sub>2</sub> coating was more effective and showed longer lifetime than IrO<sub>2</sub> coating. Also, an increased coating cycle and an electrochemically coated ZrO<sub>2</sub> could enhance the lifetime of a DSA.

**Keywords** : DSA, MMO, lifetime, cathodic protection, concrete

## 1. Introduction

Rebar corrosion in concrete structures can be easily protected because pH of concrete is high. However, penetration of chloride into concrete, neutralization, and increased amount of saline sand *et al.* can corrode the rebar in concrete construction. Therefore, appropriate protection should be applied for the integrity of concrete structures, and thus electrochemical cathodic protection is usually used.<sup>1)-3)</sup>

Properties of the anode for cathodic protection need low overvoltage for oxygen evolution and high corrosion resistance. It is well known that DSA has been the best anode ever since.<sup>4)-9)</sup> DSA is mainly composed of RuO<sub>2</sub>, IrO<sub>2</sub>, ZrO<sub>2</sub>, Co<sub>2</sub>O<sub>3</sub>, and also Ta<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, MnO<sub>2</sub> are added to DSA for better corrosion resistance. In recent years, 3-components or multi-components anodes (MMO, Mixed metal oxide) are studied because 2-component anodes have low corrosion resistance. These newly developed electrodes show lower overvoltage for oxygen evolution and

higher corrosion resistance than 2-component anodes.

The lifetime of DSA is also one of the very important factors. Thus, RuO<sub>2</sub>, IrO<sub>2</sub>, RhO<sub>2</sub>, ZrO<sub>2</sub> are well used for life extension, and many researches are focused on life extension by lowering oxygen evolution potential and minimizing dissolution of oxide coatings. This work aims to evaluate the influence of constituents of MMO and coating cycles and ZrO<sub>2</sub> coating on the electrochemical properties and lifetime of DSA electrodes.

## 2. Experimental methods

To make stable RuO<sub>2</sub>, IrO<sub>2</sub> or ZrO<sub>2</sub> sol at room temperature, ruthenium chloride hydrate (RuCl<sub>3</sub> · 3H<sub>2</sub>O, Kojima Chemical Co.) and iridium (III) chloride hydrochloride hydrate (IrCl<sub>3</sub> · XHCl · YH<sub>2</sub>O, Aldrich) were used, and isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH, Aldrich) was used as a solvent. Zirconyl nitrate (ZrO(NO<sub>3</sub>)<sub>2</sub>) was used for electrochemical coating.

Base material to be coated used titanium plate (grade II) and its size was 10×80×0.5 mm. After mechanical polishing using SiC paper #220, Ti plate was immersed for 30

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minutes in 35% HCl solution at room temperature and rinsed. Sol-gel coating on Ti plate was performed as follows; One cycle coating process consists of dip-coating (1.0cm/min), 1st drying (130°C, 10 min.), and 2nd drying (450°C, 10 min.). Several cycles of coating processes are performed and followed by the final heat treatment at 450°C for 1 hr.

Polarization test (scan rate; 1 mV/sec) and cyclic polarization test (scan rate; 1 mV/sec) were performed using a Potentiostat (Model EG&G 273A) at 25°C, 1 M H<sub>2</sub>SO<sub>4</sub> and 25°C, 0.5 M H<sub>2</sub>SO<sub>4</sub> respectively. Saturated calomel electrode was used as a reference electrode and graphite electrode as a counter electrode.

Lifetime was evaluated according to NACE Standard TM 0294-94<sup>10)</sup> in 3% NaCl, 4% NaOH, and simulated pore water (0.20% Ca(OH)<sub>2</sub> + 3.20% KCl + 1.00% KOH + 2.45% NaOH + 93.15% H<sub>2</sub>O). Applied current was constantly 320 mA/cm<sup>2</sup> and the experiment was continued before electrode potential reaches 4 V(SCE).

### 3. Results and discussion

In order to form a stable single component coating of IrO<sub>2</sub> or RuO<sub>2</sub> sol at room temperature, iridium(III) chloride hydrochloride hydrate (IrCl<sub>3</sub> · XHCl · YH<sub>2</sub>O, Aldrich), ruthenium chloride hydrate (RuCl<sub>3</sub> · 3H<sub>2</sub>O, Kojima Chemical Co.) were used and isopropanol ((CH<sub>3</sub>)<sub>2</sub>CHOH, Aldrich) was used as a solvent. Concentrations of single component sols were 0.01431 mol of Ir as IrCl<sub>3</sub> and 0.097 mol of Ru as RuCl<sub>3</sub>. 0.5 mol of Zr in the form of ZrO (NO<sub>3</sub>)<sub>2</sub> was used for electrochemical coating.

Fig. 1 shows the result of life assessment for the 5 cycles - coated anode with single component IrO<sub>3</sub>. The method of lifetime assessment is referred to NACE TM0294-94. The experimental solution used were consisted of 30 g/ℓ

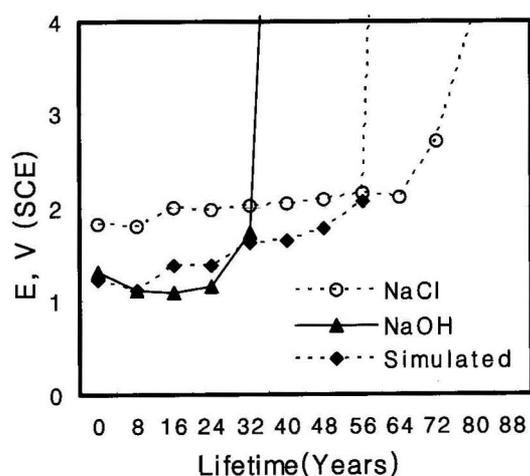


Fig. 1. Lifetime of 5 cycles-coated IrO<sub>2</sub> anode

NaCl, 40 g/ℓ NaOH, and simulated pore water(0.20% Ca(OH)<sub>2</sub> + 3.20%KCl + 1.00%KOH + 2.45%NaOH + 93.15%H<sub>2</sub>O) at room temperature. This figure shows the potential differences among corrosive environments at the beginning of experiment. The potential in a NaOH solution increased sharply near at 32 years of calculated lifetime, which means that the lifetime of this anode is estimated less than 32 years when it is served for concrete corrosion protection. The potential in a NaCl solution rose sharply at the calculated life time of 72 years and that in simulated concrete solution shows the beginning of peak at the calculated life time of more than 56 years. These data are not compatible with NACE TM0294-94 which requires at least 40 years of lifetime as an anode. Therefore, this anode is judged to be not suitable for the protection of rebar in concrete structures.

Fig. 2 is the result of lifetime assessment of the 5 cycles coated anode with the single component of RuO<sub>2</sub>. The method of lifetime assessment is also referred to NACE TM0294-94 as Fig. 1. This anode shows more stable potentials than that of IrO<sub>2</sub> coated anode, and the calculated lifetime is evaluated as more than 88 years all among in 3 types of test solutions. Only the potential of anode in NaOH solution shows the increasing tendency to some extent at the calculated lifetime of 48 years.

The comparative figures of lifetime expectancies for IrO<sub>2</sub> and RuO<sub>2</sub> coated anodes in each solution are shown in Fig. 3. As shown in this figure, RuO<sub>2</sub> coated anodes are superior to IrO<sub>2</sub> coated ones on the base of the lifetime.

Fig. 4 shows the effect of coating cycle on the lifetime of the RuO<sub>2</sub> coated anode. In Fig. 4 (a) which shows the result in 3% NaCl solution, the 7 cycles coated specimen has a quite more sharp increasing potentials than those of other specimens. The 5 cycles coated specimen has a lowest potentials and shows most stable pattern. In Fig.

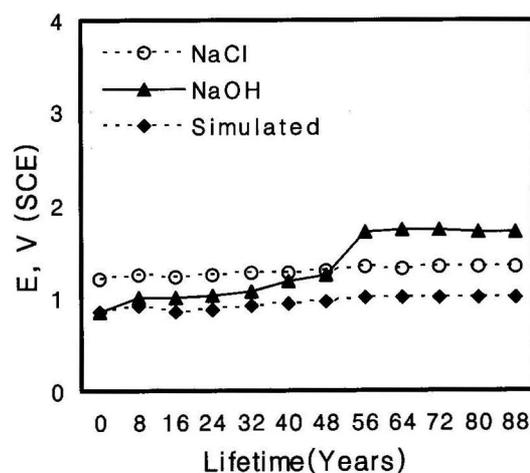
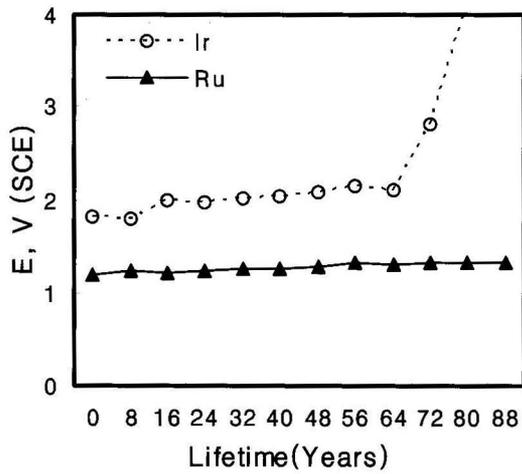
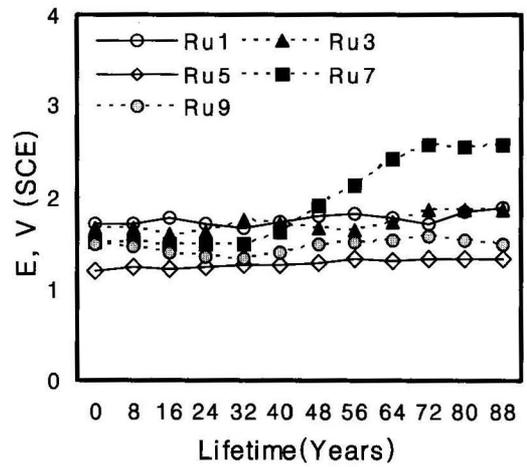


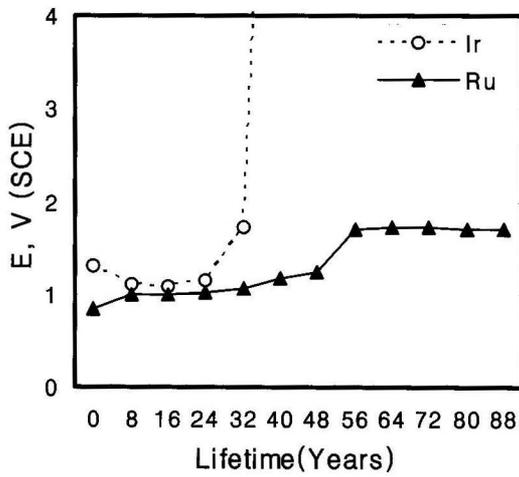
Fig. 2. Lifetime of 5 cycles-coated RuO<sub>2</sub> anode



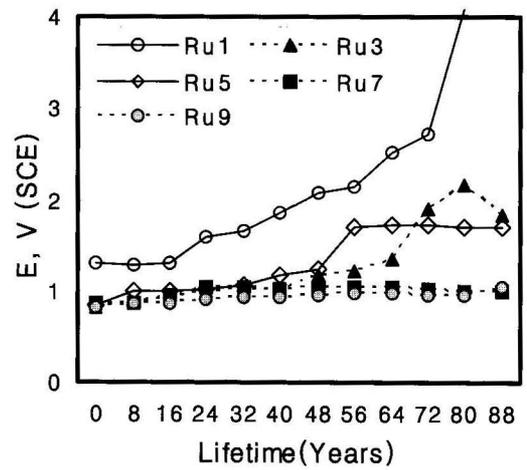
(a)



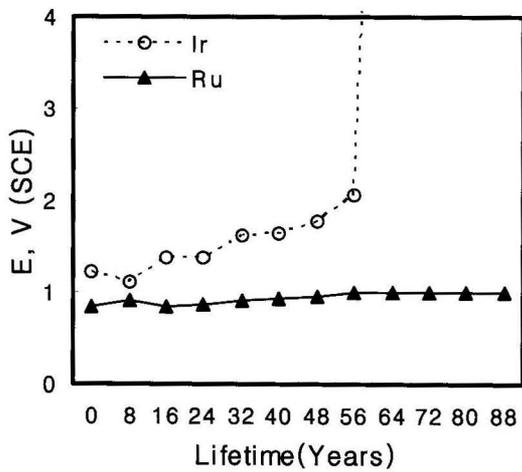
(a)



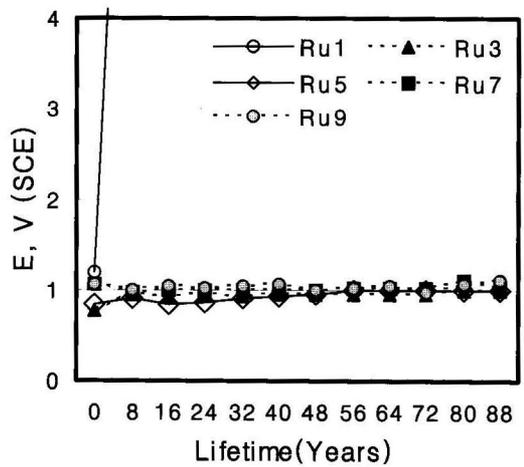
(b)



(b)



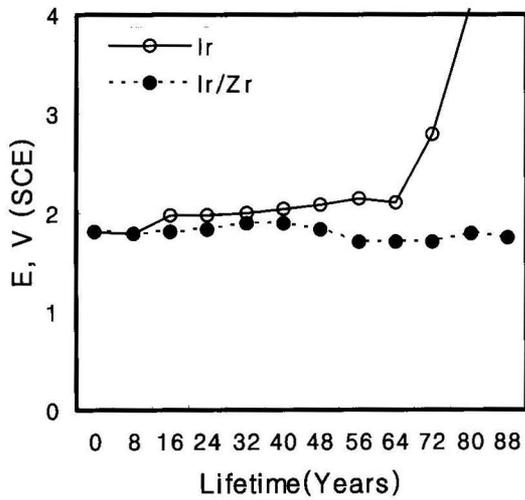
(c)



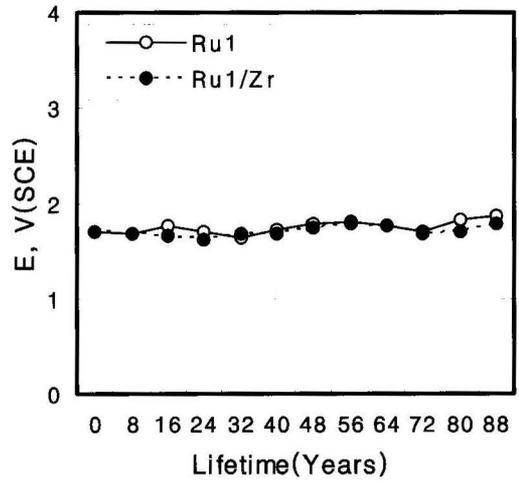
(c)

**Fig. 3.** Comparison of the lifetime between IrO<sub>2</sub> and RuO<sub>2</sub> anodes (5 cycles-coated) (a) 3% NaCl, (b) 4% NaOH, (c) Simulated Pore Water

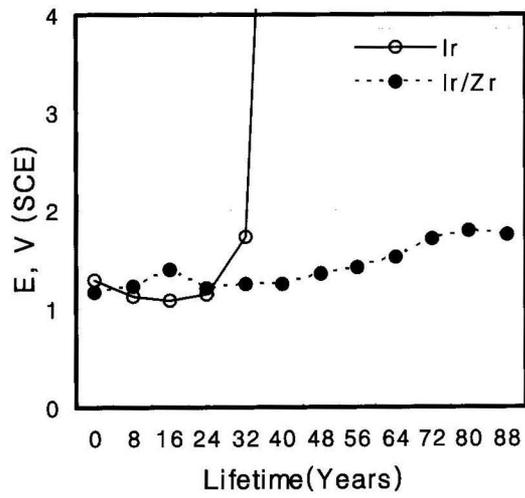
**Fig. 4.** Effect of coating cycles on the lifetime of RuO<sub>2</sub> anodes (a) 3% NaCl, (b) 4% NaOH, (c) Simulated Pore Water



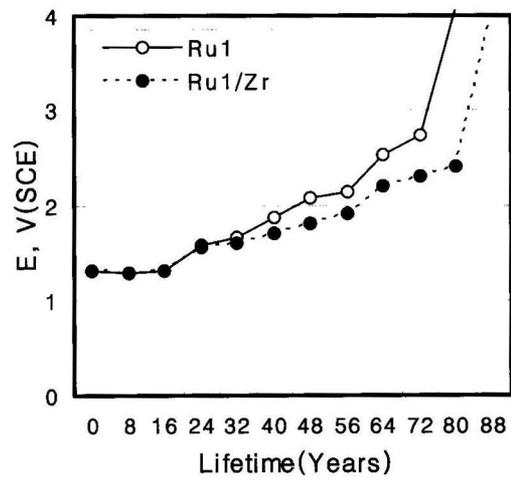
(a)



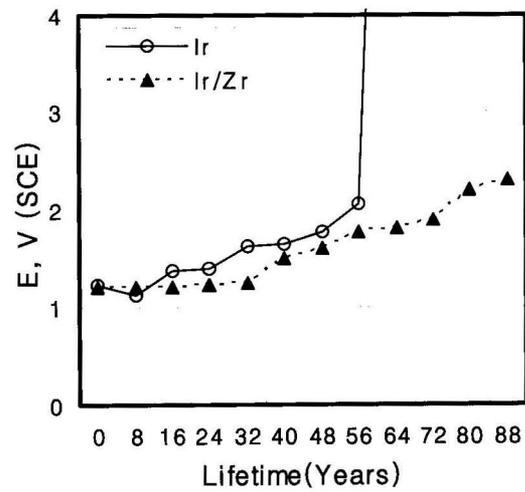
(a)



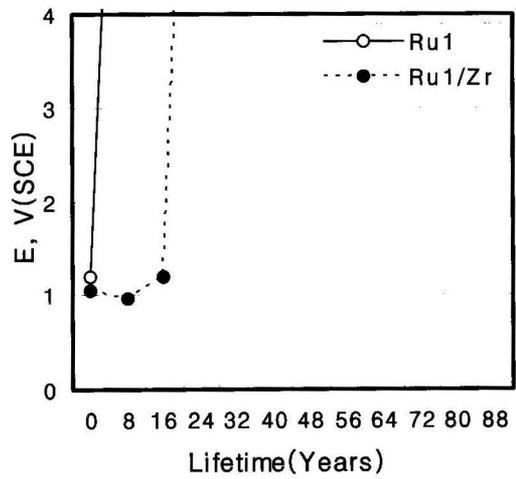
(b)



(b)



(c)



(c)

Fig. 5. Effect of electrochemical ZrO<sub>2</sub> coating on the lifetime of IrO<sub>2</sub> anodes ; (a) 3% NaCl, (b) 4% NaOH, (c) Simulated Pore Water

Fig. 6. Effect of electrochemical ZrO<sub>2</sub> coating on the lifetime of RuO<sub>2</sub> anode ; (a) 3% NaCl, (b) 4% NaOH, (c) Simulated Pore Water

4 (b) which shows the result in 4% NaOH solution, the 1 cycle coated specimen has an unstable potential which exceeds the limit of 4 V(SCE) at 80 years of calculated lifetime. However, when the number of coating cycles

increases, the specimens have more stable potentials.

In case of Fig. 4(c) that shows the result of simulated concrete solution, the potential of the 1 cycle coated specimen increases dramatically after a very short time

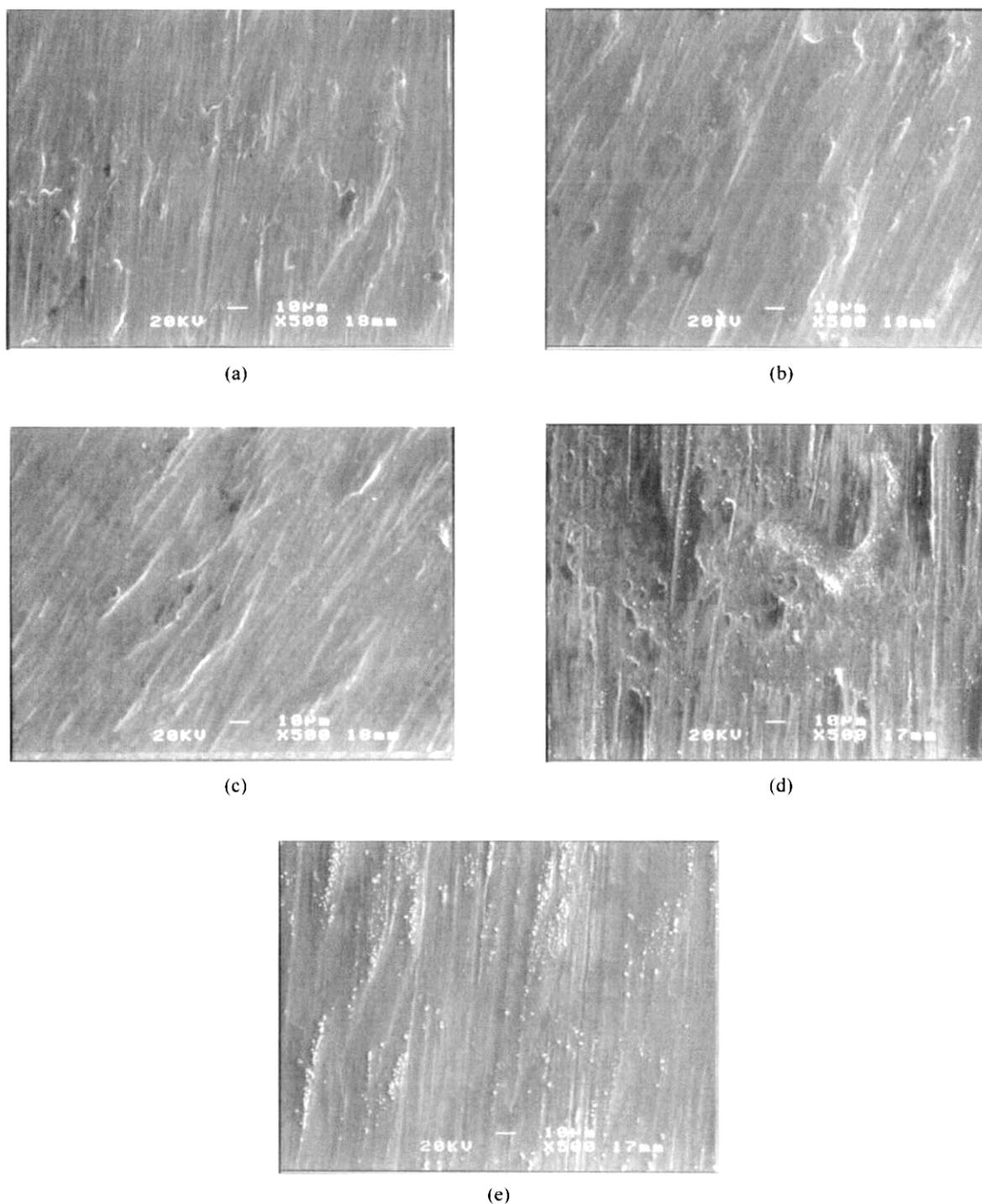


Fig. 7. Surface morphology of several anodes; (a) IrO<sub>2</sub> anode + electrochemical ZrO<sub>2</sub> coating, (b) RuO<sub>2</sub> anode + electrochemical ZrO<sub>2</sub> coating, (c) RuO<sub>2</sub> + IrO<sub>2</sub> sol coating, (d) RuO<sub>2</sub> + SnO<sub>2</sub> sol coating, (e) RuO<sub>2</sub> + ZrO<sub>2</sub> sol coating

from the beginning of experiment. This means that only one cycle coated anodes are not adequate for the cathodic protection in concrete structures. However, multiple coated anodes in the way of 3, 5, 7, 9 cycles and etc. show very stable potentials regardless of the number of coating cycles, and the calculated lifetimes of them showed more than 88 years.

Fig. 5 shows the effect of electrochemical  $ZrO_2$  coating on the lifetime of 1 cycle coated  $IrO_2$  anode. The only  $IrO_2$  coated anode in 3% NaCl solution shows that the its potential rapidly rises after 64 years to exceed the critical potential of 4 V(SCE)(Fig. 5a). However, when  $ZrO_2$  is electrochemically coated on this anode in addition, the potential of the anode became stable until 88 years of lifetime. In 4% NaOH solution as well(Fig. 5b), the potential of only  $IrO_2$  coated anode rises sharply to pass the critical potential of 4V(SCE), but only additional  $ZrO_2$  coating on this anode made the potential very stable until 88 years of the lifetime. From the evaluation results in simulated pore water (Fig. 5c), the potential of the anode coated singularly with  $IrO_2$  rises sharply after 56 years of calculated lifetime to exceed the critical potential of 4 V(SCE). However, additional electrochemical  $ZrO_2$  coating on this anode, stable potentials can be shown up to 88 years of the lifetime.

Fig. 6 shows the effect of electrochemical  $ZrO_2$  coating on the lifetime of 1 cycle coated  $RuO_2$  anode. In both cases of only  $RuO_2$  coated anode and additional  $ZrO_2$  coated anode in 3% NaCl solution, the potentials of them show stable potentials until 88 years of the lifetime (Fig 6a). These are different results from the case of  $IrO_2$  coated anodes and  $RuO_2$  coating is more effective for the life extension of anodes than  $IrO_2$  coated anodes. When 1 cycle coated  $RuO_2$  anodes are tested in 4% NaOH solution (Fig. 6b), the potential gradually increases after 24 years of calculated lifetime and then over the critical potential of 4 V(SCE) at 72 years. However, additional  $ZrO_2$  coating on these anodes makes the increasing rate of the potential to be slow down after the 24 years of calculated lifetime and exceeded the critical potential of 4 V(SCE) after 80 years. This behavior shows that the lifetime of anode can be improved by the additional electrochemical  $ZrO_2$  coating on them. In case of the evaluation result in simulated pore water (Fig. 6c), electrochemically additional  $ZrO_2$  coating on  $RuO_2$  anodes also improved the lifetime of concrete cathodic protection anodes from the lifetime graph. Electrochemical  $ZrO_2$  coating did prolong the time to exceed the critical potential from 8 years to 16 years.

Fig. 7 shows SEM (Scanning Electron Microscope) photographs for the anodes that have coating condition

of (a)  $IrO_2$  5 cycles followed by one cycle of additional  $ZrO_2$  electrochemical coating, (b)  $RuO_2$  5 cycles followed by one cycle of  $ZrO_2$  electrochemical coating, (c) 5 cycles of  $RuO_2 + IrO_2$  coating, (d) 5 cycles of  $RuO_2 + SnO_2$  coating, (e) 5 cycles of  $RuO_2 + ZrO_2$  coating. As shown in these photographs, almost oxide coatings were uniform, and even the direction of polishing could be identified. The precipitation of other phases or a sort of mud-crack cannot be found out, but some of precipitates are observed in the specimen coated with (d)  $RuO_2 + SnO_2$  sol and (e)  $RuO_2 + ZrO_2$  sol.

From the results of experiments above, it is judged that the electrochemical coating of  $ZrO_2$  improves the lifetime and electrochemical characteristics of anodes because this coating makes the surfaces of anodes to be uniform.

Fig. 8 shows the effect of coating cycles on the polarization curves of  $RuO_2$  coated specimens in 1M  $H_2SO_4$  solution at room temperature. Solutions were aerated conditions and the potential scanning rate was 1 mV/sec. Only the 1 cycle coated specimen shows a little bit higher corrosion potential, but other specimens don't show big differences regardless of the coating cycles. They also show similar oxygen evolution potentials regardless of the number of coating cycles.

Cyclic polarization curves performed in 0.5 M  $H_2SO_4$  solution at room temperature are shown in Fig. 9. Solutions were also aerated conditions and the potential scanning rate was 1 mV/sec. Because the specimen(Ti) without coating shows quite a big hysteresis loop of cyclic scanning along the current axis, oxide film on the surface has an effect to block current flow as scanning positive direction so that cathodic polarization curve is shown

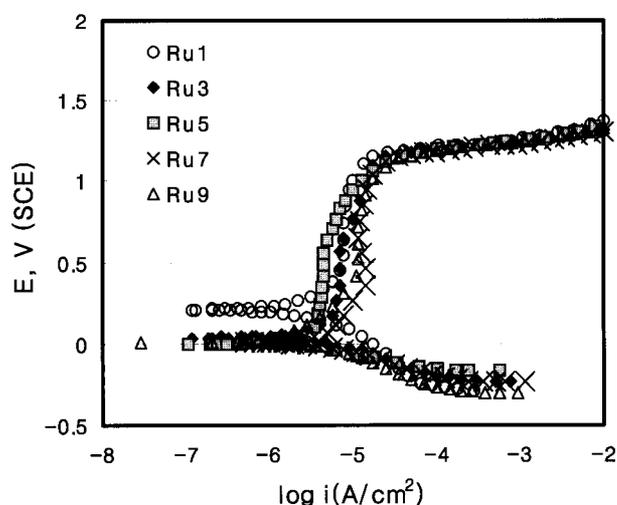


Fig. 8. Effect of coating cycles on polarization behavior of  $RuO_2$ -anode in 1M  $H_2SO_4$  at room temperature

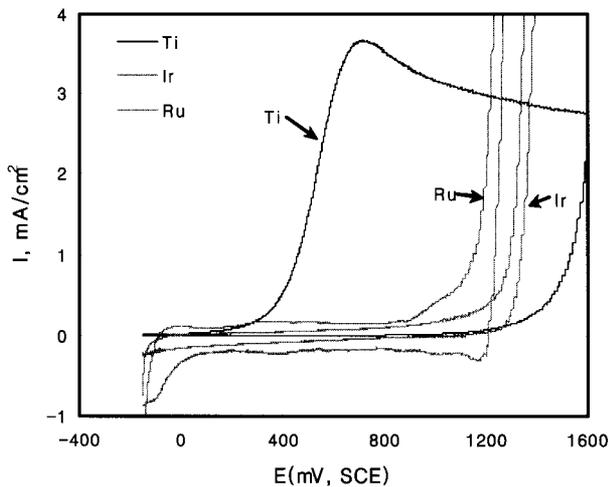


Fig. 9. Cyclic polarization curves of Ti-matrix, RuO<sub>2</sub>, and IrO<sub>2</sub> anodes in 0.5M H<sub>2</sub>SO<sub>4</sub> at room temperature

under +0.5 V(SCE). In the case of 5 cycles coated IrO<sub>2</sub> anode(Ir) on the Ti base metal, the current hysteresis curve of anode becomes smaller. On the other hand, 5 cycles coated RuO<sub>2</sub> specimen(Ru) on the Ti base metal shows very small hysteresis loop. The hysteresis loop of Ti shows relatively large area of current density and doesn't show the area of cathodic current density, whereas the anodes coated with RuO<sub>2</sub> or IrO<sub>2</sub> show similar areas of anodic and cathodic current densities.

#### 4. Conclusions

1) From the results of lifetime assessment in anodes coated with single component of IrO<sub>2</sub>, it was not suitable for cathodic protection for concrete rebars since these anodes have a lifetime of under 40 years. However, the lifetime of anode coated with single RuO<sub>2</sub> was evaluated as over 88 years, which showed the RuO<sub>2</sub> coated anode superior to IrO<sub>2</sub> coated one.

2) In the result of lifetime assessment in anode that were

coated with IrO<sub>2</sub> and additionally coated with ZrO<sub>2</sub> once more, the lifetimes of anodes were all improved by electrochemical ZrO<sub>2</sub> coating in three environments of 3% NaCl, 4% NaOH, and simulated pore water solutions. In the case of anode coated with RuO<sub>2</sub> one time, the final additional ZrO<sub>2</sub> coating also improved the lifetime, but the degree of it was less than that of IrO<sub>2</sub>.

3) When additional IrO<sub>2</sub>, SnO<sub>2</sub>, ZrO<sub>2</sub> coating were mixed with RuO<sub>2</sub> or IrO<sub>2</sub> coated electrode, some precipitation can be observed on their surfaces. However, it is judged that the lifetime and electrochemical characteristics of them can be improved when the additional ZrO<sub>2</sub> coating is added on them because ZrO<sub>2</sub> makes its surface geometry uniform.

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