



Title	A SELECTIVE CATALYST FOR TITANIUM ANODES: DEVELOPMENT AND OPTIMIZATION : . Catalyst Structure, Activity and Durability
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 32(1), 19-28
Issue Date	1984-10
Doc URL	http://hdl.handle.net/2115/25149
Type	bulletin (article)
File Information	32(1)_P19-28.pdf



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A SELECTIVE CATALYST FOR TITANIUM ANODES : DEVELOPMENT AND OPTIMIZATION

I. Catalyst Structure, Activity and Durability

By

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(Received December 13, 1983; in revised form February 21, 1984)

Abstract

A composite electrocatalytic coating with improved anionic selective features for chlorine evolution has been developed. This coating is intended for both chlorate cells and sea water electrolysis where oxygen evolution is undesirable. It has been optimized by correlating (1) its steady state polarization characteristics (electrocatalytic activity), and (2) its durability (or catalyst lifetime), with (3) its structure (from x-ray diffraction), (4) its composition (ratio of ingredients), (5) its thermal treatment (temperature and time) and, (6) its loading (grams of catalyst per square metre). There is an optimum in composition, loading and thermal treatment of the catalyst which produces a structure with both optimal catalytic activity and optimal durability.

Introduction

In the second decade of their industrial application, RuO₂/TiO₂-coated titanium electrodes are now a unique anode material used world-wide for caustic-chlorine, chlorate and sea water electrolysis cells.¹⁻⁴ More than 80% of the total chlorine production (over 30 million tons per year) employs catalytically activated titanium anodes (ATA). In addition, there are industrial processes which need even more selective electrocatalysts to provide maximal efficiency. For instance both chlorate production and sea water electrolysis have competing electrode reactions as follows :

- (a) Evolution of chlorine which hydrolyzes almost completely to HOCl and OCl⁻ (total available chlorine). In a chlorate cell the hypochlorite species undergo a chemical conversion to chlorate which gives maximal

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current efficiency.⁵⁾

- (b) Evolution of oxygen by the Foerster reaction. Chlorate is also produced at the anode but at lower efficiency (6) than by reaction (a), hence this is considered as a side reaction



- (c) Evolution of oxygen by electrolysis of water. This is usually negligible.

The reversible potentials for chlorine and oxygen discharge are close together, so a selective electrocatalyst is needed to suppress the Foerster reaction by providing a high oxygen overpotential. In addition, the catalyst must resist corrosion at high anodic current density in solutions containing chloride, chlorine and hypochlorite.

Oxide catalysts usually produce oxygen more easily than the corresponding bare metal (similarity factor). Ruthenium is one of the less expensive and more available precious metals and its mixed oxide with titanium ($\text{RuO}_2/\text{TiO}_2$) is a highly active catalyst for chlorine evolution while being quite durable.⁷⁾ For this reason it has been widely employed for coating titanium anodes. Chloride ions inhibit the formation of surface oxides on platinum group metals by being adsorbed onto the surface (8) — with the exception of platinum itself which does form surface oxides and thereby exhibits a higher anodic polarization.⁹⁾ Among base metals, tin has a remarkable overpotential¹⁰⁾ but corrodes in solutions containing hypochlorites.¹¹⁾ A palladium tin compound (PdSn_2), however, is expected to provide both selectivity (high oxygen overpotential) and a lower corrosion rate. Trasatti¹²⁾ pointed out the ability of transition metal ions to form covalent bonds with a metal surface, leading to high coverages and partial surface blocking. Phosphate ions are known to adsorb onto palladium and thus might contribute to its selectivity as a catalyst. Palladium itself could perhaps be the sole electrocatalyst but $\text{RuO}_2/\text{TiO}_2$ is cheaper, more active and more resistant to corrosion. Thus, a composite coating of $\text{RuO}_2/\text{TiO}_2$ and PdSn_2 has been optimized as an anionic selective catalyst for chlorate cells and sea water electrolysis.

The scope of the present paper is to describe the catalytic properties, polarization characteristics, corrosion stability and lifetime of this selective catalyst.

Experimental

The procedure for applying a catalytic coating onto a titanium substrate has been described in detail elsewhere.¹³⁾ The difference between the usual

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RuO₂/TiO₂ coating and this one is the addition of tin and palladium chlorides at various ratios. The materials, RuCl₃·3H₂O, PdCl₂ (Johnson & Matthey), TiCl₄ and SnCl₂ (Merck) were of reagent grade purity and were applied as an isopropanol solution containing 10 mg/ml of the metals, mixed in different ratios. Usually five coatings were painted on the titanium substrate to obtain a loading of 10 g/m². Heat treatment was in air at 450 to 500°C (cf (14)).

Results and Discussion

1. X-Ray Diffraction Analysis

Crystal structures were determined for various mole ratios of RuO₂, TiO₂ and PdSn₂. Figure 1 shows a typical curve for a satisfactory coating. The peaks correspond to reflections from the titanium substrate, from rutile solid state solutions of RuO₂ and TiO₂ and from PdSn₂ (11). The rutile peaks are between those of pure RuO₂ and pure TiO₂ (cf 13, 15). Ruthenium dioxide always exists in a rutile solid solution with TiO₂ and so forms a separate phase from the other constituents. The phase structure of the coating depends on the mole fractions of the components. Palladium and tin may form a number of phases, *i. e.* Pd or PdO, PdSn, PdSn₂ and SnO₂ as the Sn/Pd ratio increases. Only when the atomic ratio Sn/Pd is between 1 and 2 do PdSn and PdSn₂ appear. Corrosion tests have shown that whenever the ratio is greater than 2, SnO₂ appears and the coating stability decreases so that the coating soon dissolves during anodic electrolysis.

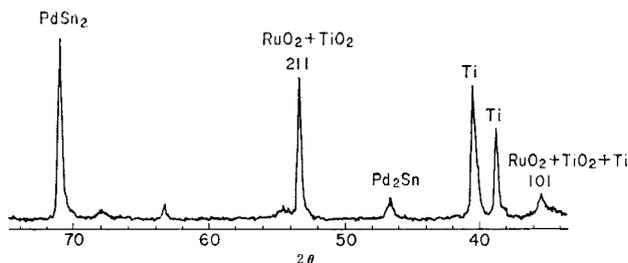


Fig. 1. X-ray diffraction radiograph for the composite electrocatalyst with optimal phase structure and catalytic activity (Ru 14 atm.%, Ti 35 atm.%, Pd 17 atm.% and Sn 34 atm.%).

X-ray diffraction has been used to determine the chemical composition of coatings and to follow the changes in catalyst activity and durability.

2. Coating Composition and Activity

Polarization characteristics were measured as a function of coating composition at industrial production conditions (NaCl 300 g/L, 80°C, pH 2.0~2.5).

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Figure 2 shows Tafel lines for $\text{RuO}_2/\text{SnO}_2$ coatings at a loading of 10 g/m^2 . At over 30 mole.% RuO_2 , the lines nearly coincide over a wide range of current densities, and are similar to those for $\text{RuO}_2/\text{TiO}_2$ at the same ratios (cf 13, 16). At lower mole ratios, the potential increases at ever lower current densities. However, these coatings corrode rapidly because of SnO_2 dissolution and could not be used industrially.

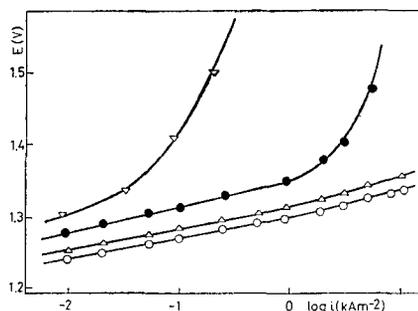


Fig. 2. Polarization characteristics of $\text{RuO}_2/\text{SnO}_2$ catalytic coatings for titanium anode in brine ($\text{NaCl } 300 \text{ g} \cdot \text{dm}^{-3}$, at 80°C and $\text{pH } 2.0$) as a function of their composition (molar ratio) for the chlorine evolution reaction: \circ —65-100 mole.% RuO_2 , \triangle —40 mole.% RuO_2 , \bullet —25 mole.% RuO_2 , ∇ —17 mole.% RuO_2 .

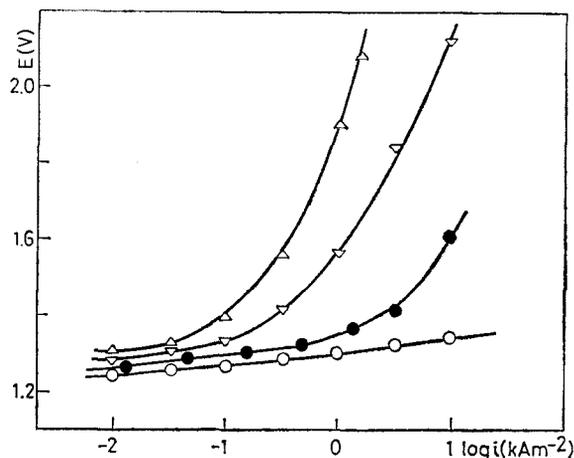


Fig. 3. Polarization characteristics of the composite catalytic coating (Pd, Sn, Ru, Ti) at constant Pd-Ti content as a function of Ru/Sn atomic ratio for chlorine evolution in brine ($300 \text{ g} \cdot \text{dm}^{-3} \text{ NaCl}$, $\text{pH } 2.0$ at 80°C): ∇ —0 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 48 atm.% Sn; \triangle —4 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 44 atm.% Sn; \bullet —9 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 39 atm.% Sn; \circ —14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn.

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The catalytic activity of PdO is close to that of RuO₂ for chlorine evolution, hence the Tafel lines do not change as the mole ratio changes, (cf. 17, 18). The resistance to corrosion also does not change but the cost increases as the ratio of palladium rises.

Figure 3 shows the Tafel lines at different Ru/Sn ratios at constant Ti and Pd contents. The coating activity decreases as the Ru/Sn ratio decreases, especially at high current densities. The coating with 14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd and 34 atm.% Sn has a high electrocatalytic activity, approaching the corresponding RuO₂/TiO₂ catalyst with RuO₂ > 30 mole.%.

Figure 4 shows the effect of various ratios of Pd/Sn at constant Ru and Ti contents. Any increase in Sn above 34/17 causes a pronounced decrease in catalytic activity while a decrease below this gives no improvement. X-ray diffraction shows that activity always decreases when SnO₂ appears, *i. e.* when Sn/Pd > 2.

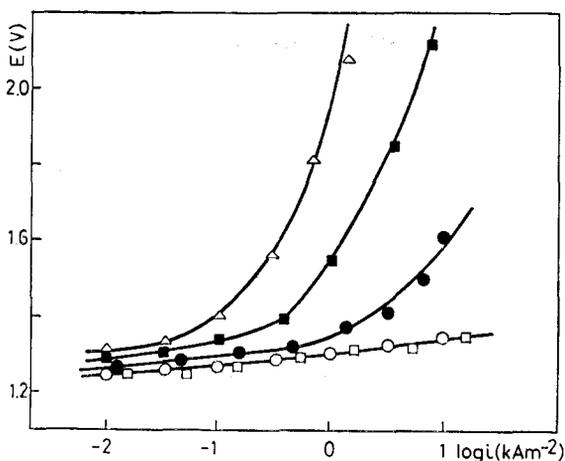


Fig. 4. Polarization characteristics of the composite catalytic coating at constant Pd/Ti atomic fraction (14 atm.% Ru, 35 atm.% Ti) as a function of Pd/Sn atomic ratio for chlorine evolution in brine (NaCl 300 g·dm⁻³, pH=2.0, 80°C): \triangle —3 atm.% Pd, 48 atm.% Sn; \blacksquare —7 atm.% Pd, 44 atm.% Sn; \bullet —12 atm.% Pd, 39 atm.% Sn; \circ —17 atm.% Pd, 34 atm.% Sn; \square —27 atm.% Pd, 24 atm.% Sn.

Figure 5 summarizes the effect of composition. The potential at 1 kA/m² is plotted against the ratio of (Ru+Pd) in the coating. Both the standard RuO₂/TiO₂ (cf 13) and the composite coating need about 30 atm.% noble metal. Below that level, the activity decays faster when the coating contains tin. SnO₂ as a separate phase decreases the conductivity, the activity and the

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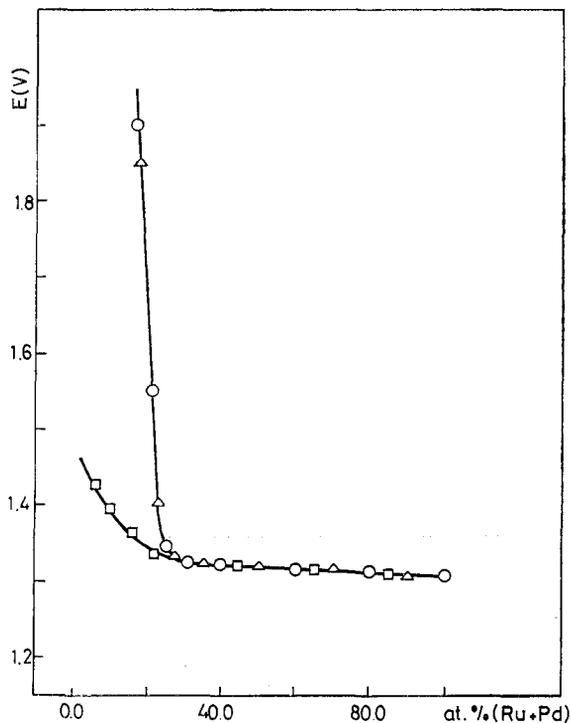


Fig. 5. The effect of precious metals (Pd+Ru) content in electrocatalytic coating on titanium anode potential for chlorine evolution in brine at constant current density ($\text{NaCl } 300 \text{ g} \cdot \text{dm}^{-3}$, at 80°C , $\text{pH} \sim 2.0$ and $i = 1.0 \text{ kA} \cdot \text{m}^{-2}$): ○—35 atm.% Ti, 17 atm.% Pd, 48 atm.% (Ru+Sn); △—35 atm.% Ti, 14 atm.% Ru, 51 atm.% (Pd+Sn); □—100 atm.% (Ru+Ti).

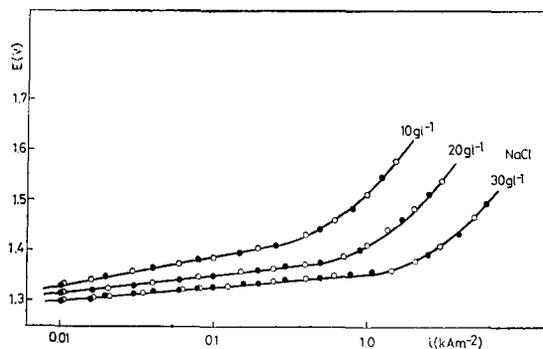


Fig. 6. Polarization characteristics of two different catalytic coatings: ○—40 mole.% RuO_2 , 60 mole.% TiO_2 ; ●—14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn, for anodic chlorine evolution both at low temperature (25°C) and brine concentrations ($\text{pH} \sim 7.0$) plotted as a function of salt content.

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durability of the coating while at higher palladium levels, the stable and active but expensive PdSn is formed.

Figure 6 is a comparison of the regular RuO₂/TiO₂ (40 mole.% RuO₂) and the composition coating (14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd and 34 atm.% Sn). The two coatings were operated at low temperature in dilute brine (similar to sea water). They show almost equal activities over the whole range of current densities and salt concentrations. The Tafel line shifts upward increases its slope from 30 to 60 mV/decade as the salt concentration decreases. In addition the lines deviate upward at higher current densities, especially at low salt concentrations.

3. Baking Temperature Effects

At the optimal coating composition (atm.% : Ru=14, Ti=35, Pd=17, Sn=34), heating between 300 and 600°C gives the separate well-distinguished phases of rutile RuO₂/TiO₂ and PdSn₂. Below 300°C. the diffraction peaks are small, pointing to incomplete conversion to these phases and hence to the presence of residual chloride ions. Above 700°C., the peaks are split and the RuO₂ and TiO₂ become separate rutile phases while PdSn₂ remains unaltered (cf 13, 19, 20).

In the 300 to 700°C. range, the diffraction peaks gradually shift to higher angles as the temperature rises, reflecting the change in the crystal structure (cf. 13, 21). The width of the peaks also decreases, pointing to growth of crystal size. Average lattice dimensions increase from 15 nm at 300°C to 75 nm at 700°C.

Increasing the baking time has roughly the same effect as increasing the temperature, i. e. increase in conversion of chloride to form desired catalyst, increase in grain size and separation of the mixed rutile crystals. An extended thermal treatment will lead to oxidation of the titanium substrate to form a non-conductive layer between the titanium and the catalyst. This occurs more readily if the oxygen concentration in the furnace is increased. Since the oxide layer causes a serious deterioration of the anode, overheating must be avoided.

All of the desired properties of the electrode depend on the coating structure and therefore on the heat treatment. Figure 7 shows the effect of temperature on the anode potential during chlorine evolution at 3 kA/m², both for the composite coating and the regular RuO₂/TiO₂ coating. The optimal temperature range is 420 to 550°C both for voltage as shown here and for durability (cf 11) as shown in short term corrosion tests. Below 400°C., the catalytic activity is low because of incomplete conversion to the desired phases. At higher than 600°C. the activity is also low and the

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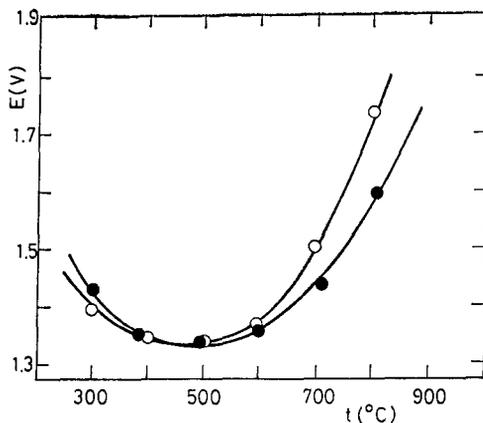


Fig. 7. The effect of temperature for thermal processing of titanium anodes on their potential for chlorine evolution at constant current density ($i = 3 \text{ kA} \cdot \text{m}^{-2}$) and for optimal catalysts compositions: ●—14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn; ○—40 mole.% RuO_2 , 60 mole.% TiO_2 . Electrolysis conditions: NaCl $300 \text{ g} \cdot \text{dm}^{-3}$; pH—2.0; 80°C ; final processing time for catalytic coating, 60 min.).

coating deteriorates rapidly because of the insulating TiO_2 layer that forms. Above 550° , cracks in the coating are visible under the SEM and these appear to initiate growth of the TiO_2 layer.

4. Catalysts Loading Effects

Tests were carried out for coatings of the optimal composition heated at 500°C . X-ray diffraction analyses have shown that for loadings above 3 g/m^2 , the phase structure is uniform. For thinner coatings, an intermediate TiO_2 layer appears during the heating step.

In Fig. 8 the anode potential at 3 kA/m^2 is plotted against the loading. The electrocatalytic activity reaches its maximum at 5 g/m^2 and remains there as the loading increases.

The durability of thin coatings is diminished by the growth of an intermediate TiO_2 layer during electrolysis, eventually resulting in passivation. Thicker coatings protect the substrate from oxidation by anodically evolved oxygen. Figure 9 displays plots of voltage versus time for chlorine evolution under membrane cell conditions at 3 kA/m^2 . Coatings with from 5 to 10 g/m^2 exhibit both high catalytic activity and high durability. At loadings of more than 10 g/m^2 , the cracks seen in SEM microphotographs allow substrate oxidation and lower the life expectancy of the anodes. For this reason the optimal loading is from 5 to 10 g/m^2 and the preferred loading which was used throughout the paper is 10 g/m^2 .

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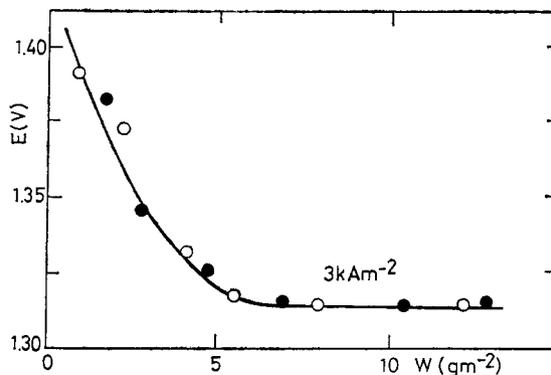


Fig. 8. The effect of total amount of composite electrocatalyst at its optimal composition (14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn) on the potential of titanium anode for chlorine evolution at constant current density ($3 \text{ kA} \cdot \text{m}^{-2}$), compared with the same features of regular $\text{RuO}_2/\text{TiO}_2$ catalytic coating under equal conditions ($\text{NaCl } 300 \text{ g} \cdot \text{dm}^{-3}$, $\text{pH} = 2.0$, 80°C .)

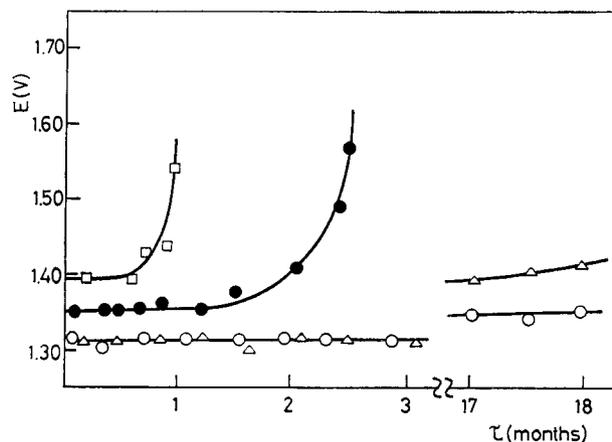


Fig. 9. Titanium anode time-potential dependence for the chlorine evolution reaction at constant current density and an optimal composite coating structure (14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn) as a function of total amount of the catalyst: \square — $1 \text{ g} \cdot \text{m}^{-2}$, \bullet — $3 \text{ g} \cdot \text{m}^{-2}$, \triangle — $5 \text{ g} \cdot \text{m}^{-2}$ and \circ — $15 \text{ g} \cdot \text{m}^{-2}$. Electrolysis conditions: $\text{NaCl } 300 \text{ g} \cdot \text{dm}^{-3}$, $\text{pH} = 2.0$, 80°C , $3 \text{ kA} \cdot \text{dm}^{-2}$.

Concluding Remarks

In conclusion, the interrelationships between structural features, processing parameters, polarization characteristics and durability not only establish

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the optimal composition and loading, but also reveal the mechanism causing anode deactivation. In addition, the role of the heat treating conditions in controlling the phase structure and hence the electrode properties has been emphasized.

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