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A SELECTIVE CATALYST FOR TITANIUM ANODES : DEVELOPMENT AND OPTIMIZATION

II. Selectivity Features

By

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Abstract

It has been pointed out in the previous paper¹⁾ that the addition of the palladium-tin compound (PdSn₂) to the regular RuO₂/TiO₂ rutile coating gives almost the same activity and corrosion resistance during chlorine evolution as the regular rutile coating. An optimized composition (14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd and 34 atm.% Sn) has now been shown to combine high activity for chlorine evolution, good corrosion resistance and low activity for oxygen evolution, both in chlorate cells and sea water electrolysis. The high selectivity stems not only from high oxygen overpotential but also from its adsorption behaviour.

Introduction

A composite electrocatalytic coating has been developed for anodes to be used in chlorate cells and for sea water electrolysis^{1,2)} where chlorine must be selectively evolved. The catalyst consists of two phases, a rutile solid solution of RuO₂/TiO₂ and an intermetallic compound PdSn₂. These two phases are at a ratio which gives the desired catalytic activity and corrosion resistance while having a low content of precious metal. This composite coating has a higher oxygen overpotential than RuO₂/TiO₂ and therefore suppresses the oxygen evolution reaction. As pointed out in the previous paper, the chlorine overpotential and the corrosion resistance are practically identical to those of RuO₂/TiO₂³⁾.

The purpose of the present paper is to disclose the selectivity of the new coating for the chlorine and oxygen evolution reactions.

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Experimental

The procedure for applying the coating to the titanium substrate has been described in detail elsewhere³. Figure 1 shows the electrochemical apparatus used to measure the electrode potentials. The electrolytic cell, a stirrer, thermostat and pH probe were immersed in the solution in a glass vessel. For chlorate production, the vessel contained 2 L of 300 g NaCl/L with added sodium dichromate or $\text{Na}_2\text{HPO}_4 + \text{NaH}_2\text{PO}_4$ or both, all of reagent grade purity. The cell was small and essentially acted as a generator of available chlorine while the large retention volume of the reactor served for its conversion to chlorate. For sea water electrolysis, the reactor contained 50 ℓ of electrolyte to slow down concentration changes. In both cases, the temperature and pH were automatically maintained at the desired setpoints (within 0.05 units for the pH). The electrical set-up consisted of a constant current power supply, multirange milliammeter (Iskra, Kranj, Yugoslavia) and a vacuum tube voltmeter (Keithly 610 C).

The tip of the Lugging capillary was about 0.03 cm in diameter and touched the anode, thereby reducing the pseudo-ohmic polarization at higher current densities to negligible values. The potentials were also corrected for ohmic losses by the interrupter technique. The cathode was bare titanium and both it and the anode were 3.0 cm × 3.3 cm (10 cm²). They were placed vertically, facing each other and were 3 mm apart. The interelectrode gap was separated from the retention volume by the glass cell body except for the circulation tubes (5 mm dia., 20 mm length). Rapid flow was generated through the cell by the gas lift of the cathodic hydrogen. This high recirculation ensured that the change in concentration through the cell was very small (about one part in 800). The production rate and gas composition were

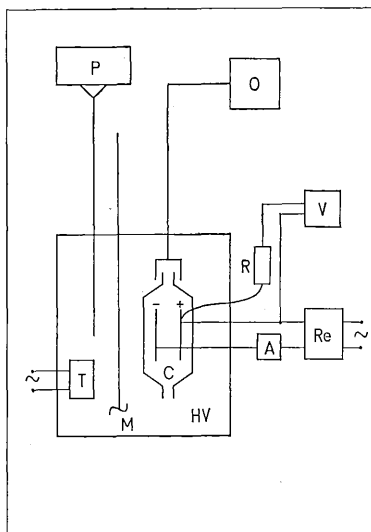


Fig. 1. The set up for simultaneous investigations of electrode activity and Faradaic yields in the chlorate cells process and sea water electrolysis: C—the cell, HV—the holding volume, M—stirrer, T—temperature control thermostat, P—automatic titrator-pH-state, O—Orsat apparatus for gas analysis, A—multi-range milliammeter, Re—rectifier, R—reference SCE, V—VTVM.

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followed by an Orsat apparatus⁴⁾. To assess cathodic losses the rate of H₂ evolution was measured for a caustic cell which was operated in parallel at the same current density. Available chlorine content was determined by potentiometric titration with sodium arsenite.⁵⁾

All measurements were carried out at well established steady states and each point on the graph represents at least five identical experimental measurements.

Results and Discussion

1. Selectivity

The selectivity was evaluated at both chlorate-producing and sea water electrolysis conditions. Although chlorine evolution is the main anodic reaction, at pH values above 7 and especially at low chloride concentrations, oxygen evolution becomes significant due to the discharge of hypochlorite (and to some extent, discharge of water). The optimized composite catalyst¹⁾ was compared to the regular RuO₂/TiO₂ rutile coating³⁾ at identical experimental conditions. Anodic and cathodic current efficiencies were determined by precise gas analysis⁴⁾ and gas rate control. Figure 2 shows the % oxygen vs. hypochlorite concentration in cell gas produced from dilute brine at a current density of 1 kA/m². The oxygen readings were corrected to the

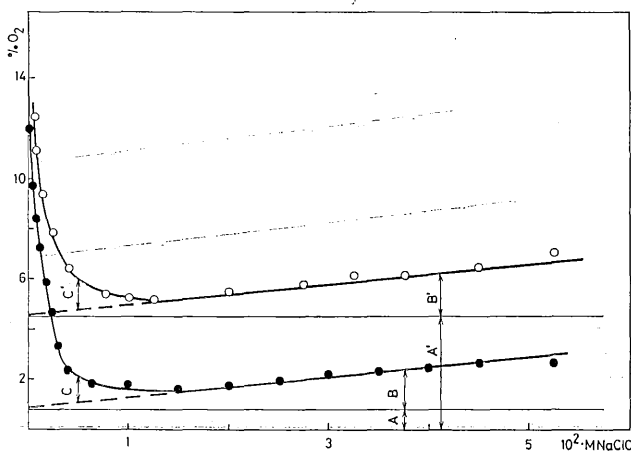


Fig. 2. Oxygen content in the cell gas recalculated for maximal hydrogen current yields in diluted brine (NaCl 30 g · dm⁻³) electrolysis plotted as a function of available chlorine concentration in the bulk at constant current density ($i = 1.0 \text{ kA} \cdot \text{m}^{-2}$) and low temperature (25°C, pH—7~9): ○—40 mole.% RuO₂, 60 mole.% TiO₂, ●—14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn.

values they would have had at 100% cathode efficiency. As the hypochlorite increases to 0.01 molar, there is a rapid drop in % oxygen, especially for the composite coating. Above this concentration, the oxygen increases and eventually rises linearly with the hypochlorite concentration with both coatings having the same rate of rise. This behaviour indicates that there are two oxygen evolution processes. One is the discharge of hypochlorite (the Foerster reaction)⁸ and its rate is controlled by mass transport^{6,7} rather than by the nature of the catalyst. The other is the discharge of water and its rate is controlled by the nature of the catalyst. The presence of hypochlorite blocks the sites where water is discharged, decreasing its contribution to A (Fig. 2) for the composite coating and A¹ for the regular coating at maximal coverage. The rapid decrease in oxygen in the low hypochlorite region resembles a typical adsorption isotherm in the reverse position, thus supporting the explanation proposed above.

The most important conclusion from Fig. 2 is that the nature of the catalytic coating can cause the bulk of the oxygen evolution to be suppressed while chlorine evolution is maintained. Fig. 3 shows current efficiencies *vs.* hypochlorite concentrations corresponding to the data in Fig. 2. The improvement is about 7% in the straight line region, hence the composite catalyst is favoured for sea water electrolysis and similar applications.

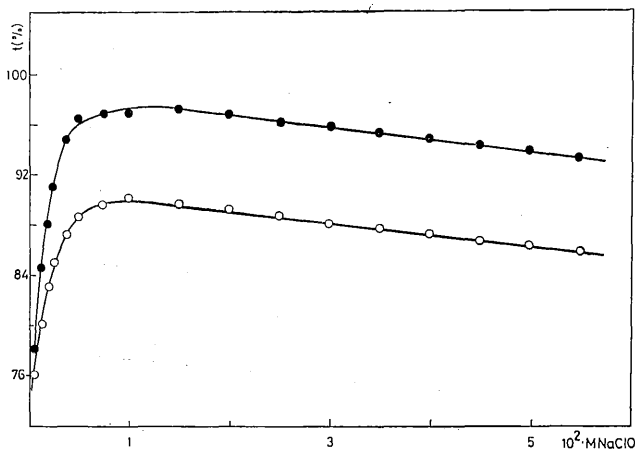


Fig. 3. Faradaic yields (t) for chlorine evolution in diluted brine ($\text{NaCl } 30 \text{ g} \cdot \text{dm}^{-3}$) plotted as a function of available chlorine concentration scanned onto two anode catalytic coatings at constant current density ($i = 1.0 \text{ kA} \cdot \text{m}^{-2}$) and low temperature (25°C , $\text{pH} = 7 \sim 9$): ○—40 mole.% RuO_2 , 60 mole.% TiO_2 , ●—14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn.

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The same selectivity is shown for chlorate cells in the presence of phosphate buffers.⁹ At high hypochlorite concentrations characteristic of alkaline brine solutions, the rate of oxygen evolution controlled by mass transport can be very high (Fig. 4). The adsorption of both hydroxide and hypochlorite species must be suppressed. In phosphate-free brine, oxygen evolution is directly proportional to hypochlorite concentration as expected for mass transfer rate control. In the presence of phosphate, however, the composite electrode has a lower rate of oxygen evolution, apparently due to adsorption of phosphate ions on the active sites. Regular $\text{RuO}_2/\text{TiO}_2$ does not exhibit this property.⁹ Experiments with radioactive ions prove that phosphate ions are strongly adsorbed on palladium.

The selectivity of the composite electrode has also been investigated as a function of current density in dilute brine at low temperatures (Fig. 5).

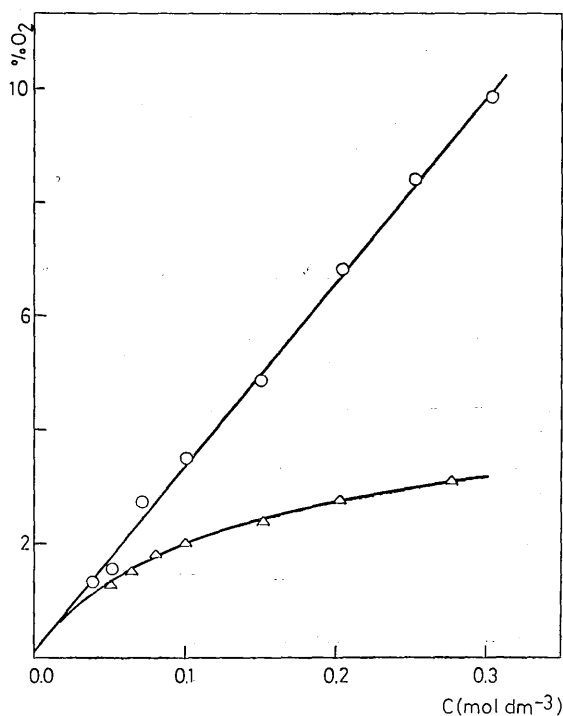


Fig. 4. Dependence of oxygen gas content in the chlorate cell on the available chlorine concentration at constant current density ($i=3.0 \text{ kA} \cdot \text{m}^{-2}$) in presence and absence of phosphate buffer for the composite catalytic coating (14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn): \circ —sodium dichromate buffer ($3 \text{ g} \cdot \text{dm}^{-3}$), \triangle —equimolar primary and secondary sodium phosphate buffer system ($3 \text{ g} \cdot \text{dm}^{-3}$).

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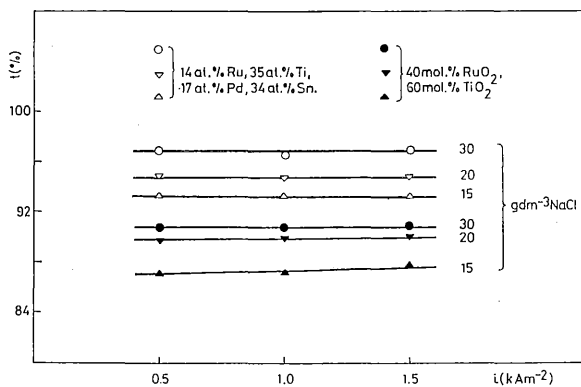


Fig. 5. Dependence of anodic current yields for chlorine evolution in diluted brine as a function both of the current density and salt concentration at low temperature (25°C) and constant available chlorine content ($1 \cdot 10^{-2}$ M NaClO).

While this coating gives higher efficiencies than the normal one, the theoretically predicted effect of current density (cf. 6, 7) was not observed (there was no change in efficiency with current density).

2. Durability

The efficiencies and anode potentials of the two catalysts were recorded against time for industrial chlorate cell conditions (Fig. 6). In concentrated

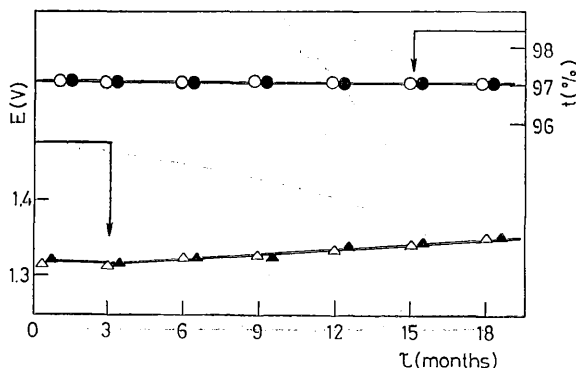


Fig. 6. Chlorate current yields and anode potential plotted as a function of continuous electrolysis duration at constant current density ($i = 3 \text{ kA} \cdot \text{m}^{-2}$), temperature (60°C) and solution parameters ($300 \text{ g} \cdot \text{dm}^{-3}$ NaCl, $\text{pH} = 6.5$, $\text{Na}_2\text{Cr}_2\text{O}_7$ $3 \text{ g} \cdot \text{dm}^{-3}$) for two catalytic coatings: \circ and \blacktriangle —14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn, \circ and \triangle —40 mole.% RuO_2 , 60 mole.% TiO_2 (circles—the current efficiency, triangles—the anode potential).

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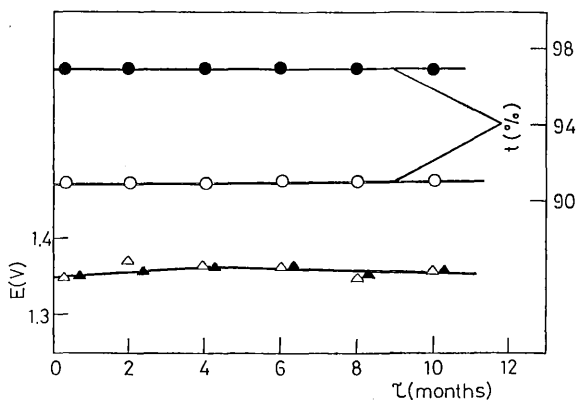


Fig. 7. The time function of available chlorine current efficiency (t) and the anode potential for two catalytic coatings at constant current density ($i=1.0 \text{ kA} \cdot \text{m}^{-2}$) in diluted brine ($\text{NaCl } 30 \text{ g} \cdot \text{dm}^{-3}$, $\text{pH}=6.5\sim 7.6$, $\text{NaClO } 1.0 \times 10^{-2} \text{ M}$) at low temperature (25°C): \circ and \triangle —40 mole.% RuO_2 , 60 mole.% TiO_2 , \bullet and \blacktriangle —14 atm.% Ru, 35 atm.% Ti, 17 atm.% Pd, 34 atm.% Sn; (circles—the current efficiency, triangles—the anode potential).

brine, optimal pH, high current density and low hypochlorite level, the catalysts have nearly the same potential and efficiency (cf 6, 7) over a 6 month period. The efficiency was nearly constant but the anode potential rose about 30 mV over 18 months.

During nearly a year in dilute brine ($\text{NaCl}=30 \text{ g}/\ell$) however, the composite coating gave about 6% higher efficiency (Fig. 7). The activity and stability of the coatings were nearly equal.

Concluding Remarks

In conclusion, the experiments with the composite coating and the regular $\text{RuO}_2/\text{TiO}_2$ have unambiguously shown that these catalysts have almost equal durability and activity in dilute brine (sea water electrolysis) as well as in concentrated brine (chlorate cell conditions). The composite coating however suppresses oxygen evolution due to the increased oxygen overvoltage on tin and the adsorption behaviour of palladium. This achievement has shown that small changes in the regular $\text{RuO}_2/\text{TiO}_2$ coating can have important effects on its behaviour as an anode catalyst.

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