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Effect of substitution of SnO_2 for TiO_2 on the surface and electrocatalytic properties of $RuO_2 + TiO_2$ electrodes*

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The effect of substituting SnO_2 for TiO_2 in $RuO_2 + TiO_2$ electrodes has been studied by varying the SnO_2 content systematically in a series of oxides of general composition 30 mol % RuO_2 + x mol % SnO_2 + $(70 - x)$ mol % TiO_2. The surface properties have been investigated by voltammetric curves, the electrocatalytic activity by using O_2 evolution from 1 mol dm^{-3} $HClO_4$ solutions as a test reaction. It has been observed that only the surface area changes at intermediate compositions as a result of morphological modifications, while the electrocatalytic activity increases dramatically as the substitution of SnO_2 for TiO_2 becomes complete. Reasons for that are discussed. The present results do not support the claim that SnO_2 depresses the electrocatalytic activity of oxide electrodes for oxygen evolution.

1. Introduction

Dimensionally stable anodes (DSA®) consist of a mixture of precious metal and non-precious metal oxides. The former impart the electrocatalytic properties, the latter the long-term stability [1]. In the search for new materials and for the optimization of the existing ones, two of the aims are: (i) to improve the stability, and (ii) to enhance the selectivity. Since the active component offers little choice, the two properties are modulated by changing the other components of the mixture [2].

There is evidence that SnO_2 improves the stability of oxide anodes [3, 4]; at the same time, its presence is claimed to improve the selectivity for chlorine production [5–7]. These qualities imply that SnO_2 possesses a high overpotential for oxygen evolution in a potential range where no transition to higher-valent soluble forms is possible.

With reference to the above situation, this work was prompted by the lack of any systematic comparative study of the properties of TiO_2, the commonest "diluent" of DSA® [8], and of SnO_2. Therefore, we have undertaken a detailed investigation of the effect of replacing TiO_2 with SnO_2 in $RuO_2 + TiO_2$ electrodes. The complete work consists of four parts: (a) oxygen evolution from acid solution on mixtures prepared dissolving the precursors in isopropanol; (b) oxygen evolution on mixtures prepared by dissolving the precursors in water [9]; (c) chlorine evolution; and (d) oxygen evolution on mixtures with variable Ru/non-precious metal ratio.

In a previous paper concerning $RuO_2 + IrO_2$ mixtures [10], it has been shown that the morphology of the mixture is of paramount importance for the electrocatalytic and stability performances. In this respect, the solvent in which the precursors are dissolved has been shown to govern the kinetics of decomposition and the degree of solid solution of the resulting mixture.

2. Experimental details

Electrodes were prepared by thermal decomposition of the following precursors: $RuCl_3 \cdot 3H_2O$, $SnCl_2 \cdot 2H_2O$, and Ti(IV) propoxide (propyl orthotitanate). The salts in the appropriate molar ratio were dissolved in isopropanol, spread onto the surface of a Ti plate by brushing and fired at 400° C. 10 mm × 10 mm × 0.2 mm Ti plates were used as a support. Ti was first sandblasted and etched for 5 min in boiling oxalic acid (100 g dm^{-3}). Calcination of each layer was performed in an oxygen gas stream for 10 min. After the desired loading was achieved, the samples were finally annealed at the same temperature for 1 h.

The catalyst loading was kept constant at 1 mg cm^{-2}. Starting with a 30 mol % RuO_2 + 70 mol % TiO_2 composition, the mole content of RuO_2 was kept constant while substituting SnO_2 for TiO_2 in 10 mol % steps. A total of eight electrodes were prepared according to the following general formula: $Ru_{0.3}Ti_{(0.7-x)}Sn_xO_2$.

The appropriate Teflon holder for mounting the electrodes [11] and the cell [12] have been described

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* Dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

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previously. AMEL equipment was used throughout. The temperature was maintained at 25 ± 0.1°C by immersing the cell in a water thermostat. Potentials were measured and are reported against a hydrogen electrode in the same solution (RHE). The supporting electrolyte, unless otherwise stated, was $1\,mol\,dm^{-3}$ $HClO_4$. Solutions were prepared with doubly distilled water and deaerated with purified nitrogen before and during the runs.

Voltammetric curves were recorded at $20\,mV\,s^{-1}$ in the potential range 0.4 to 1.4 V/RHE. They were integrated graphically to obtain the charge q^* in the same potential range. Quasi-stationary current-potential curves were performed by increasing the potential in 10 mV steps starting from 1.2 V and reading the current at each potential after 5 min. Reaction orders were determined at a constant ionic strength of $1\,mol\,dm^{-3}$ by adjusting the pH between ~0 and ~2 with appropriate mixtures of $NaClO_4$ and $HClO_4$. A single current determination was made for each electrode at each pH, by stepping the potential from 1.20 to 1.42 V. In such a way, the determination suffers from a minimum of complications due to the previous history of the electrode surface. In view of the nature of the reference electrode, the resulting reaction order with respect to H^+ is at constant overpotential.

3. Results and discussion

3.1. *Voltammetric charge*

Figure 1 shows the dependence of q^* on the SnO_2 content. Three sets of data are reported. Since q^* has been shown to monitor the state of an oxide surface [10, 13], the charge was determined (i) with the fresh electrodes, (ii) after the Tafel line determination and (iii) after the measurement of the order of reaction.

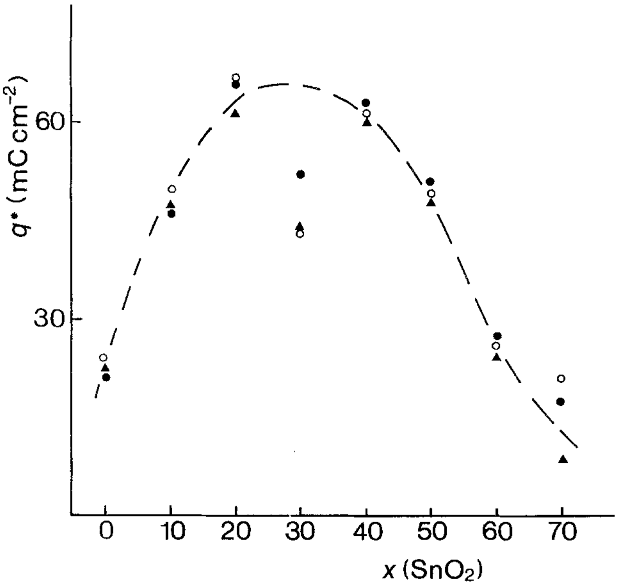


Fig. 1. Dependence of the voltammetric charge at $20\,mV\,s^{-1}$ in $1\,mol\,dm^{-3}$ $HClO_4$ solution on SnO_2 content for 30 mol % RuO_2 + x mol % SnO_2 + (70 − x) mol % TiO_2 electrodes. (●) Fresh electrodes; (○) after Tafel line experiments; (▲) after reaction order experiments.

The charge is seen to go through a maximum for intermediate compositions. This has also been observed with RuO_2 + IrO_2 mixed oxides [14]. The interpretation is that finer particles are obtained in this composition range, which points to poor mixing of the three components. q^* is almost the same at the two ends of the range, thus suggesting that the morphology of the layer is not affected by the nature of the non-precious metal. Since RuO_2 only can contribute to the surface charge in the explored potential region [15], the increase in charge for the ternary oxides is attributed to an increase in the number of exposed Ru sites.

There is very little variation of q^* with the number of runs. This suggests that the layer is mechanically stable. Although finer particles are formed, they are not eroded by the evolving gas, thus indicating that the process of sintering is satisfactory even though that of mixing is not. The value of q^* for the sample at 30% SnO_2 is anomalous and may be related to non-uniformity of the preparation procedure. The appreciable decrease of q^* for this specific sample with use also testifies to the different morphological features of the samples. Nevertheless, its behaviour will be discussed with the other electrodes.

The q^* values given in Fig. 1 are total charges, i.e. they derive from the integration of the whole voltammetric curve. Usually anodic and cathodic charges are separately equal. With fresh electrodes q_a^*/q_c^* has been found to be, on average, ~1.05. The somewhat higher ratio is essentially due to the fact that 1.4 V is just prior to oxygen evolution so that an excess anodic charge may be included. After extensive oxygen evolution the ratio increased to about 1.15. However, at the end of the runs the ratio was found to have decreased to almost the same initial value. Therefore, oxygen evolution produced only a temporary charge unbalance.

3.2. *Open circuit potential*

The open circuit potential (o.c.p.) was measured with fresh electrodes and after the kinetic runs, in parallel with the charge. No special trend in the value of E_{OC} was observed with the SnO_2 content. The values are scattered in a range of about 20 mV around the value typical for RuO_2 [16]. This indicates that the surface reactions at open circuit are governed by the redox behaviour of RuO_2 while TiO_2 and SnO_2 have no appreciable influence. However, after extensive oxygen evolution the E_{OC} was observed to become somewhat more positive, which, in line with the q_a^*/q_c^* ratio, indicates a temporary surface modification. In fact, at the end of the experiments, E_{OC}, like the charge ratio, also recovered the initial values.

3.3. *Tafel slopes*

Tafel slopes for oxygen evolution were not observed to depend substantially on the SnO_2 content. However, some systematic dependence can be recognized in Fig. 2 where the range of variation can be seen to

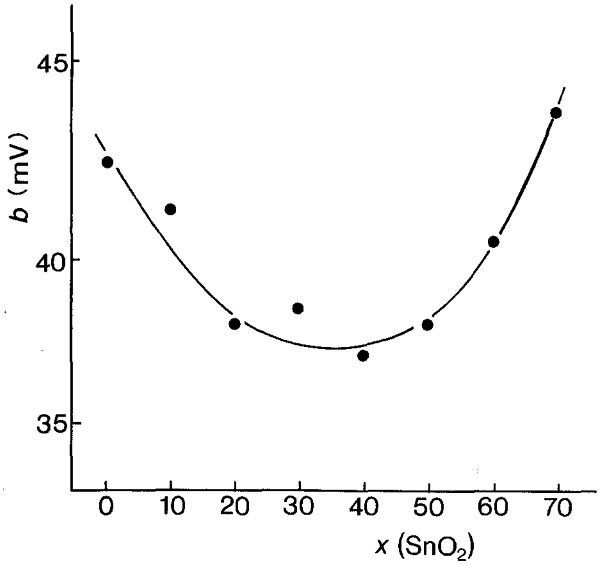


Fig. 2. Dependence of the Tafel slope on SnO_2 content for oxygen evolution on 30 mol % RuO_2 + x mol % SnO_2 + (70 − x) mol % TiO_2 electrodes from 1 mol dm^{-3} $HClO_4$ solutions.

be ~7 mV. Higher Tafel slopes are observed at the extrema of the composition range, i.e., for the binary oxides. The Tafel slope shows an opposite behaviour with respect to charge, *viz.* a decrease at intermediate compositions. In practical terms, lower Tafel slopes are indicative of higher electrocatalytic activity.

Although no direct corrections of ohmic drops were carried out experimentally, deviations of E from the linear portion of the Tafel lines were plotted against current [17]. Linear plots indicated that the deviations are substantially due to uncompensated ohmic drops thus ruling the existence of a second Tafel line. Figure 3 shows that the R values vary systematically with composition. Since the solution composition does not vary, the IR drop is associated with the nature of the layer and of the oxide/support boundary. The higher value of R for $RuO_2 + SnO_2$ may indicate a poorer doping of the TiO_2 film (which always forms on the Ti surface) by the components of the oxide overlayer because of lack of composition uniformity. The lower values at intermediate compositions are probably due to the many parallel paths that a very porous layer can establish.

3.4. *Order of reaction*

Figure 4 shows typical log j against pH plots. If the points at higher pH are taken to be as valid as the others, a reaction order slightly different from zero (0.05 to 0.09) is obtained. However, the systematic deviation of the last two points for all electrodes suggests that this is probably related to a lower accuracy of the (RHE) scale at high ionic strength and low H^+ concentration. Therefore, an order of reaction at constant overpotential $\nu(H^+)_\eta = 0$ is the most probable. The chemically significant reaction order is that at constant potential, $\nu(H^+)_E$, related to the former by the equation:

$$\nu(H^+)_E = \nu(H^+)_\eta - \gamma \qquad (1)$$

where γ is the *observable* transfer coefficient [18], given by

$$\gamma = \left(\frac{d \log j}{dE}\right)\left(\frac{RT}{F}\right) \qquad (2)$$

According to Fig. 2, the Tafel slope shows a slightly systematic variation with composition. However, since the graphically derived ohmic drop also shows the same pattern, it is thought that in fact the Tafel slope changes with composition much less in fact, the behaviour in Fig. 2 being related to the inclusion of

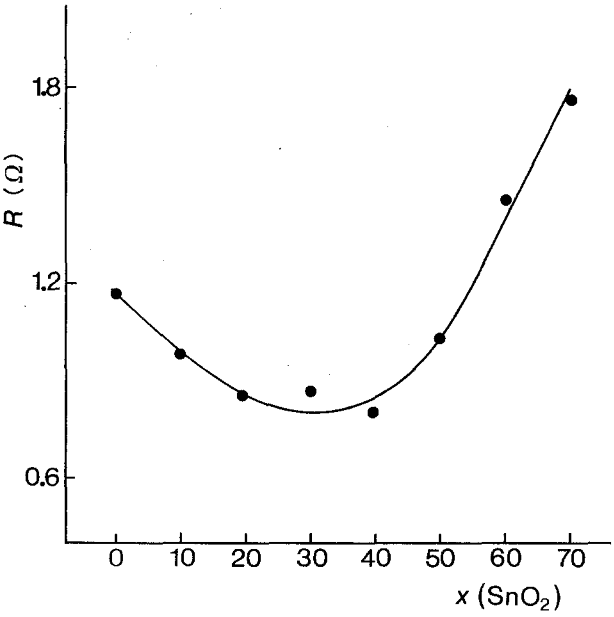


Fig. 3. Graphically derived uncompensated ohmic component for oxygen evolution on 30 mol % RuO_2 + x mol % SnO_2 + (70 − x) mol % TiO_2 electrodes from 1 mol dm^{-3} $HClO_4$ solutions.

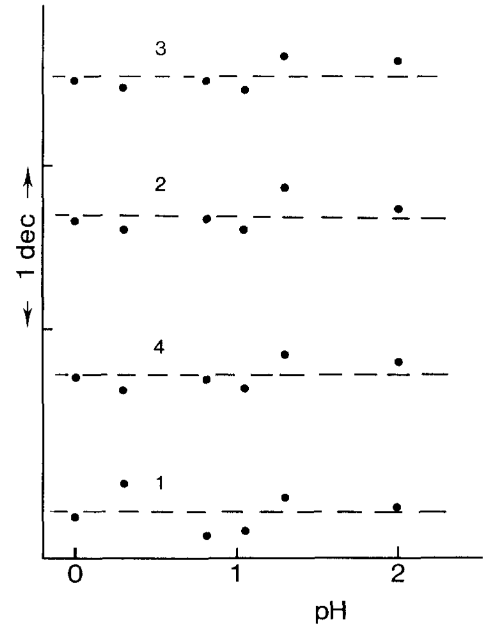


Fig. 4. pH dependence of current density at 1.42 V/RHE for oxygen evolution on 30 mol % RuO_2 + x mol % SnO_2 + (70 − x) mol % TiO_2 electrodes from 1 mol dm^{-3} $HClO_4$ solution. Electrode composition: (1) x = 0, (2) 20, (3) 40 and (4) 70.

residual *IR* effects in the graphical determination of the Tafel slope. At any rate, taking the average value of the transfer coefficient, the reaction order at constant *E* common to all electrodes is $\nu(H^+)_E = 1.48 \pm 0.08$. The significance of a fractional reaction order in oxygen evolution at oxide electrodes has already been discussed [19]. It has been attributed [20] to the variation with pH of the electric potential at the reaction site as a consequence of the mechanism of charging of the surface related to the acid-base properties of oxides. In the pH range 0 to 2 RuO_2, TiO_2 and SnO_2 are strongly positively charged since their pzc's are in the range 5 to 7 [21].

3.5. *Electrocatalytic activity*

Electrocatalytic activities are customarily evaluated on a relative scale by comparing the current density at constant electrode potential. However, in order to be significant, the comparison must be carried out at constant real surface area too. No absolute determination of the real surface area is available for these oxide electrodes, but q^* has been shown to be proportional to the number of surface active sites [22]. Since j is also proportional to the number of exposed Ru atoms, j/q^* can be taken as a surface normalized current density.

Figure 5 shows the dependence of j/q^* on composition. The electrocatalytic activity is seen to be minimum for the TiO_2 + RuO_2 electrode and maximum for the TiO_2 + SnO_2 electrode. At intermediate compositions the electrocatalytic activity stays substantially constant.

The increase in apparent electrocatalytic activity might be related to a higher surface segregation of Ru in SnO_2 than in TiO_2. However, if this were the case, it would be clearly reflected in the value of q^*. Another hypothesis is that the significance of q^* may be different at 0% and at 70% SnO_2. This is indeed possible but it should be noted that the current density enhancement ratio is ~ 6, which means that the surface concentration of Ru atoms in SnO_2 should be 6 times higher while the charge exchanged by a Ru site in the explored potential range during voltammetry would be 6 times lower, which is hardly conceivable. Therefore, the enhancement of electrocatalytic activity from 0 to 70% SnO_2 is real and not related to geometric (surface area) or surface concentration effects.

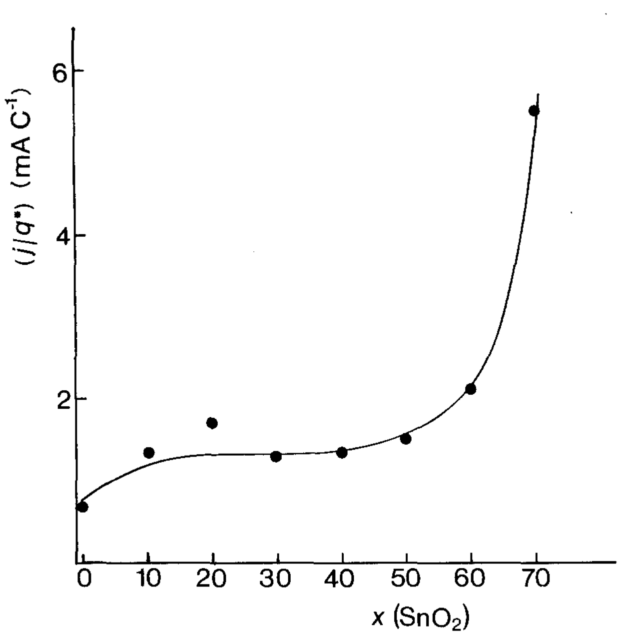


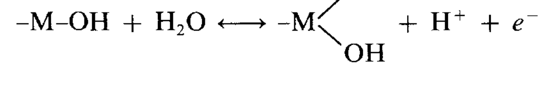
Fig. 5. Current density normalized to unit surface charge as a function of SnO_2 content for oxygen evolution from 1 mol dm^{-3} $HClO_4$ solutions on 30 mol % RuO_4 + x mol % SnO_2 + $(70 - x)$ mol % TiO_2 electrodes.

4. Conclusions

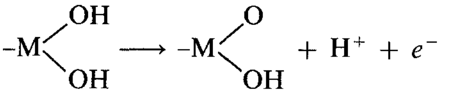
The replacement of TiO_2 with SnO_2 in 30 mol % RuO_2 + 70 mol % TiO_2 electrodes results in an increase in surface area at intermediate compositions and a 6-fold increase in electrocatalytic activity at complete substitution. Therefore, the present study shows that the addition of SnO_2 to TiO_2 + RuO_2 activates these electrodes for oxygen evolution. It is interesting that the results of this paper are in fact corroborated by some of the data in a patent [6]. If at constant concentration of Pd (8%) and of Ru (2%), Sn is substituted for Ti from 50 up to 80%, the overpotential for oxygen evolution is reported to *decrease* from 0.93 to 0.75 V. The reason may be related to the different lattice spacing of SnO_2 and TiO_2, the latter being almost the same as for RuO_2 [23]. As a consequence, intimate mixing can be realized between RuO_2 and TiO_2, while this may not be the case for RuO_2 and SnO_2. A structural study is needed to corroborate these views. This has been done in the case of RuO_2 + IrO_2 + SnO_2 mixtures [3].

The observed increase in the electrocatalytic activity for oxygen evolution is in line with the observation [24] that in RuO_2 + SnO_2 mixtures the maximum activity is reached at much lower RuO_2 content than in the case of RuO_2 + TiO_2 mixtures. This indicates that RuO_2 and SnO_2 give rise to synergetic effects, or alternatively, that RuO_2 and TiO_2 interact more closely so that the RuO_2 activity is depressed by TiO_2 but not by SnO_2. It is to be noted that the sharp increase in activity is observed only as no more TiO_2 is present. A small amount of TiO_2 is presumably able to counterbalance the effect of the presence of SnO_2. If this is the case, long-term performances should clearly discriminate between the two possibilities.

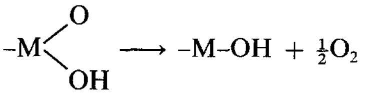
The kinetic parameters do not appear to change with composition. Tafel slope and reaction order remain the same, only the exchange current changes. This can be understood in terms of modification with composition of the strength of the interaction of adsorbed intermediates with the electrode surface. The kinetic mechanism is independent of composition and can be interpreted [12, 20] as a slow second electron transfer at an active site whose potential changes 59 mV per pH unit:



$$\text{-M-OH} + H_2O \longleftrightarrow \text{-M}\begin{matrix}\diagup OH \\ \diagdown OH\end{matrix} + H^+ + e^- \qquad (3a)$$



$$-\mathrm{M}{<}^{\mathrm{OH}}_{\mathrm{OH}} \longrightarrow -\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{OH}} + \mathrm{H}^+ + e^- \quad \text{rds} \qquad (3b)$$



$$-\mathrm{M}{<}^{\mathrm{O}}_{\mathrm{OH}} \longrightarrow -\mathrm{M{-}OH} + \tfrac{1}{2}\mathrm{O}_2 \qquad (3c)$$

The kinetic equation [19] is:

$$j \propto [\mathrm{H}^+]^{-(1+\alpha)} \exp\,[(1 + \alpha)\,EF/RT] \qquad (4)$$

The above mechanism appears to be typical of RuO_2 both in acid and alkaline solution [25], and can be characterized by the slow oxidation of the surface oxide to a higher valency state followed by the fast decomposition of the higher oxide [12]. In terms of mechanism (3) TiO_2 would make step (3b) more difficult thus retarding the oxidation of the surface oxide. Conversely, SnO_2 either accelerates it, or more probably fails to have any effects because of lack of intimate interaction. The main conclusion is that synergetic effects, either positive or negative, are possible only if intermixing at an atomic level is achieved. In this respect, the temperature and procedure of oxide preparation (including the choice of the solvent for the precursor) are expected to have a dramatic impact on the properties of mixed oxides, as shown previously for the case of $RuO_2 + IrO_2$ [10, 14].

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