

ELECTROCATALYSIS OF H₂ EVOLUTION ON Rh
OXIDE AND Rh+Ru MIXED OXIDE CATHODES

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High performance oxide electrocatalysts such as RuO₂ and IrO₂, are usually prepared by thermal decomposition of appropriate precursors dissolved in suitable solvents and spread onto metallic supports [1]. These oxides are good electrocatalysts for H₂ evolution, although less than Pt; however, they exhibit the intriguing advantage of insensitivity to metallic impurities [2].

Previous work [3] in this laboratory showed that Rh oxide (RhO_x) can even be more active than RuO₂. In this work we report on studies of hydrogen evolution on pure RhO_x as well as on RuO₂ + RhO_x mixed oxide electrodes.

Figure 1 shows quasi stationary curves for hydrogen evolution in 0.5 mol dm⁻³ H₂SO₄ recorded with Ti/RuO₂ and Ti/RhO_x electrodes prepared by thermal decomposition of MCl₃ acid solutions (c_M = 0.1 mol dm⁻³ and c_{HCl} = 10 w %) at 400°C in air. The Ti/RhO_x electrode shows a better performance than the Ti/RuO₂ electrode.

Although RhO_x is mentioned in patents and in a few papers as a component of activated anodes, the first paper regarding the surface and bulk structure of coatings prepared by thermal decomposition of RhCl₃ solutions on Ti and quartz supports, in a temperature range between 400° and 600°C was published only recently [4]. Cyclic voltammetry showed that the RhO_x oxide is unstable towards cathodic reduction [3]. However the reduced oxide proved to be particularly active for the hydrogen evolution reaction.

The activity of an oxide-based electrode can be modulated using different, intimately mixed, components. Rh+Ru oxide electrodes were prepared from (RuCl₃ + RhCl₃) acid solutions at 400°C. XPS analysis indicate that the surface of Rh+Ru oxide electrodes is enriched with the Rh phase (Fig. 2).

Cyclic voltammetric studies in H₂SO₄ 0.5 mol dm⁻³ showed that the surface charge is strongly dependent on the oxide composition (Fig. 3). The stability with respect to reduction has been investigated by progressively decreasing the negative limit of potential; it has been found that Ru+Rh oxide electrodes are stable under cathodic conditions for Rh contents ≤ 70%.

The activity for hydrogen evolution of Ru+Rh oxide electrodes increases until ca. 40% Rh, then it remains almost constant (Fig. 4). Thus, maximum activity can be achieved with an amount of RhO_x that does not affect the cathodic stability of electrodes.

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References

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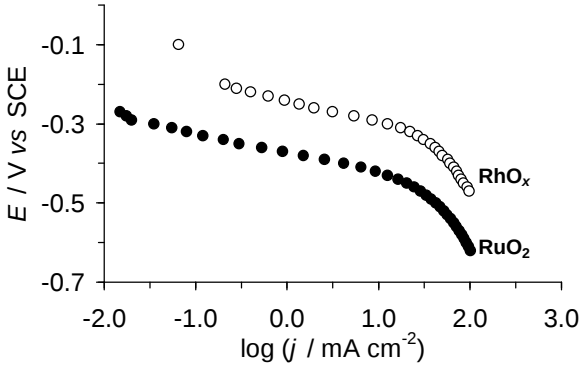


Fig.1 – Ti/RuO₂ and Ti/RhO_x steady state polarization curves for hydrogen evolution in 0.5 mol dm⁻³ H₂SO₄ solution.

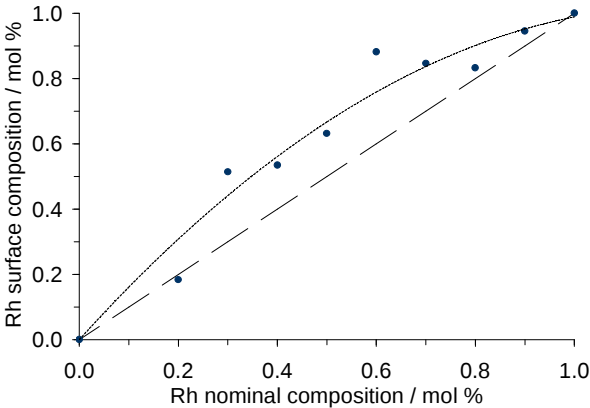


Fig. 2 - Surface (XPS) vs. bulk nominal composition of RuO₂ + RhO_x mixed oxide electrodes

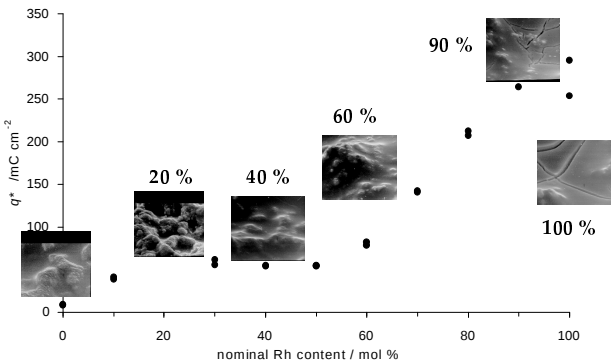


Fig. 3 - Dependence of the voltammetric charge on the nominal composition of the mixed oxides. SEM pictures are also shown for some of the compositions.

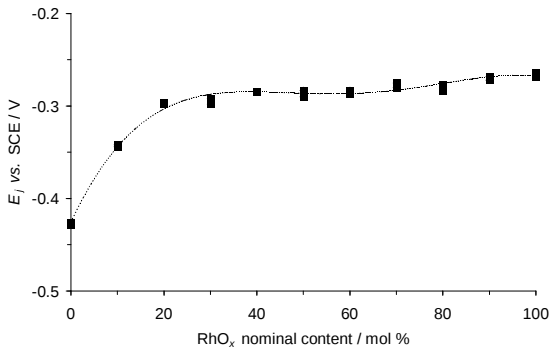


Fig. 4 - Potential at constant current as a function of composition for hydrogen evolution on RuO₂ + RhO_x.