

PHYSICOCHEMICAL AND ELECTROCHEMICAL CHARACTERIZATION OF RUTILE TYPE MIXED OXIDES $Ru_xMn_{1-x}O_2$ ON TITANIUM

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RuO_2 is the principal component of the electrodes known as DSA[®]. Generally, this is mixed with other oxides that can form a rutile type solid solution or well defined compounds. On this context, mixed oxides of Ru with Ti, Ir, Sn among others have been widely studied [1], although other potentially promissory combinations such as Ru and Mn have received scarce attention. Thus, the purpose of the present work is the structural and electrochemical characterization (intrinsic and apparent electrocatalytic activity and stability) of Ru-Mn mixed oxide activated electrodes, which could have application as anodes in electrosynthesis processes.

The titanium/Ru-Mn mixed oxide electrodes were prepared by thermal decomposition of their nitrates at 370°C by means of the spray-pyrolysis technique [2]. Through XRD analysis and the application of the Rietveld method, it was verified that the oxide film consists in a mixture of a rutile type solid solution which formula is $Ru_xMn_{1-x}O_2$ ($0.6 \leq x \leq 1$), RuO_2 and β - MnO_2 . This last phase was superficially eliminated by treating the electrodes with HCl.

The intrinsic electrocatalytic activity for the chlorine electrode reaction (CIER) was evaluated in chlorine saturated NaCl-HCl solutions by measurements of the specific polarization resistance (R_p) at different chloride concentrations and pH values. Figure 1 shows the dependence of R_p with the atomic ruthenium fraction in the precursor solution (f_{Ru}) at various pH values, where it is observed a minimum in R_p (highest activity) at $0.7 < f_{Ru} < 0.9$.

The apparent electrocatalytic activity was also analyzed through polarization curves (j^{ap} vs. η) in a wide range of overpotentials (η). The j^{ap} vs. f_{Ru} dependencies at different pH and η values were determined (Figure 2). These results are similar to those corresponding to R_p vs. f_{Ru} dependencies.

Finally, the stability of the electrodes was evaluated in anodic conditions by means of accelerated tests in H_2SO_4 0.5 M at a current density of 1 A cm⁻². It was verified a raising of the *time to failure* (τ) with the increase of the Mn content until $f_{Ru} \approx 0.7$ (Figure 3). Below this value, τ falls abruptly due to the loss of mechanical stability during the dissolution of β - MnO_2 with HCl.

In conclusion, the conditions for the preparation of Ru-Mn mixed oxides on titanium have been determined, and it has been proved the formation of a solid solution with rutile structure, $Ru_xMn_{1-x}O_2$ with $0.6 \leq x \leq 1$. The highest performance of these electrodes as anodes, electrocatalytic activity as well as stability, is obtained when $0.7 < x < 0.9$.

[1] S. Trasatti in "Electrochemistry of Novel Materials - Frontiers of Electrochemistry" edited by J. Lipkowsky and P.N. Ross, Chapter 5, VCH, New York (1994).

[2] J.L. Fernández, M.R. Gennero de Chialvo and A.C. Chialvo, *J. Appl. Electrochem.* **27** (1997) 1323-1327.

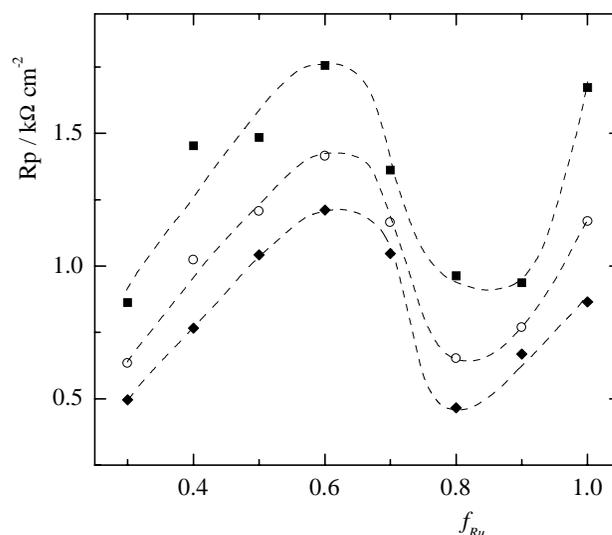


Figure 1. R_p vs. f_{Ru} dependencies in chlorine saturated (1 atm) NaCl - HCl solutions. $C_{Cl^-} = 4$ M. pH: 0.4 (■), 0.6 (○), 0.9 (◆). 30°C.

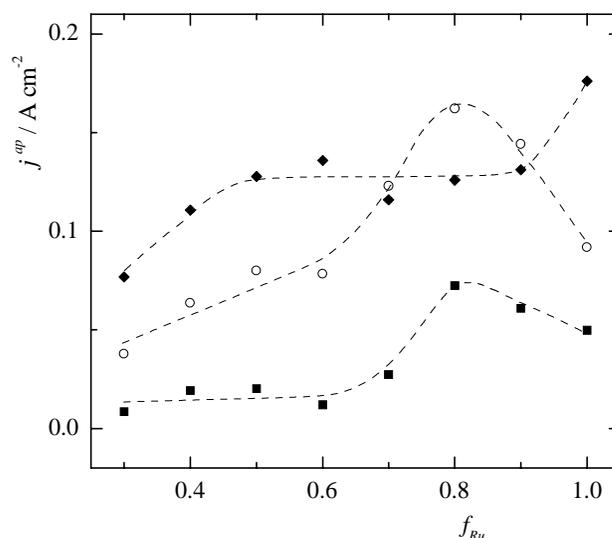


Figure 2. Apparent current density (at $\eta = 0.04$ V) vs. f_{Ru} dependencies in chlorine saturated (1 atm) NaCl-HCl solutions. $C_{Cl^-} = 4$ M. pH: 0.1 (■), 1.0 (○), 2.1 (◆). 30°C.

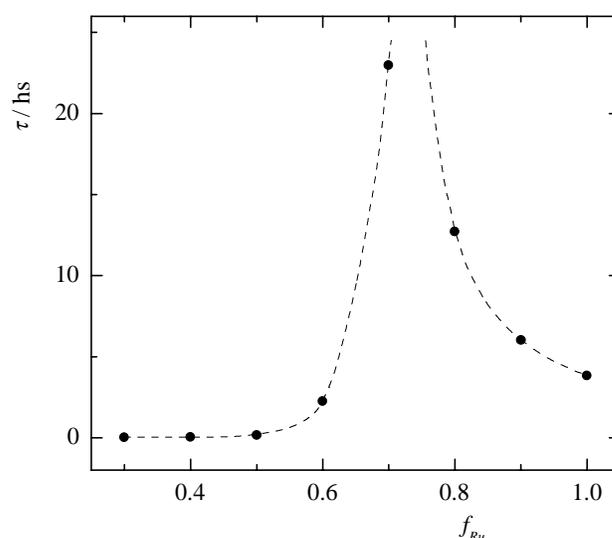


Figure 3. *Time to failure* vs. f_{Ru} dependence in H_2SO_4 0.5 M at 1 A cm⁻².