Influence of Gas Bubbling on the Properties of Ruthenium Oxy-hydroxide Coating

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It has been known for a long time that ruthenium oxy-hydroxide ($RuO_x(OH)_y$) coating can be grown at the surface of a Ru substrate by sweeping the electrode potential between pre-defined anodic and cathodic limits. The purpose of this work is to study the influence of gas bubbling during the formation of this $RuO_x(OH)_y$ coating. It will be shown that the electrocatalytic activity for the hydrogen evolution reaction (her) on $RuO_x(OH)_y$ coating prepared in presence of H_2 bubbling is increased compared to the same coating made in presence of N_2 bubbling.

The $RuO_x(OH)_y$ coatings were prepared by cycling a Ru substrate in 1 M NaOH electrolyte at room temperature, in presence of either H_2 or N_2 bubbling. In a first series of experiments, $RuO_x(OH)_y$ coatings were grown by sweeping the electrode potential between –0.5 and +0.55 V during a fixed number of cycles (30 cycles) in presence of either H_2 or N_2 gas bubbling. Typical cyclic voltammograms are shown in Figure 1, where current peak 1 corresponds to the dissolution of Ru and current peak 2 is the re-deposition of RuO_4^{2-}.

The pseudocapacity of the film grown in these conditions was determined and used as an estimate of the film thickness. The pseudocapacity value that was determined from variable sweep rate measurements performed in a potential region close to –0.2 V is 585 and 450 mF cm^{-2} for H_2 and N_2 gas bubbling, respectively (see Table1). The presence of hydrogen during the formation of $RuO_x(OH)_y$ increases the deposition rate of the coating. Films grown in a second series of experiments by varying the number of cycles exhibit the same pseudocapacitance (see Table 1).

The her on these $RuO_x(OH)_y$ coatings was studied by Tafel measurements in 1 M NaOH at room temperature. Figure 2 shows the Tafel plots obtained in steady-state conditions in the case of coatings prepared with hydrogen and nitrogen bubbling. The overpotential value at a current density of -250 mA cm^{-2}, η_{250}, is -94 mV in the case of a nitrogen bubbling and is -58 mV in the case of a hydrogen bubbling. Part of this increase in the electroactivity is due to the larger real surface area of $RuO_x(OH)_y$ deposited in the presence of hydrogen bubbling. However, Tafel measurements realized on $RuO_x(OH)_y$ deposit of the same thickness (same value of pseudocapacity) show that η_{250} is -119 mV in the case of a nitrogen bubbling and -95 mV in the case of a hydrogen bubbling. From these results, one can conclude that hydrogen bubbling has another effect on the deposit, in addition to the increase of the real surface. XPS data of the electronic structure of these films as a function of the deposition conditions will also be presented.

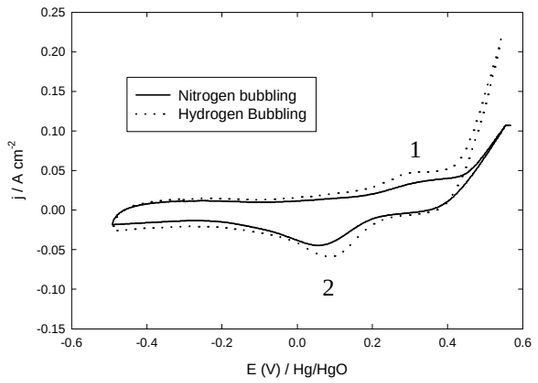

Figure 1 Cyclic voltammograms of the Ru substrate in 1 M NaOH at 20 mV s^{-1}.

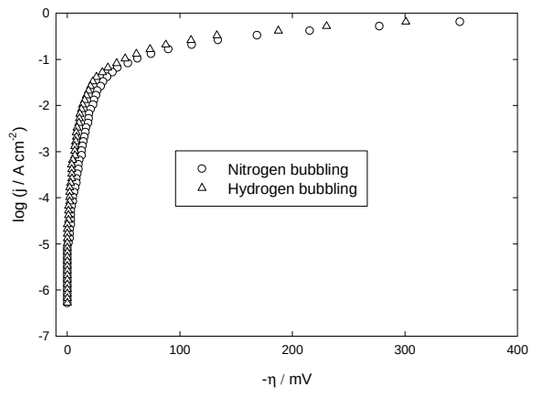

Figure 2. Tafel plots obtained in 1 M NaOH on $RuO_x(OH)_y$ coatings.

	C (mF cm^{-2})	$-\eta_{250}$ (mV)
Ru		178
$RuO_x(OH)_y$ - N_2 30 cycles	450	94
$RuO_x(OH)_y$ - H_2 30 cycles	585	58
$RuO_x(OH)_y$ - N_2 same thickness	370	119
$RuO_x(OH)_y$ - H_2 same thickness	380	95

Table 1. Summary of the pseudocapacity and η_{250} values.