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Carbon-supported Ta-based Electrocatalysts for the Oxygen Reduction and Evolution Reactions

J.C. Ruiz-Cornejo[1], D. Sebastián[1], M.V. Martínez-Huerta[2], M.J. Lázaro[1*]

[1] *Instituto de Carboquímica, CSIC, Miguel Luesma Castán 4, 50018 Zaragoza, Spain*
[2] *Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, 28049 Madrid, Spain*

*Presenting author's e-mail: *mlazaro@icb.csic.es*

Introduction

Electrocatalytic materials with high efficiency for the main reactions on bifunctional oxygen electrodes, the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), are necessary for the development of new emerging electrochemical energy storage and conversion devices. Although some noble metals such as Pt and metal oxides (RuO_2, IrO_2) possess excellent activity as bifunctional electrocatalyts, their high cost and instability hinder large-scale applications. Tantalum-based materials have demonstrated to be active and robust electrocatalysts for the ORR in acidic environment[1].They have an excellent electrochemical stability and become active for the oxygen reactions when the surface stoichiometry is tuned[2]. Carbon materials can act both as support and electron conductor phase. In this work nanocomposites based on tantalum sub-oxides on carbon black have been investigated for the ORR and OER[3].

Materials and Methods

The synthesis is based on a microemulsion path. The microemulsion (ME) was prepared by adding NaOH aqueous solution to an oil phase composed of a surfactant (Igepal CO-520), n-heptane and 3% of ethanol. Afterwards tantalum (V) ethoxide was added to the ME at room temperature under continuous stirring. The mixture reacts producing tantalum oxide-based nanoparticles within 5 min. Subsequently, carbon support (commercial carbon black Vulcan XC72R) is added to the suspension and kept under stirring overnight. The material is washed with ethanol and then with water, followed by drying at 60 ºC overnight. A final step consists of a heat treatment in inert atmosphere at a temperature from 700 to 1000 ºC. The catalysts are labeled as TaOx/C followed by the annealing temperature (700, 800, 900 and 1000 ºC). The solid-state characterization was made by transmission electron microscopy (TEM) and X-ray diffraction (XRD).

Electrochemical studies were carried out in a three-electrode cell at room temperature, using 0.1 M NaOH aqueous solution as electrolyte. A reversible hydrogen electrode (RHE) was used as reference and a glassy carbon rod as counter electrode. The catalysts were deposited on rotatory disc electrode (RDE), with a disk of glassy carbon (5 mm diameter). The electrochemical activity was studied by linear sweep voltammograms in O_2-saturated (ORR) and deareated (OER) 0.1 M NaOH electrolyte at 1600 rpm.

Results and Discussion

The Ta-based catalysts were studied for the ORR and the OER in a three-electrode half-cell configuration by using a rotating disc electrode (RDE). The electrolyte was in all studies 0.1 M

NaOH aqueous solution, saturated with O_2 for ORR tests, and the experiments were carried out at room temperature. TEM images showed that the morphology of the metal oxide particles changes from a rounded shape (700ºC) towards a prismatic and more ordered arrangement (1000ºC) as the treatment temperature increases. The average particle size increases with the temperature from 35 to 45 nm. XRD patterns showed that metal oxide nanoparticles were formed by a mix of $Na_2Ta_8O_{21}$ with other tantalum oxides and sodium tantalates. The effect of the annealing temperature of the tantalum-based catalysts on the ORR/OER activity was investigated. The increase of the annealing temperature improves the activity for the ORR as shown in Figure 1(a). The largest difference was observed between catalysts treated at 700 ºC, with low activity, and catalysts annealed at 800 ºC or higher, with more than 100 mV improvement at the same current density. For the OER the improvement take place until 900 ºC Figure 1(b).

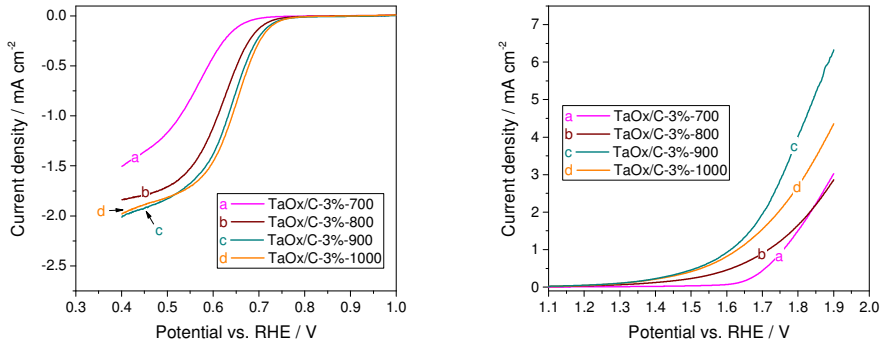

Figure 1. Effect of the temperature on (a) ORR and (b) OER polarization curves for the Ta-based catalysts. Linear sweep voltammetries at 5 mV s^{-1}, 1600 rpm, 0.1 M NaOH, 45 µg cm^{-2} of Ta.

Conclusions

The activity of the catalysts towards ORR and OER in alkaline environment is favored by using high annealing temperatures despite that the crystal size increases, decreasing the surface area. For the ORR, the activity improves until 1000 ºC. For the OER reaction the activity improves until 900 ºC. Catalysts annealed at 900 ºC and 1000 ºC exhibited the most promising bifunctional behavior in terms of activity.

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