Preparation of electrocatalysts by combining the Pechini and microwave-assisted polyol methods

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Fuel Cells are electrochemical devices that transform chemical energy in electricity. Among the several Fuel Cell types, the devices that use a polymeric membrane as electrolyte and that work at low temperatures (PEMFC), are the main systems considered for transportation or portable devices. The higher advanced technologies actually available for this kind of device use hydrogen as fuel an oxygen as the oxidant. However, liquid fuel such as methanol and ethanol, have been considered as fuel also and have attracted the attention of many research groups. The main characteristics of these substances that justify their use as fuel are related, among others, to their availability and easily storage conditions. Meanwhile, the development of devices commercially attractive depends on the utilization of electrocatalytic materials that are able to oxidize these substance at low overpotentials producing high current densities. The catalytic materials that have presented the best performance for the oxidation of methanol and ethanol are based in the use of Pt as the active material. The modification of Pt by other chemical elements such as Ru, Ir, Sn, Rh, etc ..., have shown to be able to increase the material activity. The effects of the addition of those elements are related to the modifications of the Pt electronic structure that they can induced by the elements or can be related also to the so called bifunctional mechanism in what the extra element is responsible by the formation of adsorbed hydroxyl that are necessary for the complete oxidation of the alcohols. Apart form the choice of the modifier element; the structure and morphology of the catalytic material influence directly its activity. For that reason, the electrocatalyst catalytic activity of is highly dependent on the preparation conditions and methods. The use of different preparation conditions may lead, as an example, to the obtainment of alloys, oxides or segregated metallic particles. Other important characteristics that are directly affected by the preparation conditions are the particle size and distribution. Several preparation methods described in the literature are efficient for the preparation of Pt based elecrocatalysts. Among these methods, the method is based in the Pechini thermal decomposition of polymeric precursors. The catalysts produced by this method have as a characteristic, the formation of low alloy degree, i. e., normally Pt is present in its metallic form and the other elements are present in the oxide form. This method has been used to prepare high activity materials for the electrooxidation of methanol and ethanol. Another method recently applied for the

preparation of electrocatalysts is the microwave-assisted method.

In this work we have used the Pechini and the microwave-assisted polyol method in order to prepare Pt based eletrocatalysts and we have verified their activities towards the methanol and ethanol electrooxidation.

The electrocatalysts were prepared in the form of particles dispersed on carbon Vulcan XC-72. The preparation routine consisted in to modify the carbon surface by the deposition of tin oxide using the Pechini method [1] and, in a subsequent step, in to deposit PtRu or PtRh by the microwave-assisted polyol method [2] over the previously obtained powder. Non-modified carbon was also used as support for the dispersion of PtRu and PtRh particles for comparison purposes.

The obtained materials were characterized by X-ray diffraction, transmission electronic microscopy, cyclic voltammetry, chronoamperometry and Fuel Cell tests.

The results showed that the Pechini method leads to the formation of well-dispersed SnO_2 particles over the carbon surface. The tin oxide particles present a diameter of about 5 nm. The PtRu and PtRh particles showed very regular particle sizes of about 3 nm that were deposited preferentially over the previously deposited tin oxide.

The electrochemical results showed that employed methods could lead to the production of catalysts with good catalytic activity. The effect of the tin oxide on the catalytic activity of PtRu and PtRh for methanol and ethanol was also observed.

ACKNOWLEDGMENTS: FAPESP, CNPQ, CAPES-PNPD.

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