Investigation of the Borohydride Oxidation Processes on Hydrogen Storage Alloys

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The borohydride oxidation reaction has been studied in a variety of materials, with the aim of preparing more efficient catalysts, and by employing a number of techniques, so to understand the reaction mechanisms. Hydrogen storage alloys have previously been investigated as electrocatalysts [1] for this reaction. The results have shown that exposure to sodium borohydride leads to the hydriding of the metal alloys, which are also capable of partially/slowly oxidizing the borohydride ions, while the hydrogen simultaneously produced by hydrolysis or partial oxidation of BH₄⁻ is stored in the hydride form. In this work the main steps of the alloys hydriding by expositions to borohydride ions and the reactions occurring during the borohydride oxidation process were investigated by electrode polarization and galvanostatic chrono-potentiometry using thin porous coating (TPC) rotating disk and ring electrodes (RRDE, carbon disk and gold ring) in 1.0 M KOH solutions in the presence of NaBH₄. Differential electrochemical mass spectrometry was used to monitor the hydrogen evolved from the working electrodes in the presence of BH₄⁻.

Several metal hydride alloys were considered, including LaNi₄.7Sn₀.2Cu₀.1 and LaNi₄.78Al₀.22, with and without deposition of platinum, palladium and gold. Elemental analyses were made to confirm the noble metal loading in the materials. Diffuse Reflectance Infrared Fourier Transform spectrometry (DRIFTS) was used to characterize the physic-chemical interactions of the noble metals and the alloy surface atoms. In situ X-ray diffraction was employed to analyze the changes in the alloy structure and the size of the unit cell, as well as in the structure of the deposited metals, during the hydride absorption and borohydride oxidation reaction.

Results have shown that the extent of hydride formation depends on the rate of the BH₄⁻ hydrolysis, the hydrogen storage capacity of the alloy, and kinetics of H atom diffusion inside the alloy. The activity for the direct BOR is low in both bare metal hydride alloys, but the rate of the BH₄⁻ hydrolysis and the hydrogen storage capacity are higher, while the rate of H diffusion is slower in the bare LaNi₄.78Al₀.22. Results of RRDE indicated formation of BH₃OH species during the borohydride oxidation process for all alloys, except for the bare LaNi₄.7Sn₀.2Cu₀.1 alloy.


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