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Sustainable Hydrogen Production by Electrolysis Promoted by Ethanol Oxidation

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Hydrogen produced by steam reforming of natural gas makes up the majority of the hydrogen market. Unfortunately, this technology has contributed to the carbon emissions. Electrolytic hydrogen produced by primary renewable energy sources (solar, wind, etc.) is free of carbon emissions and it is a non-suitable way to produce hydrogen on board of a vehicle. This limitation can be overcome by a low cost and free-carbon emission technology of electrolytic hydrogen production assisted by the facility of an alcohol oxidation in the anode compartment, in substitution to oxygen evolution reaction (limited by thermodynamic restriction) in the electrolytic cell. This electrolytic way to produce hydrogen assisted by ethanol oxidation is denominated "Electrochemical Reforming of Ethanol at Low Temperature for Hydrogen Generation". Additionally, an important aspect to be mentioned is that, this system is technically similar to a direct ethanol fuel cell employing a membrane electrode assembly component, with the difference that in the cathode compartment occurs the hydrogen evolution reaction. A new class of catalytic material specially for hydrogen generation should by developed with the characteristic that it is insensitive to ethanol reduction so that it does not compromise the efficiency of hydrogen production, due to the ethanol membrane crossover. Thus, this abstract describes the development of non-noble metal catalysts for hydrogen evolution reaction (HER) in alkaline medium (4 M KOH in the cathode compartment). In the anodic compartment, the same solution is used after addition of 1 M ethanol. The system is operated at the temperature range of 25 – 85 °C). The measurements were made in an electrolysis metallic cell, the gap between electrodes of 6cm^2 was 2 mm. All catalysts were characterized by X-ray diffraction, Raman spectroscopy, TEM and SEM. Two class of materials were developed: (i) MoS_x and (ii) NiM (M= B, Co, Mo) intermetallic compounds. The MoS_x was obtained by electrodeposition from $(NH_4)_2MoS_4$ precursor on black pearls high area carbon matrix doped with nitrogen. The activity of MoS_x for the HER is very good and similar to the Pt electrode and was not sensitive for reducing ethanol. The synthesis method used for preparation of NiM intermetallic was the powder metallurgy, where the metallic components were grinding in a ball mill. After grinding, the materials were heat treated at various temperatures under inert argon atmosphere in order to form the intermetallic compound according to each specific phase diagram. The Ni_2B and NiMo intermetallic materials showed an improvement of the HER and were not affected by the presence of ethanol, while the HER on Ni_3B was inhibited in presence of ethanol.

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