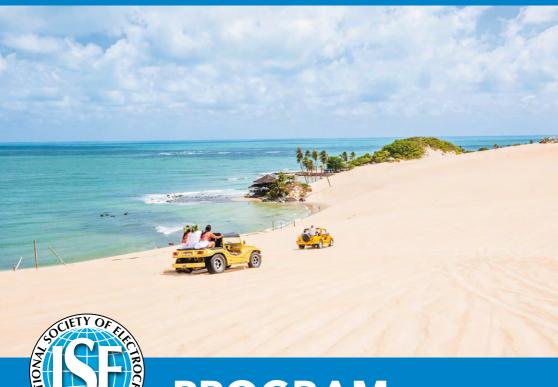
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Effect of iron impurities in the activity of Mo₂C/C for the hydrogen evolution reaction in alkaline electrolyte

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Coupling electrochemical devices to a renewable electric energy system can enable the direct conversion of electrical to chemical energy stored into hydrogen molecules. This electrochemical production of hydrogen is made through the hydrogen evolution reaction (HER), which involves the use of a catalyst that must be an abundant and non-precious metal-based material, such as molybdenum carbide, rather than commonly used noble metals (Pt, Ir, and Ru). Exploration of the potential of this application requires the understanding of all dynamics of HER, which means, all the possible variables that would affect the electrocatalysis of the reaction. In this work, the effect of iron impurities in the NaOH electrolyte on the activity of carbon supported molybdenum carbide (Mo₂C/C) for HER has been investigated. The Mo₂C/C material was produced using (NH₄)₆MoO₂₄ and Glucose as Mo and C sources by a hydrothermal step, followed by pyrolysis in an inert atmosphere. The electrochemical activities for the HER were evaluated by DC and AC experiments employing NaOH electrolytes containing different levels of iron contamination: iron-removed (EF0) and non-purified (EF1) NaOH solutions, and with the addition of an iron contaminant at increasing contents (EF2, EF3, and EF4). XRD analyses of synthesized Mo₂C/C evidenced the production of orthorhombic Mo₂C (ICSD 43322). Rietveld refinement indicates that the material is composed of 95% Mo₂C plus 5% MoO₂ particles dispersed on carbon, showing high efficiency in the conversion of precursors into the desired product. Mo₂C particles presenting crystallite sizes of 15 nm were produced, which is consistent with the average value of particle sizes (9.52 nm), as measured by transmission electron microscopy (TEM). Moreover, TEM images showed a good distribution of material on the carbon support. Electrochemical linear sweep voltammetry experiments used for HER investigations on the Mo₂C/C materials were carried out at each electrolyte, before and after a 2 h chronopotentiometry (CP) at the cathodic current of 10 mA cm⁻² for eventual iron incorporation into the electrode. The analysis of results obtained before CP shows that the Mo₂C/C activities at 10 mAcm⁻² are very close to each other, except for the EFO condition. However, at 100 mAcm⁻², activities followed the sequence EF3~EF0>EF2>EF4>EF1. On the other hand, all materials lost activity for the HER after the electrochemical CP iron incorporation. Interestingly, Mo₂C/C in EF0 and EF1 conditions resulted in larger losses of activity, compared to those seen for the iron-added electrolytes. The EDS mapping analysis by TEM for the samples after CP demonstrated no iron on the electrode in the case of EFO condition. In contrast, for EF1, results denote that the Mo₂C/C particles contain an unexpectedly high coverage of iron. The addition of iron into the electrolyte (EF2, EF3, EF4) led to an increase in the iron deposition, and a higher presence of segregated iron particles. The improved stability of electrodes under EF3 condition may be attributed to a synergetic effect caused replacing the activity of Mo₂C/C inactive sites by iron deposits, without blocking the still active Mo₂C/C sites.

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