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Kształtowanie właściwości wodorochłonnych proszku aktywnego $La(Ni,Co)_5$ poprzez magnetronowe osadzanie powłok wysokoentropowych

Abstract:

The thesis deals with surface modification of powdered (particle size fraction of 20 – 50 µm), hydrogen storage material (HSM) of $LaNi_{4.5}Co_{0.5}$ stoichiometry, using magnetron sputtering. Three kinds of high entropy alloys (HEAs) with MCrFeCoNi composition (where M = Mn, Ti or V) have been used as targets for powder particles modification. The applied deposition conditions ensured average thickness of HEA layers on the level of 0.5 µm.

In the literature part, the properties of HSMs are widely discussed. The literature review includes the theoretical- and experimental assessment upon the methods of surface modification of powdered materials applied for hydrogen storage. Characterization of high entropy alloys and criteria for the components selection of these alloys for HSM surface modification are described and justified. In the chapter "Measurement methods used in the dissertation", the methodology of powder composite HSM electrodes preparation as well as the methods of electrochemical- and structural research tests have been briefly outlined.

The experimental part contains a description of surface modification route of the parent $LaNi_{4.5}Co_{0.5}$ alloy powder by magnetron sputtering, as well as thorough electrochemical- and structural analysis results carried out within the dissertation. Interpretation of obtained results includes characterization of such parameters of modified HSMs as specific capacity, its cycle stability, exchange current density of H_2O/H_2 system, hydrogen diffusivity and high rate dischargeability. The results are also discussed in view of practical consequences for the performed modifications.

The surface modification of the $LaNi_{4.5}Co_{0.5}$ hydrogen storage powder particles by magnetron sputtering allowed to obtain amorphous HEA layers of good homogeneity on the powder particles. The galvanostatic charging / discharging tests revealed the specific capacity changes caused by HEA modification. Capacity fade caused by cycling allows for the corrosion behavior of the modified electrodes to be determined. The analysis of galvanostatic discharge curves enabled the assessment of both the hydrogen sorption efficiency and the kinetics of degradation processes of the electrode material modified by HEA layers. Hydrogen diffusivity

of the tested materials was evaluated using a chronoamperometric method at long discharge times (> 1500 s). The potentiodynamic polarisation method has been used to characterize protective properties of individual HEA materials. The beneficial role of manganese as a target component in view of HEA passivation in the KOH environment has been pointed out. Surface analyzes after magnetron sputtering modification were carried out using scanning electron microscopy (SEM) with EDS microanalysis and X-ray phase analysis (XRD).

The structural characteristics of the modified $LaNi_{4.5}Co_{0.5}$ powder composite electrodes indicate that the sputtered layers obtained on the HSM substrate have shown a number of similarities for all HEAs applied. The modified electrode materials exhibit almost identical initial specific capacity of 305 ± 10 $mAhg^{-1}$ for all HEA coatings. For the obtained HEA layers, the effect of inhibition of corrosion degradation and significant improvement of high rate dischargeability are particularly distinct for HEA-Mn modification. The strongest corrosion inhibition effect for all HEA coatings has been observed within the range of 10 - 35 cycles, with the slope of the $\log Q = f(N)$ dependence close to zero. Degradation effects appear for successive cycles, however, they are evidently weaker compared to the unmodified material. The obtained HEA layers do not inhibit the transport of atomic hydrogen within the electrode material. On the other hand, the obtained HEA coatings distinctly increase the H_2O/H_2 exchange current densities which should be considered as a very advantageous result. The HEA layers have cathodic character in the tested alkaline environment, therefore, a perceptible efficiency of corrosion inhibition in longer time intervals needs strict continuity (good tightness) of these coatings.