ELECTROCHEMICAL HYDROGENATION OF $LaNi_5$ BASED ALLOYS DOPED WITH Zr, Mg AND Al OR Ga

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Nickel-metal hydride batteries attract considerable attention as secondary sources of electrical energy due to their relatively high current density and environmental safety. However, despite their advantages (high power, durability, resistance to temperature fluctuations, low resistance, no memory effect, and environmental friendliness), nickel-metal hydride batteries have a number of disadvantages. In particular, in devices with high energy consumption, such as electric vehicles, they do not provide sufficient discharge capacity. A classic anode material widely used in Ni–MH batteries is a binary intermetallic $LaNi_5$ or its doped derivatives. However, the actual energy capacity of the binary phase is significantly lower from the theoretical one, which is due to electrode degradation and passivation of its surface in an alkaline electrolyte [1]. Therefore, the main objective of the work is to form high-entropy systems to improve the stability, sorption and electrochemical characteristics of the anode materials. An additional objective was to determine which dopants are more effective: aluminium or gallium.

The synthesis of two alloys, $La_{11.67}Zr_5Ni_{73.33}Mg_5Al_5$ and $La_{11.67}Zr_5Ni_{73.33}Mg_5Ga_5$, was carried out by melting pure metals in an arc furnace under an argon atmosphere. To ensure the homogeneity the obtained alloys were sealed in silica ampules under vacuum and annealed at 400°C for two weeks. After that, they were quenched in cold water without breaking ampoules. Phase analysis of the samples was carried out on data sets obtained by powder X-ray diffraction (XRD) using a powder diffractometer DRON-2.0M (Fe$K\alpha$-radiation, $20° \leq 2\theta \leq 120°$). Refinement of the crystal structure of observed phases was performed according to the Rietveld procedure using the WinPLOTR software. The qualitative and quantitative composition of the phases was confirmed by energy-dispersive X-ray spectroscopy using an electron microscope TescanVega3 LMU with Oxford Instruments EDX system.

The major phases observed in both samples, as well as the binary prototype, crystallize in the $CaCu_5$-type structure (space group *P6/mmm*, Pearson code *hP6*). In addition to the main phase, the reflections from $ZrNi_5$ ($AuBe_5$-type structure, space group *F*-43*m*, Pearson code *cF*24) were present on the powder patterns of the samples. The EDX analysis confirmed the average compositions of the samples and the composition of each phase observed by XRD in particular.

Electrochemical hydrogenation of $La_{11.67}Zr_5Ni_{73.33}Mg_5Al_5$ and $La_{11.67}Zr_5Ni_{73.33}Mg_5Ga_5$ (charging time t_{ch} = 4.00 h, charging current I_{ch} = 1.0 mA) confirmed that they intercalate hydrogen, demonstrating high efficiency 96.15 % and 87.64 % accordingly. Discharge time is 3.85 and 3.51 h, correspondingly. For $La_{11.67}Zr_5Ni_{73.33}Mg_5Ga_5$, regular increase in cell volume of the main phase of 0.54 % was observed; cell volume of the minor phase decreases by 0.38 %. For $La_{11.67}Zr_5Ni_{73.33}Mg_5Al_5$, relative decrease in cell volume of the main phase was 1.11 %; cell volume of the minor phase decreases by 1.28 %. After 50 charge-discharge cycles, partial amorphisation of the electrode material was observed, but the structure of the material remained unchanged as the result of electrochemical processes.

1. Ewe H., Justi E.W., Stephan K. *Energy Conversion*. 1973. Vol.13 (3). P. 109-113.

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