Electrochemical studies of \( \text{La}_{0.6}\text{Ce}_{0.2}\text{Nd}_{0.2}\text{Ni}_{4}\text{Co}_{0.4}\text{Mn}_{0.3}\text{Al}_{0.3} \) electrodes with different mass ratio of metal hydride and carbonyl nickel powders

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Abstract. Metal hydride materials are actively used as anode materials for Ni-MH batteries. Various high conductive additives (graphite, nickel, copper, etc.) to the active hydrogen storage material are used to increase the electrical conductivity and mechanical stability of the electrodes. In this work, metal hydride electrodes based on AB\textsubscript{5} type alloy mixed with carbonyl nickel in various mass ratios are prepared and studied. The electrochemical properties of the prepared electrodes, such as activation performance, maximum discharge capacity, and high rate dischargeability are investigated in detail.

1. Introduction
Energy storage is one of the key factors for the sustainable development of a new energy systems based on resource-saving renewable energy technologies. Inexpensive, reliable and efficient energy storage methods will be an important part of new renewable energy [1]. Electrochemical energy storage is one of the most intensively developing areas for the renewable energy storage. Electrochemical batteries can be used not only as power sources for mobile and portable devices, but also for hybrid and electric cars and balance the load in renewable energy networks [2].

Ni-MH batteries have a number of advantages for practical applications, such as high specific energy density, resistance to overcharge/overdischarge, fast charge-discharge kinetics, environmental friendliness and safety. The main component of Ni-MH batteries, which affects their characteristics, is a hydrogen-absorbing material used as an anode. Intermetallic compounds are capable of reversibly absorbing and releasing hydrogen under normal conditions [3]. The intermetallic compounds (IMC) for anodic materials can be represented by the general formula \( A_mB_nH_x \), where \( A \) is a hydride forming metal (La, Ce, Mn, Ti, Zr, V, Mg), and metal \( B \) does not interact with hydrogen under normal conditions (Ni, Co, Fe, Mn, Cr, Al and others). Depending on the metal \( A \) to metal \( B \) ratio, the IMCs can be classified in several basic types: \( AB_5 \), \( AB_2 \), \( AB_{3.5} \), \( AB \), \( A_2B \), Ti-, V-based solid solutions. The characteristics of each type of alloys differ significantly in terms of hydrogen storage capacity, discharge capacity, activation and stability due to their different composition and crystal structure [4]. Metal hydride materials in electrochemical energy sources require to have a high reversible hydrogen capacity (> 1% mass), high catalytic activity, corrosion resistance in the electrolyte, and mechanical stability and a long service life [5].

Along with the hydrogen storage properties of IMCs, the preparation of metal hydride electrodes is of great importance for improvement of their electrochemical properties: metal hydride particle size
[6-8], electroconductive additives [9, 10], binding components [11], compaction pressure [12, 13]. The main electro conductive additive is nickel, due to its high electrocatalytic activity. Different nickel content in the metal hydride electrode affects its electrochemical properties [9]. However, there is a lack of studies of the mass ratio effect on the metal hydride electrode properties.

The aim of this work is to study the electrochemical properties of a metal hydride electrode prepared in various mass ratios with electro conductive additive carbonyl nickel.

2. Experimental details

The AB$_5$ type intermetallic compound with nominal composition La$_{0.6}$Ce$_{0.2}$Nd$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ is prepared in an arc furnace under argon atmosphere. The purity of the starting metals is at least 99.5%. The stoichiometric amount of metals is remelted three times to achieve high homogeneity of the alloy. After melting, the surface of prepared alloy (about 50 g) is cleaned from oxide films; alloy is crushed into small pieces (5-8 mm). A 20 g sample is wrapped in a molybdenum foil and sealed in a stainless-steel tube sample holder with titanium powder under argon atmosphere. The sample is annealed at 1223 K for 20 hours with subsequent quenching in ice water.

XRD patterns of the annealed alloys are obtained from X-ray diffractometry (Bruker’s D8 ADVANCE diffractometer). Samples for XRD analysis are prepared by mechanical grinding to a fine powder. The step size was 0.02º and the exposition time was 1 s. The 2θ angles scanned were in the range from 15 to 80. Crystal structure and phase composition are performed using Jana2006 and Crystal Impact Match software using JCPDS PDF-2 Data Base.

In case of electrochemical studies metal hydride electrodes are prepared from a powder fraction with particle sizes of 40-60 µm. The electrodes in the form of a tablet with a diameter of 10 mm and a thickness of 1 mm with a total weight of 0.5 g are prepared by cold pressing at a pressure of 25 MPa for 3 minutes. Three electrodes with a mass ratio of metal hydride material and carbonyl nickel 1:4, 1:3, 1:2 are manufactured. The prepared tablets are pressed between the nickel foam plates attached to the current collector.

Electrochemical measurements are carried out in a standard three-electrode cell with a 6M KOH solution as an electrolyte and Hg/HgO reference electrode. Commercially available Ni(OH)$_2$ with a larger capacity is used as the counter electrode. The experiments are carried out on a multichannel potentiostat R-20X8 from Electrochemical Instruments. Activation of the metal hydride electrodes includes 10 charge cycles performed at a current density of 100 mA/g for 4.5 hours and a subsequent discharge at the same current density to a cut-off potential -0.65 V. The relaxation time between the charge and the electrode discharge is 0.5 hours. After activation, the high rate dischargeability performance of the electrodes is measured in the range of discharge current densities of 100 - 1200 mA/g. The electrode is charged at a current density of 100 mA/g for 4 hours.

3. Results and discussion

3.1. Structural characterization.

Analysis of XRD pattern of the La$_{0.6}$Ce$_{0.2}$Nd$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ alloy shows a high homogeneity of the obtained sample after annealing (Figure 1). Narrow diffraction peaks indicate a high degree of crystallinity of the sample. The crystal structure corresponds to the hexagonal CaCu$_5$ type with unit cell parameters: $a = 0.5013$ nm, $c = 0.4038$ nm.
3.2. Electrochemical activation performance

The activation process of metal hydride electrode sample 1:4 as example is shown in Figure 2. The charge curve can be divided into three areas. At the initial stage of the charge, the potential increases rapidly with a slight increase in the electrode capacity. This region corresponds to the formation of \( \alpha \)-solid solution in the metal hydride alloy. The second region with a practically unchanged equilibrium charge potential (plateau region) corresponds to the formation and saturation of the \( \beta \)-hydride phase. At the end of the process, a second plateau with a higher potential appears on the charging curve, where hydrogen is released at the electrode and corresponds to complete saturation of the metal hydride electrode. During the discharge process, the metal hydride releases hydrogen and transfers from the \( \beta \)-hydride phase to \( \alpha \) phase.

As the metal hydride electrode is fully activated, the equilibrium potentials of the charge and discharge decrease and increase, respectively, thereby reducing the hysteresis value. This effect is also characterized for gas phase activation of metal hydride powders [14, 15].
As shown in Figure 3, the samples reach the maximum discharge capacity at the second or third cycle. Sample 1:2 is characterized by a certain decrease in discharge capacity during cyclic activation from 308 mAh/g (2nd cycle) to 291 mAh/g (10th cycle), which is likely because of metal hydride particle decrepitation and precipitation on the bottom of the electrochemical cell. It is well known that AB_5 type alloys are characterized by a significant change (up to 20–25%) of the unit cell volume during hydrogen sorption – desorption [16, 17]. The contact area of active species increases with an increase of particle content, which leads to an improvement in the kinetics of the proceeding processes. At the same time, internal stresses arising from the expansion of particles lead to the gradual destruction of the electrode and the precipitation of metal hydride particles. In this case, carbonyl nickel serves not only as an electrically conductive additive and catalyst, but also as a medium for partial compensation of internal stresses of the metal hydride material. The highest discharge capacity at the 10th cycle is C_{max} = 320 mAh/g for a 1:4 sample. The equilibrium discharge capacity of the electrodes slightly decreases as the mass ratio of the metal hydride powder in the electrode increases (Figure 4).

![Figure 3. Activation performance of metal hydride electrodes](image1)

![Figure 4. Maximum discharge capacity of metal hydride electrodes.](image2)

An increase in the mass ratio of the active material to carbonyl nickel does not affect the equilibrium discharge potential, as shown in [9]. This discrepancy is possibly associated with the presentation on the same graph of discharge curves for different activation cycles. Figures 2 and 3 show that the maximum discharge capacity is achieved at the initial activation cycles, while the equilibrium discharge potentials increase and become constant only at the end of activation in the 7-8th cycle. Thus, the comparison of the discharge curves under the same conditions show no significant influence of the mass ratio of the components of the metal hydride electrode on the electrochemical properties.

3.3. High-rate dischargeability
High-rate dischargeability (HRD) of metal hydride electrode is one of the key characteristics for the development of Ni-MH batteries. HRD shows retention of discharge capacity during operation at high current densities.

Figure 5 shows discharge curves of sample 1:4 measured from 100 to 1200 mA/g. The electrochemical reaction in metal hydride electrodes is associated with the processes of mass transfer, charge transfer and hydrogen diffusion. Charge transfer on the catalytic surface and hydrogen diffusion in the bulk occur simultaneously and both processes are limiting the electrode reactions [1, 2].

At low current densities charge transfer, which determines the plateau width of the equilibrium potential, prevails over hydrogen diffusion. At high current densities, the rate-determining factor is
hydrogen diffusion from the bulk to the electrode surface. The maximum discharge capacity at 1200 mA/g is achieved by metal hydride sample 1:3. The discharge capacity reaches 277.2 mAh/g and corresponds to 87.9% of the initial capacity. Metal hydride sample 1:4 shows a significant drop in discharge capacity from 324.3 mAh/g at 300 mA/g to 256.8 mAh/g at 1200 mA/g (Figure 6). For cold-pressed electrodes, the optimum ratio of metal hydride material and carbonyl nickel is 1:3 due to the high discharge capacity and acceptable performance at high current densities. Currently, the most common electrodes for investigation of the electrochemical properties of metal hydride electrodes are prepared in mass ratio 1:3 [3-5] and 1:4 [6-8]. However, it should be noted the high stability of the 1:2 electrode, which retains 93.3% of the discharge capacity at 1200 mA/g can be perspective. Such a ratio of the active material and the conductive additive looks promising coupling with binders such as PTFE [9, 10], polyvinyl alcohol [11], which will improve the mechanical stability of metal hydride electrodes.

4. Conclusion
The electrochemical properties of metal hydride materials based on La$_{0.6}$Ce$_{0.2}$Nd$_{0.2}$Ni$_{4}$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ are studied for cold pressed electrodes at different mass ratios with conductive additive carbonyl nickel. In terms of activation performance, maximum discharge capacity and high-rate dischargeability the optimal ratio for cold-pressed electrodes is 1:3. Sample 1:3 shows high discharge capacity of 315 mAh/g at 100 mA/g and HRD at 1200 mA/g is not less than 87.9% of the initial discharge capacity. The use of electrodes with 1:2 ratio is promising in case of improving the mechanical stability of the electrodes.

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