TARGET COMPREHENSIVE PROGRAM SCIENTIFIC RESEARCH NAS of UKRAINE

Development of scientific principles of obtaining, storage and use of hydrogen in autonomous energy supply systems

CREATION OF MH ELECTRODES WITH A SPECIFIC COMPLEX OF TECHNOLOGICAL CHARACTERISTICS AND TESTING THEM FOR COMPATIBILITY AND EFFICIENCY OF FAROCHAN CHARGING IN PHOTOELECTROCHEMICAL (PEC) CELL

PROJECT № 11-19-21

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Goal of the work*- development of highly efficient hydrogen-absorbing materials for a reversible current source, which is charged using solar energy and discharged using oxygen (reversible photoelectrochemical MH - air cell).*

Objects of research: hydride-forming MH alloys: **$LaNi_{5-x}Mx$** (where M: Co, Mn, Al; x = 0.5-1.0); **$MmNi_{5-x-y-z}Co_xAl_yMnz$** type ABx (x = 4.8-5.1) and **$La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_x$** (x = 0; 0.7; 1.9) type ABx (x = 3.5-4, 6) , alloys type **AB_2** and electrodes based on them

Subjects of research: regularities of interaction of ABx type alloys (x = 3,5-5,1) with hydrogen in electrochemical process depending on structure, composition and manufacturing technology of alloys and electrodes.

Research methods: electrochemical methods: voltammetry, chronopotentio- and ampermetry using computerized potentiostat-galvanostat PGSTAT 4-16; physical methods: X-ray phase analysis.

To achieve this goal, the following studies were conducted

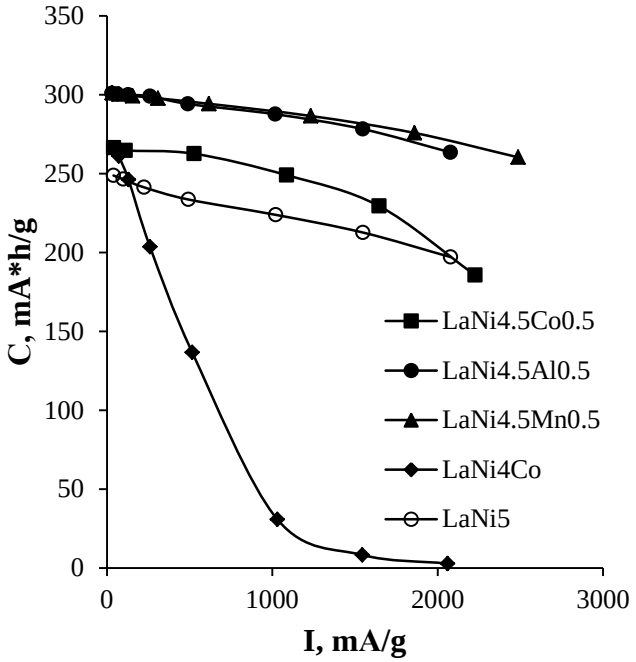
the complex of practically important characteristics (kinetics, maximum discharge capacity, Cmax., stability of hydrides) of 3-component alloys LaNi5-xMx (where M: Co, Mn, Al; x = 0,5-1,0) depending on the nature nickel substitute metal is investigated;

- the structure and phase composition of **$MmNi_{5-x-y-z}Co_xAl_yMn_z$** alloys of ABx type (x = 4.8-5.1) obtained by gas spraying, as well as electrochemical and sorption characteristics of electrodes from these alloys depending on the particle size of the alloy and preactivation were studied;
- the influence of stoichiometry and crystallization conditions on the structure, phase composition and basic electrochemical characteristics of ABx-type alloys (x = 3.5-4.6) of **$La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_x$** composition (x = 0; 0.7; 1.9) was investigated;
- the influence of the alloy composition on the ability of electrodes made of them to high-speed discharge was studied;
- Influence of the quantitative phase composition and various types of component composition on the electrochemical characteristics of the **ZrNiMnCrV** alloy

Investigation of the processes of reversible hydrogen absorption at the electrodes of $LaNi_{5-x}M_x$ alloys (M: Co, Mn, Al; x = 0.5-1.0)

Сплав	V, A^3	i_o, mA·s m^2	C_{max}, mA·h/g $^{-1}$	C_{2C}/C_{max}, %	$P_{eq.}$, бар
$LaNi_5$	86,5651	0,28	230 (6)**	67,4	2,45
$LaNi_{4.5}Co_{0.5}$	87,450	1,86	250 (5)	93,6	1,96
$LaNi_4Co$	87,6972	1,12	251 (4)	87,6	-
$LaNi_{3,9}Co_{0,7}$	88,3400	0,40	310(3)	90,3	0,50
$LaNi_{4.5}Al_{0.5}$	89,0466	3,16	299 (2)	66,7	0.47
$LaNi_{4.5}Mn_{0.5}$	88,1513	8,91	306 (1)	78,4	0.67

** - the number of the cycle to achieve maximum discharge capacity



It was found **that alloys of the type $LaNi_{5-x}M_x$, which contain Al and Mn, have good kinetic of reversible hydrogen absorption, have a high hydrogen capacity (about 300 mA * h /g), create stable hydrides, effectively absorb hydrogen at charge currents up to $2C_{.max}$ and capable of giving up to 90% hydrogen when discharged with currents up to 6 $C_{.max}$**

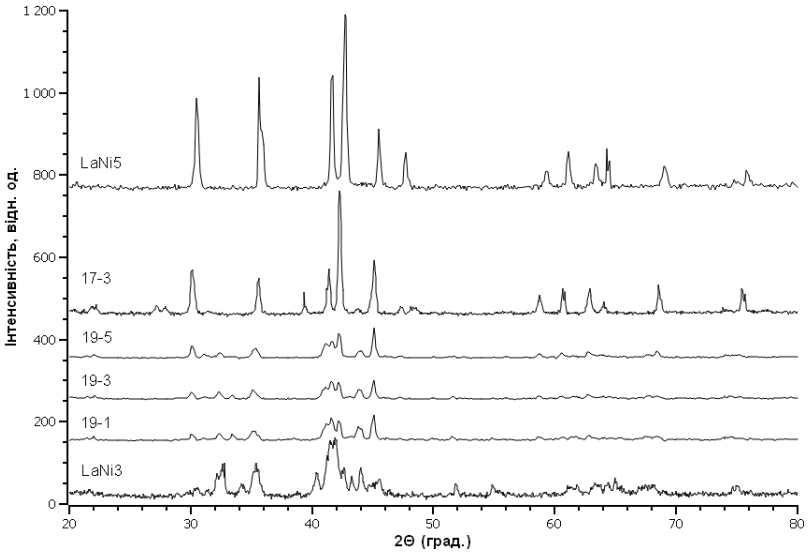
Increasing the cobalt content from 6.4 wt.% ($LaNi_{4,5}Co_{0,5}$) to 13,6 wt. % ($LaNi_4Co$) reduces the discharge efficiency with currents ≥1000 mA / g from 88% to 10%, respectively.

Electrochemical characteristics of electrodes from alloys of the Mm $(NiCoMnAl)_5$ type which were received by a method of gas spraying

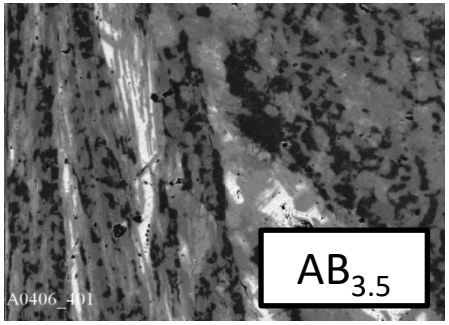
Alloys	V, A^3	b, mV	i_o, $mA \cdot cm^{-2}$	C_{max}, mA·h/г	$E_{eq.}/P_{eq.}$ V/bar
$MmNi_{3.6}Co_{0.7}Al_{0.4}Mn_{0.3}$-плав.	89,46	103	0,18	293	-0,921/0,82
$MmNi_{3.6}Co_{0.7}Al_{0.4}Mn_{0.3}$-GS	88,61	130	0,10	288	-0,921/0,82
$(Mm+La)Ni_{3.68}Co_{0.7}Al_{0.3}Mn_{0.4}Zr_{0,03}$ gas spraying (GS)	87,77	125	0,36/4,0	287	-0,895/0,28
$MmNi_{3,7}Fe_{0,7}Al_{0,5}Cu_{0,1}$-GS	88,28	0,11	0,15/1,0*	225	0,912/0,54

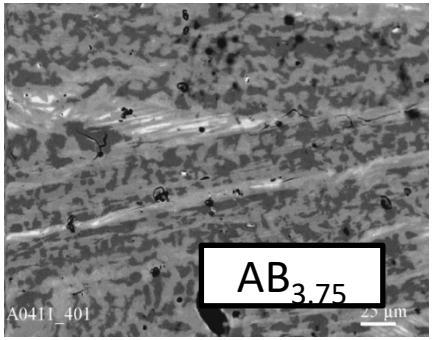
It is established that the process of hydrogen absorption on all investigated alloys is limited only by the electronic stage of charge transfer (b), and the discharge is limited by the process of hydrogen diffusion in the electrode. Alloys are easily activated (3-7 cycles) and create sustainable hydrides ($P_{eq.}$<1 bar). It is shown that the technology of obtaining alloys affects all electrochemical characteristics of the electrodes to a lesser extent than the nature of nickel-replacing metals. Complete replacement of Co by Fe leads to a decrease in the discharge capacity by 25%.

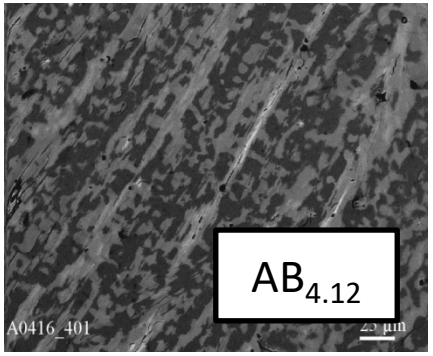
Structure and phase composition of $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}$ Co_x *(x=0;0,7; 1,9)* alloys type AB_x (x=3,5-4,6)

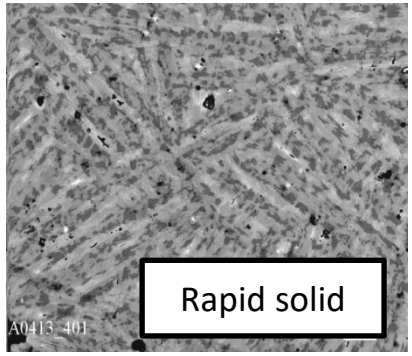


Radiographs of the studied alloys and intermetallics $LaNi_3$ and $LaNi_5$









***Structure**: main - two phases:*gray phase - AB_3 ($LaNi_3$, La_2Ni_7), lighter dark phase - $LaNi_5$, impurity white phase - heavy phase with higher La content (possibly La_2Ni_3). The study of the distribution of alloying elements (Co, Mn, Al) in alloys showed that the phases of type AB_3 do not contain these elements, and they are concentrated mainly in the dark phase of AB_5 type

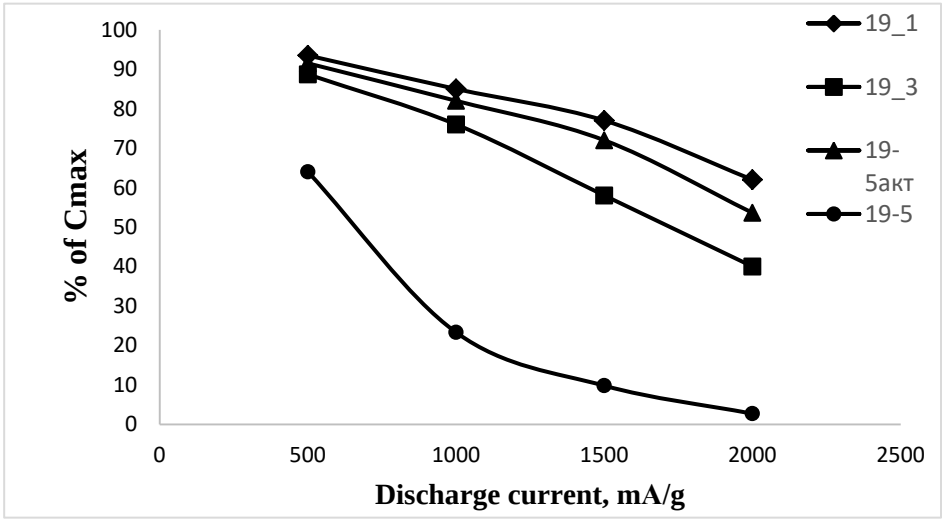
Structure, phase composition and electrochemical characteristics of electrodes made of $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_x$ alloys (x = 0, 0.7; 1.9)

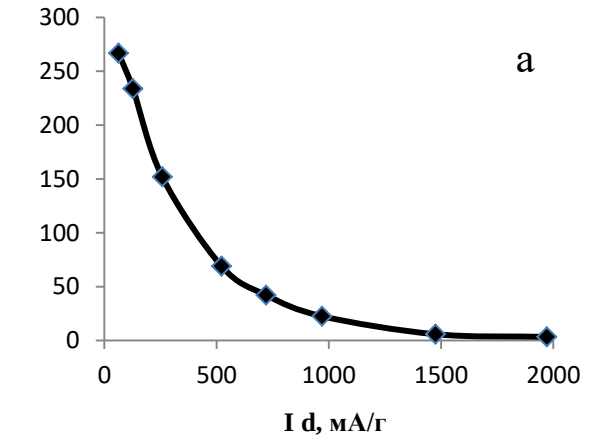
Alloys	Phases, Contents %	Cell volume,Å^3	I_{exheng}, mA/cm^2	$C_{max.}$, mA*h/g	$H_{eq.}$,V/ $P_{eq.}$, bar
19-1 ($AB_{3,5}$) $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}$	AB_3, 80,5 AB_5,19.5	561,49 88,86	2,09	165,0	-0,918/0,686
19-1T (scales) Artz melting+rapid solid	AB_3, 79,0 AB_5 21,0	559,29 88.23	1,56	193.0	-0,912/0,543
19-3 ($AB_{3,73}$) $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_{0,7}$	AB_3, 91,2 AB_5, 8,8	556,74 88,43	1,58	202.0	-0,940/1,16
19-3T (scales) Artz melting+rapid solid	AB_3, 65,1 AB_5, 34,9	558,63 88,52	2,82	207.0	-0,921/0,77
19-5 ($AB_{4,12}$) $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_{1,9}$	AB_3,40,0 AB_5,60,0	549,23 88,30	1.53	291,4	-0,915/0,61
19-5T (scales) Artz melting+rapid solid (spied 1000^o /c)	AB_3,40,9 AB_5,59,1	550,99 86,86	2,41	242.0	-0,925/0.91
17-3 ($AB_{4,6}$) $LaNi_{3,9}Co_{0,7}$	AB_5,98,0 AB_3, 2,0	88,34	2,34	305,0	-0,912/0,543

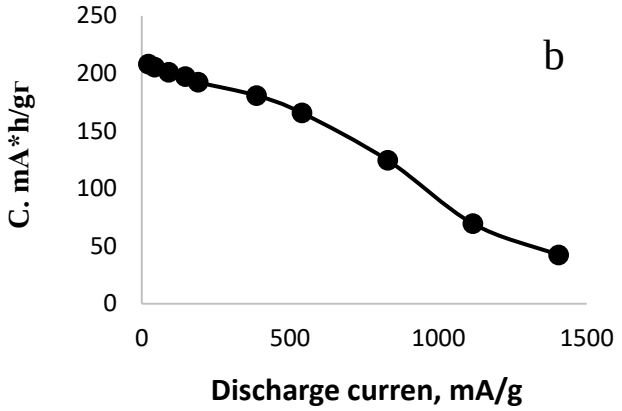
With an increase in the stoichiometric index ***x*** in alloys of the ABx type and a decrease in the content of the AB_3 phase in them, an increase in Cmax and the cyclic stability of MH electrodes is observed. Best performance are taken on electro-des with alloys **$AB_{4.12}$** and **$AB_{4.6}$**.

Thus, a change stoichiometric index x in ABx alloys can be used for optimizing the phase structure and and electrochemical characteristics of alloys for reversible hydrogen absorption.

Influence of the composition of hydrogen-absorbing alloys on the ability to high-speed discharge of electrodes made of them







With the growth of cobalt in the two-phases $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_x$ alloys, the efficiency of the discharge of electrodes with currents of 0.5-2.0 A/ g decreases. However, the activation of alloys (3-4 charge / discharge cycle I = 100 mA / g) increases the ability of the alloys to a high-speed discharge.

Behavior of electrodes from alloys (Mm + La) $Ni_{3.68}Co_{0.7}Al_{0.3}Mn0.4Zr_{0.03}$ (a) and $MmNi_{3.7}Fe_{0.7}Al_{0.5}Cu_{0.1}$ (b) under deep discharge conditions

METHODS OF OBTAINING AND CHARACTERISTICS OF ANODES AND CATHODE WHEN WORKING IN A PAIR IN PEC CELL

Photo-anodes	Method of obtaining and subsequent processing of films
A1	Electrodeposition of CdSe , annealing - 530 ° C, activation
A4	Formation of NT-TiO2 layer, annealing. Electrodeposition of CdSe,annealing - 530 ° C, activation
A5	Grinding of CdSe. Spraying a suspension (CdSe + ZnCl2 - acetone). Annealing, activation.
K-cathod	A mixture of alloy powders (LaNi4.5Mn0.5 + $LaNi_{4.0}Al_{1.0}$) + Cu por, cold pressing.

Pair anode-cathode	Potentials, V				ΔE,V	Photo-current, мAsm^2
	Open circuit		After closing			
	$-E_{an}$, V	$-E_{kat}$, V	$-E_{an}$, V	$-E_{kat}$, V		
A3-K	1.013	0.847	1.00	0.910	0.09	1.3
A4-K	1.09	0.85	0.955	0.925	0.03	2.86
A5-K	1,12	0,83	0,965	0,930	0,035	3,35

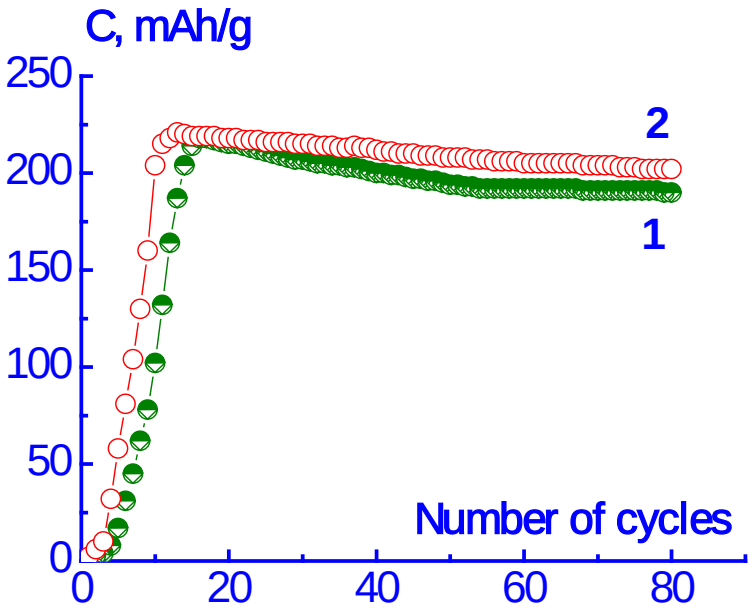
Measurements of the discharge capacity of the cathodes after charging **in the PEC cell showed that 95-100% of the current generated under the action of light at the anodes is spent on the formation and accumulation of hydrogen by the cathodes.** It was found that when the A5-K cathode - photoanode pair operates, the most optimal mode of cathode charging with hydrogen accumulation under the influence of light is realized.

Influence of the quantitative phase composition and various types of component composition on the electrochemical characteristics of the ZrNiMnCrV alloy

Large phase storage of surface alloy $ZrNi_{1,2}Mn_{0,5}Cr_{0,2}V_{0,1}$

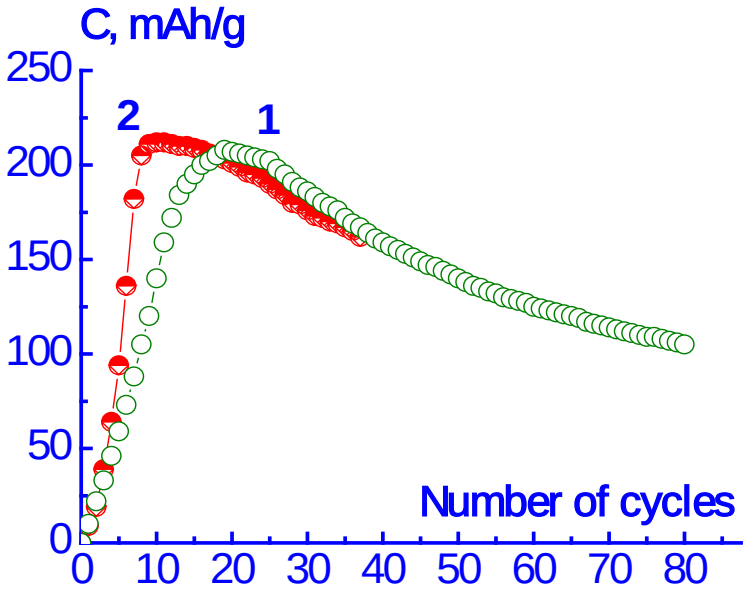
Phase (vol. %)	Sample № 1 (5 g)		Sample № 2 (40 g)	
	Exposition on air, days			
	0	2	0	2
C15	66,1	65,3	58,0	62,1
C14	22,5	23,6	20,6	16,7
Zr_7Ni_{10}	2,1	1,8	14,4	13,2
Zr_9Ni_{11}	9,4	9,3	7,0	8,0

By means of the X-ray phase analysis, it was found that when the $ZrNi_{1,2}Mn_{0,5}Cr_{0,2}V_{0,1}$ alloy is exposed to air in the form of a powder, different stability of the quantitative phase composition of its surface is observed, which depends on the sample size. When exposed to air for 2 days, in the case of a sample with a smaller mass (5 g), its certain stability was observed (fluctuations in the quantitative phase composition within 1%), and with a larger mass (40 g), polymorphism of the C15 and C14 phases was observed (the amount of phase C15 increases by 4% and the amount of phase C14 decreases by the same amount). The sample, which is more stable when exposed to air for 2 days, demonstrates greater cyclic stability during hydrogenation-dehydrogenation.



Electrodes from a sample weighing 5 g

Cathode nickel and : ferromanganese (curve 1), electrolytic manganese (curve 2)



Electrodes from a sample weighing 40 g

Cathode nickel and ferromanganese (curve 1), electrolytic nickel and electrolytic manganese (curve 2)

The activation of electrodes pressed from freshly made powders of the $ZrNi_{1,2}Mn_{0,5}Cr_{0,2}V_{0,1}$ alloy depends on the type of nickel and manganese and occurs at different rates, the cyclic stability - primarily depends on the size of the sample.

The study of alloys of the LaMm (NiAlCoMn) x (x =3.5-5.1) type showed:

1. Alloys $La_3Ni_{9.7}Mn_{0.5}Al_{0.3}Co_x$ (x = 0; 0.7; 1.9) of the AB_x type (x = 3.5-4, 2) contain two main phases of the AB_3 and AB_5 types, the ratio of which changes: with an increase in the stoichiometric index x, the phase content type AB5 increases, which, apparently, is the reason for the increase in the value of the value of the maximum discharge capacity (Cmax) and cycle resistance. The best characteristics were shown by the $LaNi_{3.9}Co_{0.7}$ ($AB_{4.6}$) alloy (Cmax = 305 mA * h / g; cycle resistance - about 300 cycles, hydride resistance)**.**
2. Alloys Mm $(NiCoMnAl)_x$ (x = 4.8-5.1), obtained by the method of gas spraying, are single-phase (phase of the AB_5 type), practically do not differ in their characteristics from the fused alloys of their analogs. The alloys are easily activated (3-7 cycles), form stable hydrides, and have a high discharge capacity (about 290 mA · h / g)

3 Alloys (Mm + La)$Ni_{3.68}Co_{0.7}Al_{0.3}Mn_{0.4}Zr_{0.03}$ ($AB_{5.1}$) and $LaNi_{3.9}Co_{0.7}$ ($AB_{4.6}$) in terms of their complex of electrochemical characteristics are of practical interest as hydrogen-absorbing cathode materials for a PEC cell.

4 It was found that with an increase in the cobalt content in both the two- and single-phase investigated alloys, the ability to high-speed discharge (currents> 500 mA / g) of electrodes sharply decreases.

5 It is shown that 95-100% of the photocurrent generated at the anode under the action of light is spent on the formation and accumulation in the form of metal hydride at the cathode.

6 The activation of electrodes pressed from freshly made powders of the $ZrNi_{1,2}Mn_{0,5}Cr_{0,2}V_{0,1}$ alloy depends on the type of nickel and manganese and occurs at different rates, the cyclic stability - primarily depends on the cooling conditions of the ingot (its size)/