PHOTOELECTROCHEMICAL CELL FOR HYDROGEN ACCUMULATION: THE CATHODES CHARACTERISTICS

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Introduction

At present, works on hydrogen production by the method of photoelectrochemical decomposition of water under the action of sunlight are being performed in many developed countries. These investigations are predominantly focused on the search for optimal materials and designs of cells with the aim to provide their efficient long operation and an acceptable cost. Earlier the authors of the work showed the possibility of using a photoelectrochemical (PEC) system including a GaAs photoanode, absorbing visible light, and a cathode intended for hydrogen accumulation and made from $LaNi_{5-x-y}Co_xAl_y$ type intermetallic compounds, absorbing hydrogen with the formation of hydrides [1]. The main aim of the work performed by the authors is to elaborate scientific and practical fundamentals of the attainment of the efficient charge of a metal hydride cathode operating in pair with a photoanode in a PEC cell. To realize this, a complex investigation of all processes responsible for the efficiency of alloys absorbing hydrogen under conditions of their use as cathodes in PEC cells and of the influences of the structure, alloying, and the surface state on these processes was performed.

Results and Discussion

The electrochemical behavior of microelectrodes of two compositions, namely $LaNi_{4.5}Mn_{0.5}$ + $LaNi_{4.0}Al_{1.0}$ (electrode No. 1) and $MmNi_{3.5}Co_{0.7}Al_{0.8}$ + $LaNi_{4.0}Al_{1.0}$ (electrode No. 2), with the equimolar contents of the components in mixtures was investigated. For operation in the PEC cell, microcathodes were made from a powder mixture of a hydrogen-sorbing alloy (≤0.03 g) and Cu powder (0.09 g), which were pressed in the form of pellets with a diameter of 6 mm in nickel mesh.

Results of the investigation of the electrochemical and sorption properties of the electrodes are presented in Table 1.

Table 1.

Electrodes	№ cycle	$E_{M/MH}$/ $E_{MH/M}$, V	$I_{-0.98V}$, mA/cm^2	$C_{pfзp.}$, мА×ч/г
№1	initial	-0,910/ -0,885	-4,1	-
	1		-12,0	150
	2		-33,3	250
№2	initial	0,850/- 0,910	5,0	-
	1		-	143
	2		9,4	177
	4			209

An investigation of the kinetics of the cathodic process on both electrodes showed that the catalytic activity of the surface substantially increased in the process of cycling of the electrode, specifically, the overpotential of the process decreased, currents in the region of potentials of maximum photocurrent yield in the PEC ($E_{-0,98}$ = –0.98 V) increased almost by an order on electrode No. 1 and slightly less on electrode No. 2 (Table 1). It is seen that the cathodic reaction on electrode No. 1 is limited by the rate of the process on the $LaNi_{4.5}Mn_{0.5}$ alloy (Fig. 1).

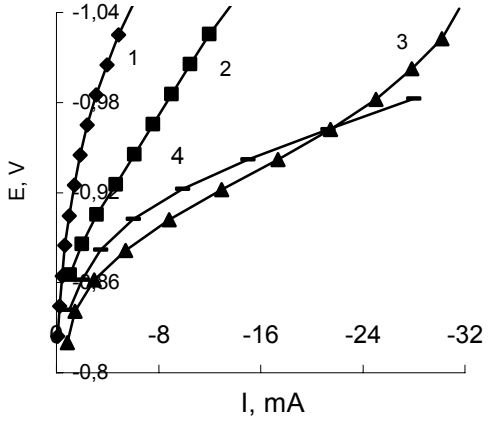

Fig.1. The kinetics of the cathodic process on electrode No. 1 and in the $LaNi_{4.5}Mn_{0.5}$ alloy:
1,2,3 – electrode No. 1; 1 – initial surface; 2 – after the first and 3 – after the second cycle.

The equilibrium and discharge curves of these electrodes have one plateau (not two plateaus), despite the substantial difference in the values of the equilibrium potentials of formation ($E_{M/MH}$) and decomposition ($E_{MH/M}$) of hydrides entering in the mixture of intermetallic compounds [2]. An investigation of the behavior of the electrode under the equilibrium conditions of polarization showed that, for both electrodes, the value of $E_{M/MH}$ is closer to the values of $E_{M/MH}$ for the alloys $LaNi_{4.5}Mn_{0.5}$ (–0.92V) and $MmNi_{3.5}Co_{0.7}Al_{0.8}$ (–0.90V), since, for the alloy $LaNi_{4.0}Al_{1.0}$, the value of this quantity is more positive by ~60 mV (–0.85 V) [2].

An investigation of the sorption capacity of the electrodes showed that both electrodes revealed an insignificant discharge capacity in the first cycle. For electrode No. 1, the sorption capacity increases abruptly in the next cycle. In the subsequent charge/discharge cycles, electrode No. 2 absorbed a much smaller amount of hydrogen, and, even in the fourth cycle its discharge capacity was smaller by 20–25% than that for electrode No. 1 (Table 1).

Thus, the ($LaNi_{4.5}Mn_{0.5}$ + $LaNi_{4.0}Al_{1.0}$) composite electrode has some advantages over the ($MmNi_{3.5}Co_{0.7}Al_{0.8}$ + $LaNi_{4.0}Al_{1.0}$) electrode. Specifically, it is activated more readily, has better kinetic and sorption properties. This is why the behavior of the electrode of this composition (K) was investigated in operation in pair with a CdSe photoanode in the PEC cell under real lightening conditions (Crimea) (Table 2).

The design of the cell developed by the authors made it possible to control the values of photocurrent, potentials of the photoanode and cathode in the process of photocharge of the cathode and perform its subsequent discharge directly in the cell.

As photoanodes, we investigated CdSe films with a thickness of 1 to 2 μm deposited on a titanium foil by the electrochemical method (the thickness of the film increases in the order A1<A2<A3).

Table 2. The results of investigation into PEC cell.

Anode-cathode	τ, min	ΔE, V	**Q**mA×h	
			$Q_{зар.}$	$Q_{раз.}$
A1-K	420	0.189	5.9	5.75
A7-K	240	0.166	3.3	3.30
A3-K	300	0.265	5.85	4.1*

* - current discharge - 100 mA/g and in other experiments - 50 mA/g.

It was established that, in the process of hydrogen accumulation by a cathode in the PEC cell, the cathode potential shifted in the cathodic direction, and the value of the shift depended on the type of the used anode. The values of photocurrents generated in the operation of the PEC cell, the character of their changes in the process of operation, and the cell potential differed for the anodes of the investigated compositions used in pair with the investigated cathode and depended on the intensity of the light flux.

Conclusions

A complex investigation of composite cathodes which consist of a mixture of the alloys, namely ($LaNi_{4.5}Mn_{0.5}$ + $LaNi_4Al$) and ($MmNi_{3.5}Co_{0.7}Al_{0.8}$ + $LaNi_4Al$), and are intended for a PEC cell was carried out. In was established that an electrode which, besides $LaNi_4Al$, contained the alloy $LaNi_{4.5}Mn_{0.5}$ was activated more readily, had better kinetic characteristics during charging and absorbed hydrogen in quantities larger by 20–25%. The possibility to accumulate hydrogen by the cathode ($LaNi_{4.5}Mn_{0.5}$ + $LaNi_4Al$) in the PEC cell with a narrow-zone photoanode (CdSe) under conditions of real solar illumination was shown. The discharge capacity of cathodes charged in the PEC cell attained 240 mA×h/g.

References

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