

METAL HYDRIDES USE FOR SOLAR ENERGY ACCUMULATION

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Introduction

The solar-to-hydrogen conversion by photoelectrochemical method of water splitting under the action of sunlight is the perspective method for solar energy accumulation [1]. The difficulty lies in the nature of the process: the water splitting energy (1.23 eV per electron) and additional losses associated with electrode overpotentials are too large compared with the quantum energy of the bigger part of sunlight spectrum. In our work it is proposed to change the reaction of hydrogen releasing at a Pt cathode by the hydrogen accumulation reaction in the metal hydride (MeH) cathode. It is assumed that this reaction would go under lower voltage that permits increase the solar-to-hydrogen efficiency. Moreover, using MeH permits obtain hydrogen in suitable technological form at once. This idea was proposed in literature now [2]. But the choice of photoanode SrTiO₃ with wide bandgap ($E_g=3.2$ eV) does not permit use MeH advantages for increasing conversion efficiency. So narrow bandgap photoanode as GaAs ($E_g=1.42$ eV) was chosen in our work. Moreover, we tried to determine MeH are the most appropriate for this application and their parameters are important in this case.

Experimental

The intermetallic alloys LaNi_{5-x}Co_x, where $0 \leq x \leq 2.5$, were selected for investigation as cathodes. The work consists of three parts: calorimetric, electrochemical and photoelectrochemical investigations. The integral enthalpy of hydrogen desorption was determined in calorimetric experiments. The calorimeter modernized IT-s-400 was used.

The samples for electrochemical investigations were prepared by pressing of the alloys powder on Ni net at 125 kg/cm². The cathodes look as tablets with 8 mm diameter and 1 mm thickness. The equilibrium potential (E_o), discharge capacity ($C_{dis.}$) and exchange current (I_o) were determined for the MeH electrodes at electrochemical investigations. The measurements were carried out with P5848 potentiostat in the three-electrodes cell with Pt counter electrode and Hg/HgO/6M KOH

reference electrode under room temperature. The electrodes were charged by current 100 mA/g and discharged by 50 mA/g.

A single-crystal GaAs was used as the photoanode at photoelectrochemical experiments. The measurements were carried out in the cell with quartz window and Ag/AgCl electrode as the reference. The cathode's and the anode's areas of cell were separated by ion-exchange membrane. The photoanode was placed in polysulphide electrolyte and cathode – in 30 % KOH solution. The spectral characteristics of photoelectrochemical current were measured at experimental setup described in the work [3]. The accumulation of hydrogen was investigated under radiation flux 75 mW/cm².

Results and discussion

The thermograms of hydrogen desorption from MeH show several hydride phases for each sample and main maximum shift to higher temperatures with increasing Co contents (Fig. 1).

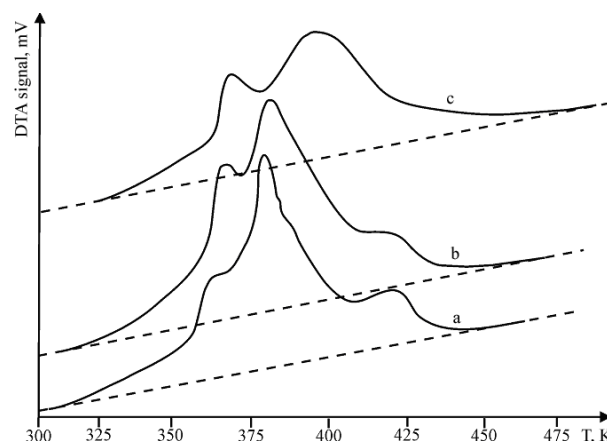


Fig. 1. The thermograms of hydrogen desorption: a - LaNi_{3.5}Co_{1.5}H_{6.77}; b - LaNi_{3.0}Co_{2.0}H_{6.68}; c - LaNi_{2.5}Co_{2.5}H_{6.55}

The results of calorimetric investigations are represented in Tab. 1. As it is clear from Tab.1, the enthalpy, $H_{des.}$ increases with increasing Co contents. The results of electrochemical investigations are represented in Tab.1 too.

The data show the anodic shift of equilibrium potential, E with increasing Co contents with agreement of H_{des} shift. The rate of selfdischarge decreases under this conditions. The electrodes with bigger Co contents (2 and 2.5 at. %) had discharge capacity 2-2.5 times bigger than $LaNi_5$ after 24 h open circuit exposure (Tab.1). The current-voltage curves show variation of hydrogen releasing kinetic: the cathode process is accelerated and goes at lower overpotential with increasing Co contents. The exchange current, I_0 was increased too.

Tab. 1.

Materials	Hdes. kJ/mole H ₂	E, V	Cdis. mAh/g	I_0 , A/cm ²
$LaNi_5$	31.6	-0.985	80	
$LaNi_4Co$	32.7	-0.951	133	7.4×10^{-4}
$LaNi_3Co_2$	36.0	-0.952	198	2.5×10^{-3}
$LaNi_{2.5}Co_{2.5}$	37.3	-0.940		

The photopotential of GaAs electrode, E_f has to be -1.1÷-1.2 V regards to Ag/AgCl electrode for effective charging under maximum power output. At the same time E_f had value -0.8÷-0.9 V that was not sufficient for MeH charging. The E_f is increased by 0.25÷0.3 V after Pt nanoparticles deposition on GaAs surface that leads to near optimum charge regime. The Pt film on GaAs surface was investigated by Auger-spectroscopy and Transition electron microscopy methods [4]. The variety of Pt nanoparticles size from several nm to several tens nm was established. The results obtained are discussed in the frame of the theory of photoexcited charge transfer in semiconductor-electrolyte system [5].

The efficiency 13-15 % for solar-to-current conversion was obtained. The MeH samples with bigger anodic potential and bigger enthalpy were charged more effective. The efficiency of

hydrogen accumulation was estimated from discharge/charge capacity relation and from hydrogen volume released under cathodes heating [6]. Both methods gave results in good agreement: from 50 to 80 % for discharge/charge capacity relation. It corresponds to the efficiency of solar-to-hydrogen conversion 6-12 %. This result is comparable with the best world results in this field [7].

Conclusions

The work shows promise for MeH use for solar energy conversion. The use of MeH permits to increase the conversion efficiency considerably. The MeH alloys with bigger anodic potential and bigger enthalpy are more perspective.

References

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