## PRODUCTION AND USE
## OF NEW MATERIALS

# New Materials for Sorption of Hydrogen

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**Abstract**—The influence of temperature, duration of thermal treatment, and oxidation modes of the aluminum base on processes in which intermetallic compounds LiLaAl are formed by the method of electrochemical cathodic intercalation was studied. The optimal modes of formation of $LiLaAl_{ox}$ compounds exhibiting high sorption capacity for hydrogen were determined.

Hydrogen is a versatile and environmentally clean kind of fuel. One of the most important tasks of hydrogen power engineering is the development of efficient systems for hydrogen storage, because none of the existing systems for hydrogen storage under high pressure, in absorbed state at low temperature, in liquid state, and in the form of metal hydrides and intermetallic compounds satisfies the requirements to $H_2$ accumulators. In the case of mobile storage systems, the mass content of $H_2$ should be no less than 6.5 wt %, and the volume content, no less than 63 kg m$^{-3}$ [1, 2]. According to the regulations by the International Energy Agency, an $H_2$ accumulator should contain no less than 5 wt % $H_2$ and release it at a temperature not higher than 373 K [1–3].

One of the most promising and presently widely studied ways to solve the above-mentioned problem is accumulation of $H_2$ by metals and alloys, based on reversible sorption of hydrogen.

The interaction of $H_2$ with metals or alloys commonly involves the following processes: physical adsorption on the surface, activated absorption in the bulk, diffusion, migration, and molecular absorption (occlusion), to form hydrides [2–10]. The nature of a metal or an alloy and presence of defects in their structure strongly affect the mechanism by which $H_2$ interacts with the base. Diffusion, or mass transfer, commonly leads to formation of interstitial or substitution solid solutions. The key factor in the sorption process is the defectiveness of the crystal lattice and existence of hydrogen dissolved in it in the form of protons [5–8]. The solubility of $H_2$ and its sorption by various matrices are affected by such factors as pressure, mechanical treatment of the surface, grain size of the metal, presence of impurity compounds on the metal surface, pH value of the solution, and electro-

lyte composition [1, 4–13]. Thus, the surface and volume properties of a material that sorbs $H_2$ and the number of defects (vacant places for hydrogen atoms) can be changed by means of various physicochemical or electrochemical methods.

The aim of this study was to examine the possibility of using the method of cathodic intercalation to obtain reversible $H_2$ sorbents based on lithium–aluminum–lanthanum (LiAlLa) alloys.

## EXPERIMENTAL

Aluminum foil (A 99.95) was conditioned with synthetic corundum of M-28 brand, twice washed with double-distilled water, and dried. Then, electrodes with a geometric working surface area of 1 cm$^2$ were subjected to a 30-min preliminary thermal treatment ($Al_{th}$; $T_{tr}$ = 200–500°C, step 50°C). After that, lanthanum was introduced into the $Al_{th}$ matrix by cathodic intercalation from a 0.03 M solution of lanthanum sulfanilate in dimethylformamide (DMF) at the cathodic polarization potential $E_{cp}$ = –2.7 V for 1 h. Then, lithium was introduced into the resulting $LaAl_{th}$ alloy from a 1 M solution of $LiClO_4$ in a mixture of propylene carbonate (PC) and dimethoxyethane (DME) taken in a 1 : 1 volume ratio at $E_{cp}$ = –2.9 V for 1 h. $LiLaAl_{th}$ phases with the highest energy storage capacity are obtained after thermal treatment of the Al base at 400°C. In the next stage, the duration of the thermal treatment was varied: the starting Al samples were treated at 400°C for 15–120 min (step 15 min), and then $Al_{th}$ samples were treated in nonaqueous solutions of La and Li salts as described above. In another set of experiments, the starting Al or $Al_{th}$ was preliminarily oxidized, in order to "develop" the electrode surface, in a
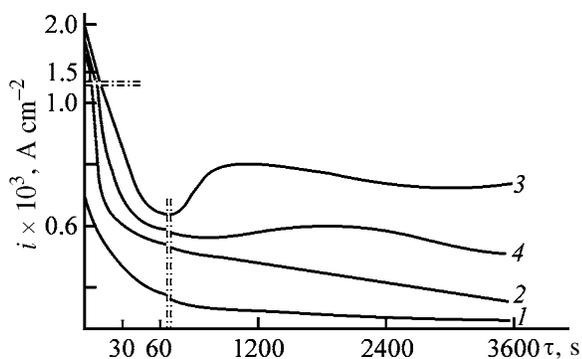
**Fig. 1.** Potentiostatic curves of cathodic intercalation of La into aluminum matrices from a 0.03 M solution of lanthanum sulfanilate in DMF. $E_{cp} = -2.7$ V (relative to a non-aqueous silver chloride electrode), 20°C. (*i*) Current density and (*τ*) time; the same for Figs. 2–5. Matrix: (*1*) Al, (*2*) Al$_{th}$, (*3*) Al$_{ox}$, and (*4*) (Al$_{th}$)$_{ox}$.

mixture of acids (g l$^{-1}$): sulfuric 150, oxalic 30, citric 30, and nicotinic 10, at anode current densities $i_a = 10$–50 mA cm$^{-2}$ (step 10 mA cm$^{-2}$) and oxidation time $t_{ox} = 10$–60 min (step 10 min). As counter electrodes in oxidation served lead plates ($S = 10$ cm$^2$). Al plates ($S = 10$ cm$^2$) were used in cathodic intercalation of La and Li. As reference electrode was used nonaqueous silver chloride electrode fabricated from an EVL-1 standard silver chloride electrode, placed in a working electrolyte solution, 1 M LiClO$_4$ in PC + DME (1 : 1). LiCl crystals were introduced into the electrolyte in order to eliminate the diffusion potential. The potential of the nonaqueous silver chloride electrode at 20°C is $-0.06$ V vs. standard silver chloride electrode, 0.163 V vs. hydrogen electrode, and 3.05 V vs. lithium electrode in the working electrolyte solution. In measurements in DMF-based solutions, an intermediate vessel with the working solution was used. The silver chloride electrode Ag$^+$/Ag is reversible and stable in the aprotic solvents used in the

**Table 1.** Diffusion-kinetic characteristics of intercalation of La into Al matrices and Li into Al–La matrices

| Electrode | $K_i \times 10^4$, A s$^{1/2}$ cm$^{-2}$ | $c^0 D^{1/2} \times 10^{-9}$, mol cm$^{-2}$ s$^{-1/2}$ |
|---|---|---|
| LaAl | 1.3 | 2.4 |
| LaAl$_{th}$ | 2.7 | 4.9 |
| LaAl$_{ox}$ | 3.4 | 6.2 |
| La(Al$_{th}$)$_{ox}$ | 5.2 | 9.5 |
| LiLaAl | 4.3 | 7.9 |
| LiLaAl$_{th}$ | 7.6 | 13.9 |
| LiLaAl$_{ox}$ | 9.7 | 17.8 |
| LiLa(Al$_{th}$)$_{ox}$ | 1.1 | 2.0 |

study [14]. In studying the sorption of H$_2$ by the formed LiLaAl, LiLaAl$_{ox}$, and LiLa(Al$_{th}$)$_{ox}$, HCl and HClO$_4$ solutions with concentrations of 0.375, 0.750, 1.500, and 2.000 wt % were used. The sorption was performed at potentials $E_{cp}$ from $-1.0$ to $-2.2$ V (step 0.1 V) in the course of 1 h. All the measurements in this study were carried out at 20°C on a P-5848 potentiostat with a KSP-4 recorder. The diffusion-kinetic parameters of the process were determined using the potentiostatic method. The initial portions of current decay in curves plotted in the coordinates $i$–$1/\tau^{1/2}$ were analyzed in terms of the Cottrell equation [15] for solid-state diffusion in thin films

$$K_i = \Delta i / \Delta(1/t^{1/2}) = zFc^*D^{1/2}/\pi^{1/2},$$

where $K_i$ is the diffusion-kinetic parameter of intercalation (A s$^{1/2}$ cm$^{-2}$); $i$, current density (A cm$^{-2}$), $F = 96\,485$ C mol$^{-1}$, Faraday number; and $D$, diffusion coefficient (cm$^2$ s$^{1/2}$).

An oxide film with a structure that is looser than the natural structure can be formed on the surface of Al (A 99.95) by selecting the temperature (200–500°C) and time (15–120 min) of thermal treatment. It was found that the optimal mode is mode I: $T_{tr} = 400$°C and $\tau_{tr} = 60$ min. Similarly, the optimal mode in the case of anodic oxidation in a mixture of acids (g l$^{-1}$): sulfuric 150, oxalic 30, citric 30, and nicotinic 10 is mode II: anode current density $i_a = 20$ mA cm$^{-2}$, $\tau_{ox} = 20$ min (Fig. 1). Under the chosen conditions of thermal treatment and oxidation, the oxide film on the surface of Al has such properties and structure which, as shown previously [16, 17], favor introduction of La into the Al electrode from a lanthanum sulfanilate solution. Upon the introduction of lanthanum at $E_{cp} = -2.7$ V and $\tau_{cp} = 60$ min, the negative potential of the formed electrode (Al$_{th}$)$_{ox}$La was about $-2.0$ V. The calculated diffusion-kinetic parameters of the processes of successive introduction of La and Li into the starting Al and aluminum and lanthanum–aluminum bases preliminarily formed in modes I and II are listed in Table 1.

Upon introduction of lithium into La(Al$_{th}$)$_{ox}$ electrodes from a 1 M solution of LiCl in PC + DME (1 : 1) in the potentiostatic mode (Fig. 2), a classical curve of cathodic intercalation was obtained [18–20]. Incorporation of La and Li atoms into the structure of thermally treated and oxidized Al (Figs. 1, 2) leads to successive distortion of the initial crystal lattice of Al and to formation of additional vacancies and structural defects and zones with increased diffusion rate.

This must facilitate sorption of $H_2$ and its accommodation at the forming vacant sites. The study demonstrated that the best parameters of the processes are achieved for the $LiLaAl_{ox}$ electrode (Figs. 1, 2; Table 1).

The quantitative and qualitative pattern of the process of $H_2$ sorption by preliminarily formed $LiLaAl_{ox}$ electrodes depends on the nature of a hydrogen-containing agent (HCl and $HClO_4$), its concentration, and cathodic polarization potential $E_{cp}$ (Figs. 3, 4).

According to Smith's classification [1, 3], all metals can be divided into three groups by their relation to hydrogen: the first comprises metals, including Li, that form with $H_2$ saltlike hydrides; the second, metals that form with $H_2$ chemical compounds with covalent bonding, covalent hydrides (Al); and the third, endo- and exothermic absorbers of hydrogen and, in particular, La [3]. Thus, the metal components of the $LiLaAl_{ox}$ alloy under study belong to different groups and, therefore, the variety of alloys formed with $H_2$ may be exceedingly wide. In cathodic polarization of the $LiLaAl_{ox}$ electrode in HCl solutions of various concentrations at a potential $E_{cp} = -1.1$ V, the rate of discharge of $H^+$ ions grows 3–4-fold when the HCl concentration increases from 0.375 to 1.5 wt % (Fig. 3). Analysis of the influence exerted by the cathode potential on the sorption of $H_2$ by the $LiLaAl_{ox}$ alloy shows (Fig. 4) that a shift of the potential in the negative direction accelerates saturation of the electrode surface with discharged hydrogen atoms and makes shorter the critical time in which the first nuclei of a new phase are formed, when prerequisites for their growth and formation of a layer of this phase are created. At $E_{cp} = -1.1$ V, this critical time is not reached under the given experimental conditions; at $E_{cp} = -1.5$ V, it is as long as 300 s, and at $E_{cp} = -2.0$ V, as short as 10 s.

In the initial stage of the current decay, the dependence $i$–$1/\tau^{1/2}$ is represented by straight lines with a sharp bend, which make intercepts $i_\infty$ on the ordinate axis (Fig. 5). This may be due to parallel occurrence of two processes: introduction of $H^+$ ions into the oxide layer ($i_{ox}$) and intercalation of discharged hydrogen ions into the metal at the inner M⎪oxide interface ($i_M$). The resistance of the protonated oxide layer is so high that, at $E_{cp} = -1.1$ V, the electrode current remains constant during approximately 18 s. And only after that there appears a concentration gradient of hydrogen ions, $dc_{H^+}/dx$, that is sufficient for ensuring the diffusion of $H^+$ ions to the inner interface with the metal of the electrode, where the fol-
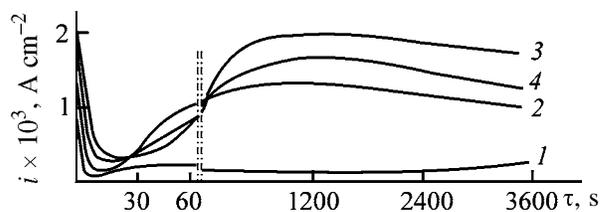


**Fig. 2.** Potentiostatic curves of cathodic intercalation of Li from a 1 M solution of $LiClO_4$ in PC + DME (1 : 1) into electrodes. $E_{cp} = -2.9$ V (relative to a nonaqueous silver chloride electrode), 20°C. Electrode: (1) LaAl, (2) $LaAl_{th}$, (3) $LaAl_{ox}$, and (4) $La(Al_{th})_{ox}$.
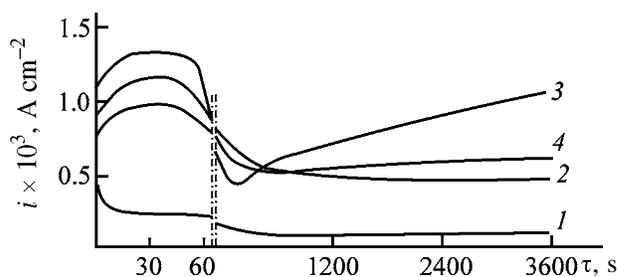


**Fig. 3.** Potentiostatic curves obtained in treatment of a $LiLaAl_{ox}$ electrode in HCl solutions at $E_{cp} = -1.1$ V. $c_{HCl}$ (wt %): (1) 0.375, (2) 0.5, (3) 1.5, and (4) 2.0.
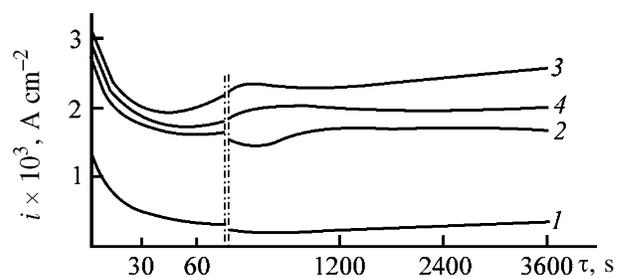


**Fig. 4.** Potentiostatic curves obtained in treatment of a $LiLaAl_{ox}$ electrode in a 1.5% HCl solution. Potential $E_{cp}$ (V): (1) 1.1, (2) 1.5, (3) 2.0, and (4) 2.2.
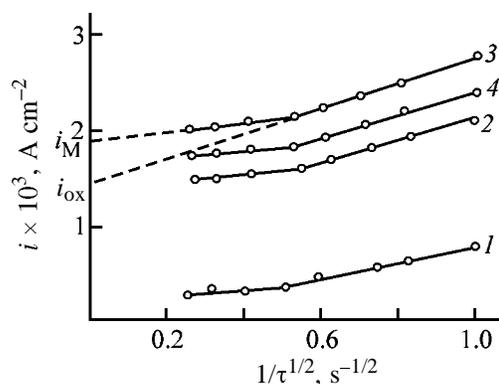


**Fig. 5.** $i$–$1/\tau^{1/2}$ dependence for a $LiLaAl_{ox}$ electrode (plotted using the data of Fig. 4).

**Table 2.** Constants of hydrogen sorption by LiLaAl$_{ox}$ electrode from a 1.5% HCl solution and $c^0D^{1/2}$ product at different cathodic polarization potentials

| $-E_{cp}$, V | $K_i \times 10^3$ (ox), A s$^{1/2}$ cm$^{-2}$ | $c^0D^{1/2} \times 10^8$ (ox), mol cm$^{-2}$ s$^{-1/2}$ | $K_i \times 10^3$ (M), A s$^{1/2}$ cm$^{-2}$ | $c^0D^{1/2} \times 10^8$ (M), mol cm$^{-2}$ s$^{-1/2}$ |
|---|---|---|---|---|
| 2.2 | 1.2 | 2.2 | 0.25 | 0.5 |
| 2.0 | 1.4 | 2.6 | 0.44 | 0.8 |
| 1.5 | 1.3 | 2.4 | 0.38 | 0.7 |
| 1.1 | 1.0 | 1.8 | 0.42 | 0.8 |

lowing exchange reactions are possible:

$$LiAl + xH^+ + xe = AlH_xLi_{1-x} + xLi$$

or

$$La + xH^+ + xe = LaH_x,$$

$$Li + xH^+ + xe = LiH_x.$$
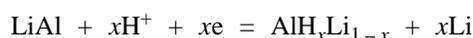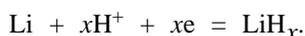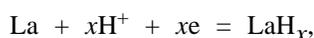
It was established experimentally that hydrogen is sorbed from HCl solutions at a higher rate. In the case of HClO$_4$, adsorption of ClO$_4^-$ anions on the alloy surface hinders introduction of H$^+$ ions into the structure of the electrode, and an additional energy is required for this process to begin. This is achieved, for example, at a significant shift of the cathodic polarization potential in the negative direction (to +0.05 V relative to Li$^+$/Li and –3.0 V relative to the nonaqueous silver chloride electrode).

Raising the concentration of HCl from 0.375 to 1.5 wt % makes the rate of hydrogen intercalation 3–4 times faster. In this case, the electrochemical parameters of the process depend on $E_{cp}$ (Table 2).

## CONCLUSIONS

(1) In the chosen modes of preliminary thermal treatment and oxidation, an oxide film whose properties and structure favor cathodic intercalation of La and Li into an aluminum electrode is formed on the Al surface.

(2) Introduction of lithium and lanthanum is accompanied by successive distortion of the crystal lattice by La and Li and formation of additional vacancies and structural defects and of zones with an increased diffusion rate. This facilitates the subsequent sorption of hydrogen and its accommodation in the structure of the LiLaAl alloys formed.

(3) Hydrogen sorption is affected by the solution concentration and nature (anionic composition) of a hydrogen-containing agent.

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