ELECTROCHEMICAL BEHAVIOR OF LEAD AND LEAD ALLOYS IN SULFURIC ACID SOLUTIONS SUBJECTED TO ULTRASOUNDS

C.D. Mateescu[1], I.V. Branzoi[2], A. Mateescu[3], F. Branzoi[4]

[1] National Institute for Materials Physics, Magurele, Ilfov, P.O. Box M.G.-7, Romania

[2] University "Politehnica" Bucharest, Splaiul Independentei 313, Romania

[3] MT ROM Trading SRL, Calea Plevnei 94, sect.1, Bucharest, Romania

[4] Institute of Physical Chemistry, Bucharest, Romania

Introduction

Lead-acid batteries represent the classical devices for energy storage. Though new generations of storage batteries are quickly developing, lead-acid batteries are still in use due to the advantages of low costs and long service life. Many studies are carried on in order to improve their electrical efficiency, to hinder the gases evolution that takes place at the electrodes, to limit the self discharge and to increase the number of cycles.

By changing the lead-antimony grid alloys with lead-calcium alloys, the auxiliary reactions (oxygen evolution at the positive plate and hydrogen evolution at the negative plate) were limited and an improved battery resulted, the maintenance free battery.

In the attempt to improve the electrical balance of the lead-acid batteries we experienced a method of electroforming the active masses in sulfuric acid solutions previously exposed in an ultrasonic field. The results proved that the ultrasonic field has a benefic influence upon the active masses.

In order to establish the influence of the ultrasonic field on the electrochemical behavior of lead and its alloys we carried studies of linear voltammetry and scanning microscopy on several lead electrodes immersed in sulfuric acid solutions exposed to ultrasonic field and compared the results with those registered for unexposed materials.

Experimental

Sulfuric acid solutions with specific gravity 1.28 gcm^{-3} were exposed in an ultrasonic field with the frequency of 25 kHz for several periods of time ranging from 3 to 20 minutes. The electric conductivity was measured immediately after removing the acid solutions from the ultrasonic field and from time to time for several days.

The electrochemical behavior of pure lead, lead antimony alloy with 1.8 % Sb and lead-calcium alloy with 0.08% Ca, in sulfuric acid solutions with the specific gravity of 1.28 g/cm^3, exposed for 12 minutes in ultrasonic field, was examined using linear cyclic voltammetry, by means of a 173 Potentiostat-Galvanostat Model (Princeton Applied Research) provided with a Digital Coulometer 179 Model. The potential scan rates were between 5 and 40 mVs^{-1}.

A single compartment electrochemical cell with the microelectrode to be studied in the middle, surrounded by a platinum gauze as counter electrode was used.

The electrodes surface was examined by scanning microscopy using a TEMSCAN 200CX Electron Microscope, after the voltammetric measurements.

Results and discussion

The electric conductivity of sulfuric acid solutions of specific gravity 1.28 g/cm^3, exposed in ultrasonic field for different periods of time, ranging from 3 to 20 minutes proved that the optimum time for exposure was 12 minutes. The maximum electric conductivity was registered after 2 days. After 5 days the electrolyte conductivity became stable. The temperature was 20 °C. The same electrolyte unexposed to ultrasounds had the electric conductivity of 345 mS/cm.

Table 1. *Conductivity variation of sulfuric acid solution with 1.28 g/cm^3 specific gravity exposed for 12 minutes in an ultrasonic field with the frequency of 25 kHz.*

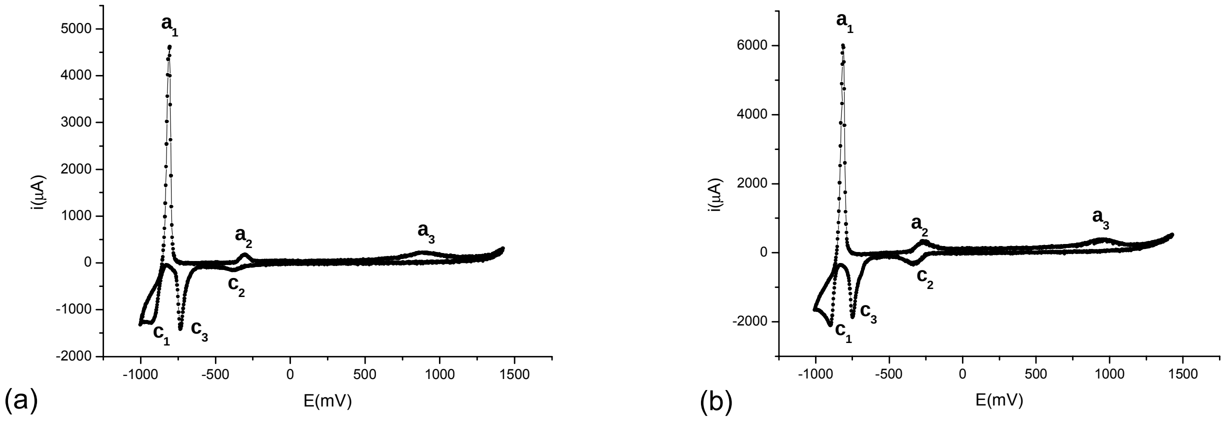
Time [days]	Immediately after exposure	1	2	5	7	9	12	15	18	21	25
Conductivity [mS/cm]	360	370	521	395	390	395	400	395	395	397	395

It is obvious that the exposure in the ultrasonic field leads to an increase of electric conductivity, explained by the increase of free ions in the electrolyte. It is interesting that this effect keeps in time.

Using the potentiodynamic method, the electrochemical redox behaviour of Pb/$PbSO_4$ system on the lead alloys electrodes in H_2SO_4 concentrated solutions was studied.

The potentiograms of several electrodes made of pure lead, lead antimony alloys and lead calcium alloys, immersed in normal sulphuric acid solution and in sulphuric acid solution subjected to ultrasounds were plotted in the potential range from –1200 mV to +1600 mV with the sweeping rate of 5 mVs^{-1} up to 40mV s^{-1}.

From figure 1, one can see that with increasing anodic polarization, first an insulating layer of $PbSO_4$, then a conductive layer of PbO_2 are successively formed on the electrode. In the PbO_2 potential domain different crystalline phases (α and β) can be formed [1-7], with possible existence of amorphous zones. When the oxidation proceeds through the porous $PbSO_4$ layer, the β – PbO_2 phase is formed at $PbSO_4$ / solution interface by a dissolution precipitation mechanism [2 – 4]. The α – PbO_2 layer has been shown to result from the oxidation of PbO in solid state. Then a PbO sublayer is covered by a non-stoichiometric PbO_n oxide whose stoichiometry coefficient n ($1<n<2$) progressively increases when approaching the oxide/solution interface. It has been also reported that the PbO_n layer conductivity increases with raising both n value and anodic polarization [1 – 7].



(a) (b)

Figure 1. The potentiograms of the lead alloy (Pb – Sb 1.8%) electrode in (a) sonnicated and (b) normal electrolyte (sulphuric acid solution of specific gravity 1.28 gcm^{-3}).

The voltammogram of lead alloy Pb + 1.8%Sb in H_2SO_4 solution of $\rho = 1.28$ gcm^{-3} shows during the positive going potential sweep a net well-defined anodic current peak (a_1) followed by a wide passive region and another anodic oxidation peaks (a_2) and (a_3) respectively.

During the reverse scan the potentiodynamic response exhibits three cathodic current peaks (c_1, c_2 and c_3). Conjugated current peaks a_1 and c_1 are related to the electroformation and electroreduction of $PbSO_4$.

The peaks a_2 and c_2 are related to the electroformation and electroreduction of antimony oxide, whereas the peak a_3 is related to the electroformation of PbO_2 with different crystalline phases (α and β). After this peak oxygen evolution takes place and the current increases sharply. The peak c_3 can be associated with the electroreduction of PbO and PbO_2 which build up underneath the initially grown $PbSO_4$ porous layer. The analysis of the potentiograms from figure 1 and the kinetic parameters from tables 2 and 3 pointed out that in sulphuric acid solutions previously exposed in an ultrasonic field, the obtained peak currents are higher and, generally, the anodic and cathodic currents are bigger and consequently, the anodic and cathodic processes are more intensified.

Table 2. *The kinetic parameters from potentiograms for lead alloys in sonnicated H_2SO_4 solutions (ρ = 1.28 gcm^{-3}) and in normal H_2SO_4 solutions (ρ = 1.28 gcm^{-3}) at a scan rate of 10mV/s and 25°C.*

Electrode	H_2SO_4 solution	Ipa_1 (mA)	Ipa_3 (mA)	Ipc_1 (mA)	Ipc_3 (mA)	Epa_1 (mV)	Epa_3 (mV)	Epc_1 (mV)	Epc_3 (mV)
Pb+1.8%Sb	Normal	4.66	0.17	1.27	1.4	-808	976	-933	-733
Pb+1.8%Sb	Sonnicated	5.97	0.35	2.06	1.86	-810	940	-900	-750
Pb+0.08%Ca	Normal	0.95	0.06	0.82	0.54	-808	1026	-958	-744
Pb+0.08%Ca	Sonnicated	1.79	0.15	1.38	1.55	-816	995	-888	-703

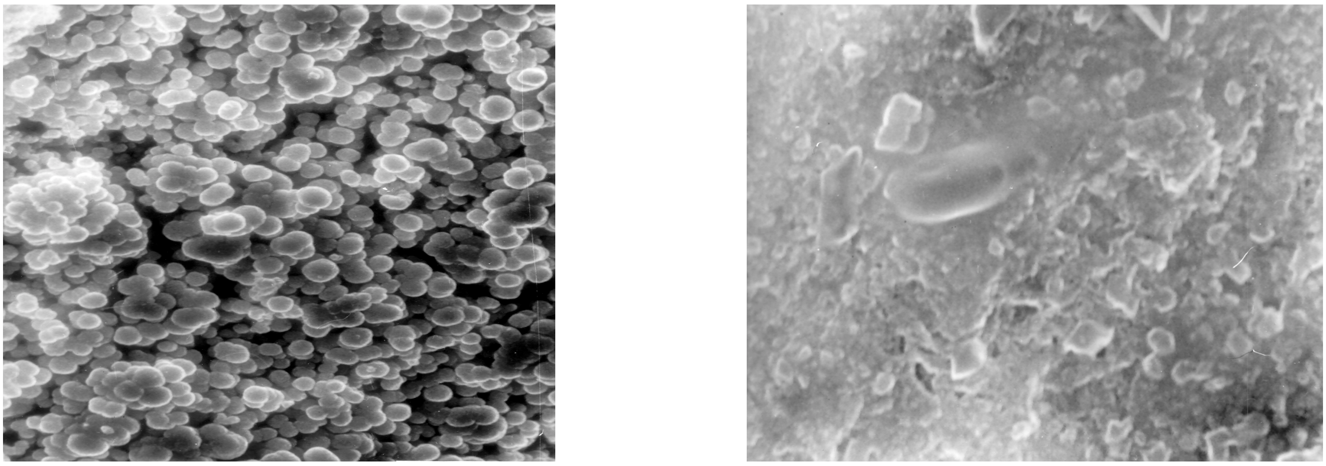
Table 3. *The kinetic parameters from potentiograms for lead alloys in sonnicated H_2SO_4 solutions (ρ = 1.28 gcm^{-3}) and in normal H_2SO_4 solutions (ρ = 1.28 gcm^{-3}) at a scan rate of 10mV/s and 25°C.*

Electrode	H_2SO_4 solution	Ipa_1 (mA)	Ipa_3 (mA)	Ipc_1 (mA)	Ipc_3 (mA)	Epa_1 (mV)	Epa_3 (mV)	Epc_1 (mV)	Epc_3 (mV)
Pb+1.8%Sb	Normal	5.1	0.18	1.44	1.83	-813	970	-980	-760
Pb+1.8%Sb	Sonnicated	9.4	0.74	2.89	3.6	-798	1030	-923	-779
Pb+0.08%Ca	Normal	4.42	0.24	1.64	1.75	-820	1006	-957	-762
Pb+0.08%Ca	Sonnicated	6.89	0.7	3.77	4.51	-820	988	-895	-798

The presence of alloying elements have led in all cases to the increase of the anodic peak currents as well as of the average of the respective currents, which represents an activation of all anodic and cathodic processes from this potential range (-1200 ÷ +1600) mV.

The coulometric measurements and the value of the kinetic parameters determined from the polarization curves pointed out the activation of the anodic and cathodic processes, the increase of the corrosion rate and the decrease of the hydrogen evolution overvoltage simultaneously with the increase of the Sb concentration from the alloy, respectively. The addition of calcium and selenium, respectively, led in all cases to the decrease of the corrosion rate, to the increase of the hydrogen evolution overvoltage and to the decrease of the hydrogen evolution current respectively. The manufacturing of the grids from Pb – Ca alloys decreases their corrosion during the functioning cycles, it reduces the gas evolution, their self-discharge, respectively, and increase time service of the lead acid batteries.

The surface of the electrodes made of lead calcium alloy with 0.08 % Ca, after polarization in sonnicated electrolyte, was examined by scanning microscopy. We hoped to observe a uniform microstructure of the surface as in the case of the active masses electroformed in electrolyte exposed to ultrasounds (figure 2 a).



(a) (b)

Fig. 2. *a) Positive active mass formed in sonnicated electrolyte. b) Lead calcium alloy electrode surface polarized in sonnicated electrolyte.*

Positive active masses formed in sulfuric acid solution exposed to ultrasounds impressed by the well-defined crystalline grains having average diameter of 2 μm, well shaped even in the depth of the plate.

On the electrode surface we notice lead sulfate crystals, with dimensions up to 2 μm surrounded by large amount of uniform, well defined small crystals, having submicron dimensions. This confirms the assumption that using electrolytes exposed to ultrasonic waves, the dimensions of the crystalline grains diminish and their uniformity improves.

For the active masses of the lead-acid batteries this effect leads to certain improvement of the electrochemical reactivity.

References

1. T.Y. POPOVA and B.N. KABANOV, *Zh. Prikl. Kim.*, 32 (1959) p.326.
2. D. PAVLOV, S. ZANOVA, G.PAPAZOV, *J. Electrochem. Soc*. 124, (1977), p.1522.
3. D. PAVLOV and Z. DINEV, *J. Electrochem. Soc*. 127, (1980), p.855.
4. D.PAVLOV*, Electrochim. Acta*, 23, (1978), p.815.
5. D.PAVLOV, *J. Electroanal.Chem*. 118, (1981), p.167.
6. J.P. POHL and W. SCHENDLER, *J. Power Sources*, 13(1987), p.297.
7. C.D. HODGMAN, R.C.WEAST, R.S.SHANKLAND and S.M. SELBY, *Handbook of Chemistry and Physics*, The Chemical Rubber Publishing Co. Cleveland, Ohio, (1962), p.262.