

Paweł NOWAK *

SEMICONDUCTING PROPERTIES OF LEAD SULPHIDE AND THEIR INFLUENCE ON THE SORPTION OF XANTHATES

Nearly stoichiometric samples of lead sulphide and the samples of the stoichiometry adjusted either to a lead-rich or sulphur-rich limit were synthesized in the form of thin films. Cycling voltammetry experiments in the solutions of pure base electrolytes as well as in solutions of potassium ethyl xanthate were performed. For the nearly stoichiometric samples spectroelectrochemical experiments in the infra-red range of the spectrum were performed, too. A strong dependence of the behavior of the sample on stoichiometry (and hence on conductivity type) was observed.

1. Introduction

The question of the possible influence of semiconducting properties of minerals on their behavior in flotation (especially on the sorption of anionic collectors) was first raised by Plaksin and his co-workers. Briefly this theory may be presented as follows. The adsorption of an anionic collector (xanthate for example) is a process of the transferal of electrons from the collector to the surface of a mineral and requires the presence of electron defects (free holes) in the valence band of the mineral. Those holes may be either already present in the mineral (due to its p-type conductivity) or may be generated in the surface of the mineral in the reaction of oxygen with the minerals surface (which is a process of abstraction of electrons from the surface). So, both the natural conductivity of p-type, as well as the presence of oxygen in the flotation pulp should facilitate the adsorption of anionic collectors. Similar concepts were developed in the U.S. Bureau of Mines (Maust, 1976). That theory, although very elegant, was not able to describe properly the

* Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Cracow

behavior of semiconducting minerals in flotation due to obvious over simplification of the real situation. Firstly, it neglects completely the possible presence of oxidation products at the mineral surface Golikov (Golikov, 1961) tried to avoid that difficulty assuming that those oxidation products peel away from the surface in the form of metal xanthate after reacting with xanthate ions from the solution). Secondly, this theory does not take into consideration the unavoidable changes in the surface stoichiometry and the resulting changes in the conductivity type under the influence of the redox processes proceeding at the surface. Lastly, the observed influence of conductivity type on adsorption of anionic collectors may be explained in another manner. It is well documented in the literature (see Maust, 1976 and the references cited therein) that the susceptibility to oxidation of a sulphide mineral depends greatly on its semiconducting properties. Obviously the enhanced oxidation of the surface should facilitate the anionic collector sorption.

So, it is clear that the semiconductor theory is not able to describe the sorption process as a whole, however one may expect that this theory might describe the initial steps of anionic collector adsorption on freshly obtained, non-oxidized surfaces.

In cycling voltammetry experiments on some sulphide minerals in xanthate solutions, so-called adsorption pre-waves preceding the main peak of xanthate oxidation were observed (Woods, 1971, Kowal, 1973). However, in the case of lead sulphide, there are great differences in the shape of voltammetric curves, both registered in pure base electrolyte as well as in xanthate solution, among different authors. Those differences are at least partly due to the different properties of the samples (not only to the differences in experimental procedure). The work of Paul and co-workers (1977) may serve as an example in which, for 4 different samples of galena completely different voltammetric curves in pure base electrolyte (HClO_4) were obtained in identical conditions. Especially interesting are the differences in the shape and height of the adsorption pre-wave in a xanthate solution.

Probably the most pronounced adsorption pre-wave may be observed in the work of Woods (1971). That author performed his experiments using natural galena samples prepared at the open air. On the other hand Lekki and Chmielewski (1987) have observed well marked adsorption pre-waves but only in the case of a surface obtained by cleavage of the sample below the surface of the solution. In the case of the samples prepared in open air this pre-wave did not appear. Contrarily, Richardson and Maust (Richardson, 1976) did not observe the adsorption pre-wave in the experiment on the cleaved sample.

It is very probable that the differences in the behavior of different samples are caused by the differences in their semiconducting properties.

2. Experimental

2.1. Preparation of the samples

The simplest and easiest control manner of obtaining the semiconductor of a given conductivity type and free charge carrier concentration is doping by foreign atoms. In the case of surface studies that manner is however rather hazardous in view of the possible enrichment of the surface in the trace element. In the present work the PbS samples of controlled stoichiometric composition were obtained by heating nearly-stoichiometric lead sulphide in a two-zone furnace under the controlled pressure of sulphur (Dalven, 1969, Gutierrez 1978). To obtain realistic times of equilibration at a relatively low temperature of heating the samples of PbS were deposited in the form of thin (200 nm) layers on the surface of gold wires (0.5 mm in diameter). Those layers were obtained by the chemical bath deposition method (Davies, 1966) and were nearly stoichiometric, slightly p-type. The semiconducting properties of PbS were controlled by measurements of conductivity, thermoelectric power and rest potentials in the solutions of lead ions.

2.2. Experimental procedure

Two types of experiments were performed. In the case of the samples with sulphur-rich or lead-rich stoichiometry the cycling voltammetry in $0.1 \text{ mol} \times \text{dm}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ solutions containing different concentrations of potassium ethyl xanthate were conducted. A typical electrochemical set-up and three electrode electrochemical cell were used. A saturated calomel electrode (SCE) was used as a reference electrode - all solutions were deoxidized using purified argon. The spectroelectrochemical measurements were performed using the cell shown in figure 1. Two spectral features were observed in the case of spectroelectrochemical measurements. First the infra-red absorption bands, characteristic of a xanthate group were observed in the spectra in the case of the adsorption of the xanthate group at the surface. Also the changes in the absorption of IR radiation on free charge carriers caused by the changes in the stoichiometry of the surface layer of the sulphide during the reaction were noticed. The absorption by free charge carriers may be observed as a monotonous rise in absorption with a rising

wavelength and may be registered at any wavenumber (at which no specific absorption due to adsorption of xanthate appears).

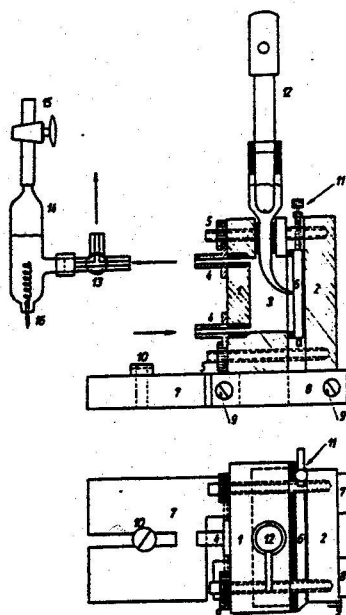


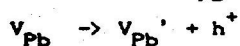
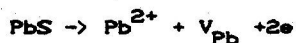
Fig. 1. The spectroelectrochemical cell: 1, 2 - teflon flow cell, 3 - solution, 4 - inlet and outlet of the solution, 5, 9, 10 - mounting screws 6 - reflection element, 7, 8 - metal base, 11 - current lead, 12 - SCE, 13, 15 - valves, 14 - counter electrode compartment, 16 - platinum counter electrode

All solutions were prepared using analytical grade purity reagents and double distilled water. The experiments were performed at room temperature.

3. Results

3.1. Surface stoichiometry of lead sulphide during polarization in solution of base electrolyte.

During the experiment presented in figure 2 a thin, nearly stoichiometric layer of lead sulphide was cycled in $0.1 \text{ mol} \times \text{dm}^{-3} \text{ Na}_2\text{B}_4\text{O}_7$ solution in the range of potentials in which no significant currents flow. However very significant changes of the free charge carrier's absorption may be observed at the extreme limits of the potential range. It is to be seen in the figure that for moderate polarization the changes of absorption in the anodic part of the curve are reversible and may be ascribed to the reactions:



giving rise to ionized lead vacancy, free hole and lead ion in the solution. In the range of cathodic potentials, the situation is much more complicated.

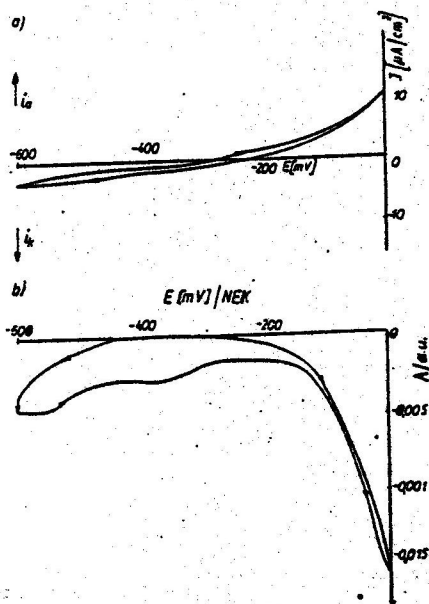
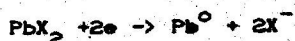


Fig. 2. Changes of current (2a) and free charge carrier's absorption (2b) during polarization of thin PbS sample in $0.1 \text{ mol} \times \text{dm}^{-3} \text{ Na}_2\text{S}_4\text{O}_7$ solution. Potential versus saturated calomel electrode. Absorption in arbitrary units.

The observed hysteresis is probably due to the slow interfacial reaction. The most interesting feature which may be seen in figure 2 is the very low free charge absorption in the range of potentials from -200 to -300 mV, the range in which the adsorption pre-wave in voltammetric experiments in xanthate solutions was observed (Nowak, 1980). So, in that range of potentials the surface stoichiometry should reflect the bulk stoichiometry (at least roughly).

3.2. The behavior of the product of adsorption of xanthate on oxidized lead sulphide surface during polarization.

When the lead sulphide oxidized in the ammonium acetate solution undergoes sorption in xanthate solution, a nearly close-packed monolayer of the adsorption product is formed (Nowak, 1980). The behavior of that adsorption product, obtained in the exchange reaction with oxidation products present at the surface during polarization is presented in figure 3. It is to be seen in figure 3 that the adsorption product obtained in such a manner does not undergo the desorption even at potentials exceeding the equilibrium potential for the reaction:



(where X denotes xanthate radical).

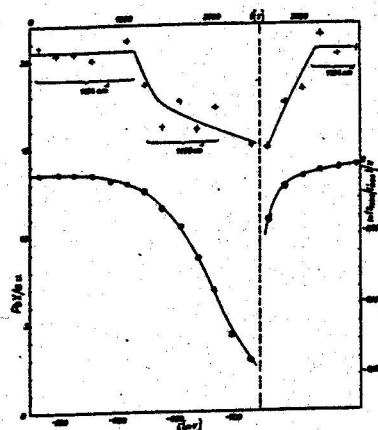


Fig. 3. The changes of the intensity of the most intense absorption band of lead xanthate (—+—) and free charge carriers absorption (—•—) during the polarization of the PbS sample covered by chemically adsorbed xanthate in cathodic direction in xanthate solution. Both free charge carriers absorption and coverage by adsorption product in arbitrary units

The desorption occurs to some extent only at potentials where significant reduction of the surface occurs. So, it may be stated that the presence of the layer of absorption product blocks very efficiently the surface - no electrochemical reactions are possible at such surfaces.

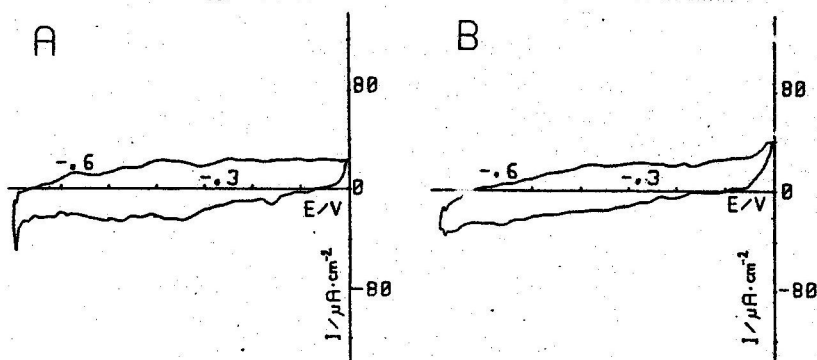


Fig. 4. The cycling voltammetry curve for lead-rich (strongly n-type) PbS sample in 0.1 mol/dm³ Na₂B₄O₇ solution (A) and in 0.003 mol/dm³ potassium ethyl xanthate solution (B). Scanning rate 0.1 V/s⁻¹.

3.4. The cycling voltammetry of PbS samples with adjusted stoichiometry in xanthate solution

The cycling voltammetry curve for a lead-rich (strongly n-type) PbS

sample in a pure base electrolyte as well as in a xanthate solution is presented in figure 4. It is to be seen that both the reaction of anodic dissolution in the pure base electrolyte and the oxidation of xanthate are significantly hindered. There is no adsorption pre-wave for the reaction of xanthate electrosorption for this type of samples too. For sulphur-rich (strongly p-type) samples the obtained curves were similar to the curve for nearly stoichiometric samples (presented elsewhere (Nowak, 1980)).

4. Discussion

It seems that on the basis of the presented results, the behavior of the lead sulphide samples in electrochemical experiments may be explained at least partly. It was shown that both the reaction of the anodic dissolution of lead sulphide as well as the anodic oxidation of xanthate strongly depends on the stoichiometry of the sulphide - for n-type samples both those reactions are significantly hindered. That is in accordance with the recent theory of the rate of electrochemical processes at semiconductor electrodes. However there is another factor influencing greatly the behavior of PbS in xanthate solution. It is well known from the literature that there are great differences in the susceptibility to oxidation between PbS samples of different types of conductivity (the p-type samples being much more readily oxidizable). So, the s-type samples are always covered to some extent by oxidation products which after reaction with xanthate give rise to the layer of the adsorption product obtained in the reaction between oxidation products of the surface and xanthate ions from the solution. It was shown that the product of xanthate sorption on the lead sulphide surface is very stable and may not be removed from the surface by cathodic polarization. Thus, depending on the experimental procedure (especially the time of the contact of the surface with air) the p-type samples will give the voltammetric curves showing well developed adsorption pre-waves (in the case of an unoxidized surface - for example the surface obtained by cleavage of the sample below the surface of the solution) or will give the curves not showing adsorption pre-waves (in the case of oxidized samples). The n-type samples should give in xanthate solutions voltammetric curves not showing adsorption pre-waves providing that polarization is not too strong (strong polarization may cause significant changes in the stoichiometry of the surface layer of the sulphide which was shown in figure 2).

Acknowledgement

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5. References

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Streszczenie

Nowak P., 1988. Półprzewodnikowe własności siarczku ołowianego i ich wpływ na sorpcję ksantogenianu. *Fizykochemiczne Problemy mineralurgii* 20 ; 125-133.

Prawie stechiometryczne próbki siarczku ołowianego w postaci cienkich warstw oraz próbki, których stechiometrię zmieniano do składu odpowiadającego nasyceniu siarką i do składu odpowiadającego nasyceniu ołowiem badano metodą voltamperometrii cyklicznej w roztworach etyloksantogenianu potasowego oraz roztworach czystego elektrolitu podstawowego. W przypadku prawie stechiometrycznych próbek zastosowano również metody spektroelektrochemiczne. Zaobserwowano silną zależność zachowania się próbek od składu.

СОДЕРЖАНИЕ

П.Новак, 1988. Полупроводниковые свойства сульфида свинца и их влияние на сорбцию ксантогенатов. Физикохимические вопросы обогащения, 20; 125-133.

Получены образцы сульфида свинца стехиометрического состава, образцы насыщенные серой и насыщенные свинцом. На этих образцах проведены измерения методом циклической вольтамперометрии в растворах инертного электролита и в растворах ксантогената.

На образцах стехиометрического состава проведены также измерения методом спектроскопии электрохимии в инфракрасной области спектра. Обнаружено сильное влияние (и связанного с этим типа проводимости) на поведение образцов.