

VOLTAMMETRIC STUDY OF THE ELECTROCHEMICAL STRIPPING OF GALENITE USING A ROTATING RING-DISK ELECTRODE

Šárka HOŠKOVÁ^a, Přemysl BERAN^b and Tomáš BERAN^c

^a *Institute of Hydrodynamics,*

Czechoslovak Academy of Sciences, 166 12 Prague 6

^b *Department of Analytical Chemistry, Charles University, 128 40 Prague 2 and*

^c *Institute for Ore Research, 252 10 Mníšek pod Brdy*

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A study was carried out of the electrochemical stripping of galenite in the form of a disk electrode with a gold ring, in 0.1M-NaClO₄ base electrolyte. It was found that lead is reduced from the galenite at potentials more negative than -1 V and remains on the surface of the electrode. The reduced lead is electrochemically stripped from the electrode at potentials more positive than -0.5 V. At potentials more positive than +0.4 V, PbS is further oxidized to Pb(IV). The degree of oxidation increases with increasing potential.

A previous work¹ dealt with the electrochemical stripping of galenite. Measurements were carried out on a synthetic sample in a plaster matrix. The dependence of the stripping of lead on the current magnitude, frequency of alternating the polarity of the sample and auxiliary electrode, electrolysis time, anions of lead salts added to the plaster, etc. was studied. These results were employed in the determination of the surface concentration of galenite in polished surfaces of natural samples. Later², similar measurements were carried out in which the stripping of cadmium, zinc and copper were study by a similar technique. Some of the measurements were combined with an optical method, AAS. These results were published without a more detailed discussion of the mechanisms of these reactions, which are certainly very complicated.

This work describes measurements carried out with a rotating disk galenite electrode with a gold ring, in an attempt to elucidate the mechanism of dissolution of lead from lead sulphide.

EXPERIMENTAL

The measurements were carried out using a bipotentiostat constructed from operational amplifiers. A scheme of the apparatus is depicted in Fig. 1 (ref.³). The dependences were recorded using a 26000 A3 XYY' Recorder from Bryans, England. The reference electrode was a K 401 calomel electrode from Radiometer, Denmark; the auxiliary electrode was a gold wire placed

in an electrode space separated by a frit. The galenite disk-gold ring electrode was prepared as described in a previous work⁴. Pure galenite from Přibram was worked to form a short rod with a diameter of c. 7 mm. The auxiliary disk part of the electrode consisted of a brass rod with a hole with a depth of 5 mm and diameter the same as that of the galenite rod, where this rod was fitted. The rod was lightly glued in place with epoxy resin. After hardening of the resin, the RRDE was finished as described in ref.⁴. The RRDE parameters were r_3 3.518 mm, r_2 2.914 mm, r_1 1.649 mm. The theoretical collection efficiency value N is not tabulated, and was thus found experimentally in an independent experiment employing copper ions in a base electrolyte of ammoniacal buffer with a concentration of 0.1 mol l^{-1} , yielding a value of $N = 0.20$. A gold RDE with r 2.379 was used to record the waves of some depolarizers. The working vessel was a five-mouth 200 ml vessel.

All the reagents were of the highest purity available, designated p.a.. Nitrogen from a steel bottle was purified by passing through an alkaline solution of sodium anthraquinone- β -sulfonate. The measurements were carried out in a sodium perchlorate base electrolyte solution with a concentration of 0.1 mol l^{-1} . The potential values are related to a saturated calomel electrode.

RESULTS AND DISCUSSION

The voltammetric behaviour of Pb^{2+} , S^{2-} and SO_3^{2-} ions, a S suspension (sulphur flowers), of PbS , PbO and PbO_2 on a gold RDE was first investigated by cyclic voltammetry in the potential range -1.5 to $+1.5$ V. Lead compounds yield a cathodic wave at $E_{1/2} - 0.5$ V. Recording of the curves in the anodic direction results in stripping of the lead deposited on the disk electrode at a potential of -0.5 V to form an anodic peak. Its height depends on the polarization time at potentials more negative than -0.5 V.

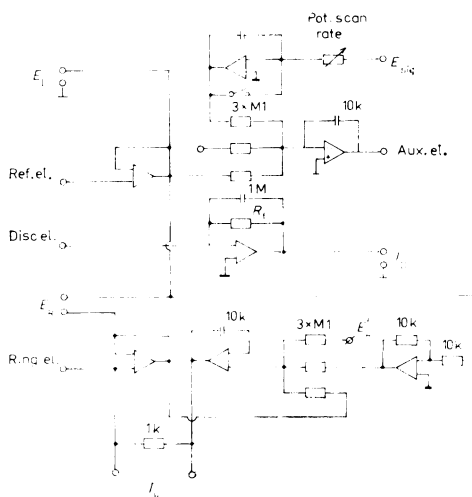


FIG. 1

Electronic scheme of the bipotentiostat

An anodic peak appears at a potential of c. +1.1 V, corresponding to the oxidation $\text{Pb}^{2+} \rightarrow \text{Pb}^{4+}$. Suspensions of PbS, PbO and PbO_2 behave similarly. A suspension of PbO_2 yields only a slight peak in the anodic region, which can be explained by a low Pb^{2+} content in the lead (IV) oxide.

Of the studied sulphur compounds, sulphite yields a clear anodic wave with $E_{1/2} +0.3$ V, in the anodic polarization direction. In the cathodic direction, the curve is identical with that of the base electrolyte. In the presence of sulphide, an anodic current was observed in the potential range +0.7 to 1.2 V as a sharp maximum. A sulphur suspension (flowers of sulphur) yielded an anodic peak in the anodic direction at $E_{1/2} -0.3$ and 0.2 V; at a potential of 0.6 V, the anodic current suddenly decreases to the level of the wave with $E_{1/2} -0.3$ V. In the cathodic direction, the curve is practically identical with that of the base electrolyte. PbS yields an anodic current as a maximum in the anodic polarization direction in the region -0.5 to -0.2 V and then at a potential of +1.25 V. The cathodic polarization curve was identical with that of the base electrolyte with increased cathodic current.

It follows from comparison of these recordings with the voltammetric curve of the galenite electrode that they cannot be employed to explain the reactions of the sulphur components of galenite as the voltammetric curves of galenite do not contain any waves or peaks comparable with the curves for sulphur compounds. Lead(II) ions yield a reversible wave at -0.5 V; thus lead deposited on the electrode will be stripped at this potential.

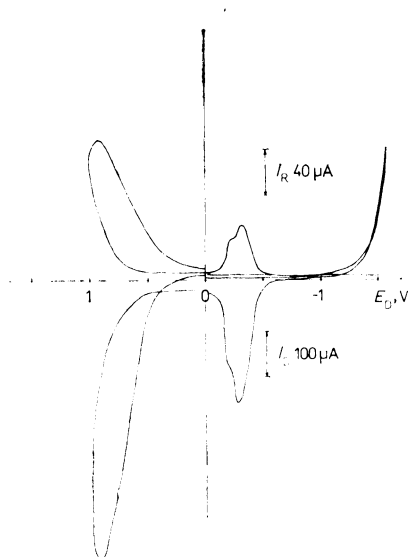


FIG. 2

I_R-E_R and I_D-E_D voltammetric curves using a rotating galenite disk electrode with a gold ring. 0.1M-NaClO_4 ; 0.6 V min^{-1} ; polarization direction $0 \rightarrow -1.5\text{ V} \rightarrow +1.5\text{ V} \rightarrow 0$; $E_R -0.65\text{ V}$; $\omega = 28\text{ rps}$

Figure 2 depicts the curves for a RRDE with a galenite disk and gold ring in a 0.1M sodium perchlorate solution. These curves were recorded only in the first cycle as repeated curves correspond to an undefined surface of the galenite disk. Consequently, the electrode was polished prior to each recording. During the recording, the ring potential was set to a value of -0.65 V at which lead(II) ions are reduced to metallic lead.

The recording of the $I_D - E_D$ and $I_R - E_D$ curves was carried out from zero to negative potential values. No wave was observed on the disk current curve, and the cathodic current begins to increase around about -1 V. The reversed polarization

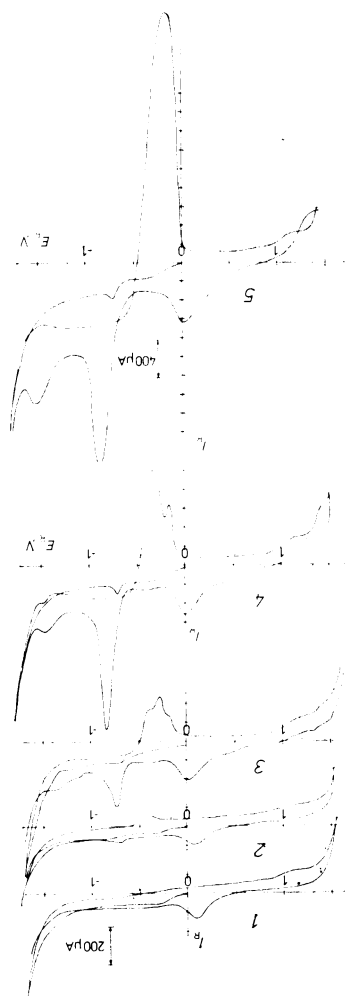


FIG. 3

$I_R - E_R$ voltammetric curves at a rotating galenite disk electrode with a gold ring at various constant E_D : 1 0.2; 2 0.4; 3 0.6; 4 0.8; 5 0.9. 6 V min^{-1} , other conditions as in Fig. 2

curve is practically identical up to a value of -0.5 V. The ring current is practically zero. As the disk potential is further increased to positive values, a marked maximum appears on the disk current curve, corresponding to the oxidation of lead (Pb produced by reduction of PbS) to lead(II) ions. This reaction produces a maximum on the ring current curve ($E_R - 0.65$ V). The current ratio $-I_R/I_D$ has a value of 0.19, which is in very good agreement with the collection efficiency of the electrode. As the disk potential continues to change, the disk anodic current begins to slowly increase at $+0.5$ V, with an equivalent increase in the ring cathodic current. When the polarization direction is changed, the current decreases on both curves.

It follows from these results that lead is reduced from a valence of (II) in galenite to metallic lead at very negative potentials of the galenite disk electrode (about -1 V), with simultaneous electrolytic decomposition of the base electrolyte. The reduced lead is deposited on the electrode surface. In the anodic polarization direction this electrolytically deposited lead is stripped at a potential of about -0.5 V. A maximum thus appears on the $I_D - E_D$ curve, with an equivalent cathodic peak on the $I_R - E_D$ curve, corresponding to the reduction of lead(II) ions, transported to the ring electrode by convective diffusion flow of the solution. It was also found that both the disk and ring peaks increase with decreasing polarization rate, when the potential change is arrested at negative values above -1 V or the reversal potential is shifted to negative values. In all three cases, the period of time during which lead is deposited on the disk electrode is prolonged.

A different procedure was necessary to definitely demonstrate that galenite (Pb(II)) is oxidized to Pb(IV) on the galenite disk electrode at positive potentials. The $I_R - E_R$ curves were recorded by cyclic voltammetry and the potential of the disk galenite electrode was set at a predetermined value between 0.1 and 1.0 V. A single cycle was recorded at a relatively high polarization rate on a newly polished galenite disk-ring electrode. Figure 3 depicts the curves obtained. An increase in the potential of the galenite disk to $+0.4$ V yields a small amount of Pb(IV). An anodic peak appears on the ring at a potential of -0.5 V, corresponding to oxidation of lead formed during cathodic polarization of the ring. This lead could come only from the galenite through oxidation at a positive potential. As the disk potential increases, the peak on the ring polarization curve constantly increases, corresponding to increased oxidation of the galenite and consequent release lead into the solution, irrespective of whether reduction in the solution to lead(II) ions occurs prior to deposition on the ring.

The results obtained yield no information on oxidation of sulphide ions as no characteristic current was obtained in either the study of the voltammetric behaviour at the gold disk electrode or a glassy carbon electrode.

Similar processes definitely occur when a chloride medium is employed in the electrochemical stripping of galenite¹; they are accompanied by chemical reactions such as that of chlorine formed at positive potentials.

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