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Composition and morphology of the film formed on a lead alloy under conditions typical of the electro-winning of copper

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ABSTRACT

The composition and morphology of the anodic film formed on a lead alloy under conditions typical of copper electro-winning was studied with the aim of establishing the mechanism by which cobalt ions decrease the oxidation rate of lead. The film was characterized by scanning electron microscopy, X-Ray Diffraction (XRD) and X-Ray Photon Electron Spectroscopy (XPS). The anodic film formed in the presence of cobalt ions was thin and compact whereas the film was thick and porous without cobalt ions. No crystalline cobalt compounds were detected by XRD and no cobalt peaks were detected by XPS. In the absence of cobalt ions in the solution, initial oxidation produces three layers on the lead surface, namely $PbSO_4$, α-PbO_2 and β-PbO_2 in contact with the solution. In steady state, there are two layers: α-PbO_2 and β-PbO_2. In the presence of a moderate cobalt ion concentration of up to and including 100 ppm, in steady state there remain the three layers: $PbSO_4$, α-PbO_2 and β-PbO_2. The results indicate that the presence of cobalt ions increases the imperviousness of the α-PbO_2 layer in hindering the oxidation of metallic lead to α-PbO_2 and also in hindering the oxidation of $PbSO_4$ to β-PbO_2.

1. Introduction

1.1. Oxidation of lead in sulphuric acid

Oxidation of lead in sulphuric acid at high anodic current densities is a significant commercial issue because lead alloy anodes are common in base metal electro-winning, including copper electro-winning (Anderson et al., 1974; Camurri et al., 2001; Cifuentes et al., 1999; Ipinza et al., 2007) and in battery applications (Bagshaw, 1997; Cifuentes et al., 1998, 2005; Lander, 1951; Nikoloski and Nicols, 2008; Ruetschi and Angstadt, 1964). The lead surface (Astakhov et al., 1964; Burbank, 1957; Ruetschi and Cahan, 1958a,b) in sulphuric acid is quickly covered with a protective, non-conducting layer of $PbSO_4$. Because of the high anodic current density at the anode surface, $PbSO_4$ is oxidised to a conducting lead oxide, PbO_2, which hinders the further oxidation of the lead alloy. PbO_2 can exist in two crystal forms: rhombic (α) and tetragonal (β). Ivanov et al. (2000a) reported that α-PbO_2 forms strong deposits composed of large, closely-packed crystals whereas β-PbO_2 deposits were reported to be considerably less strong and composed of poorly-bonded, fine, needle-shaped crystals. α-PbO_2 has a higher density and a higher hardness than β-PbO_2. α-PbO_2 only forms in alkaline or neutral solutions whereas β-PbO_2 only forms in acidic solutions (Ivanov et al., 2000b). β-PbO_2 is the low-temperature, low-pressure phase whereas α-PbO_2 is the high-temperature, high-pressure phase (Dawson, 1979) and therefore α-PbO_2 is meta-stable at standard atmospheric pressure and temperature (Burbank et al., 1971).

The oxidation to PbO_2 of the lead sulphate, formed initially on the lead surface, was thought to occur by the formation of a film of β-PbO_2 on top of the lead sulphate and the formation of α-PbO_2 underneath as a result of oxygen diffusion through the β-PbO_2 layer (Astakhov et al., 1964; Burbank, 1957; Ruetschi and Cahan, 1958a,b). Ivanov et al. (2000b) quoting Razina et al. (1956) further suggested that the PbO_2 surface layer becomes looser and less-protective during anodic oxidation, caused by reactive intermediate products (including peroxide compounds) of the oxygen evolution reaction. Rey et al. (1938) suggested that an oxidation product was lead persulphate $Pb(SO_4)_2$ which decomposed to lead mono-oxy-sulphate, $PbOSO_4$ and then to lead peroxide, PbO_2. Codaro and Vilche (1997) suggested the following reaction sequence:

$$PbO + H_2O \rightarrow \alpha{-}PbO_2 + 2H^+ + 2e^- \quad (1)$$

$$PbSO_4 + 2H_2O \rightarrow \beta{-}PbO_2 + H_2SO_4 + 2H^+ + 2e^- \quad (2)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad (3)$$

It was suggested that reaction (3) takes place on the β-PbO_2 surface. Pavlov et al. (1993) suggested that the $PbSO_4$ dissolves as Pb^{2+} and SO_4^{2-} in the solution in pores of the surface film; the Pb^{2+} ions diffuse to the

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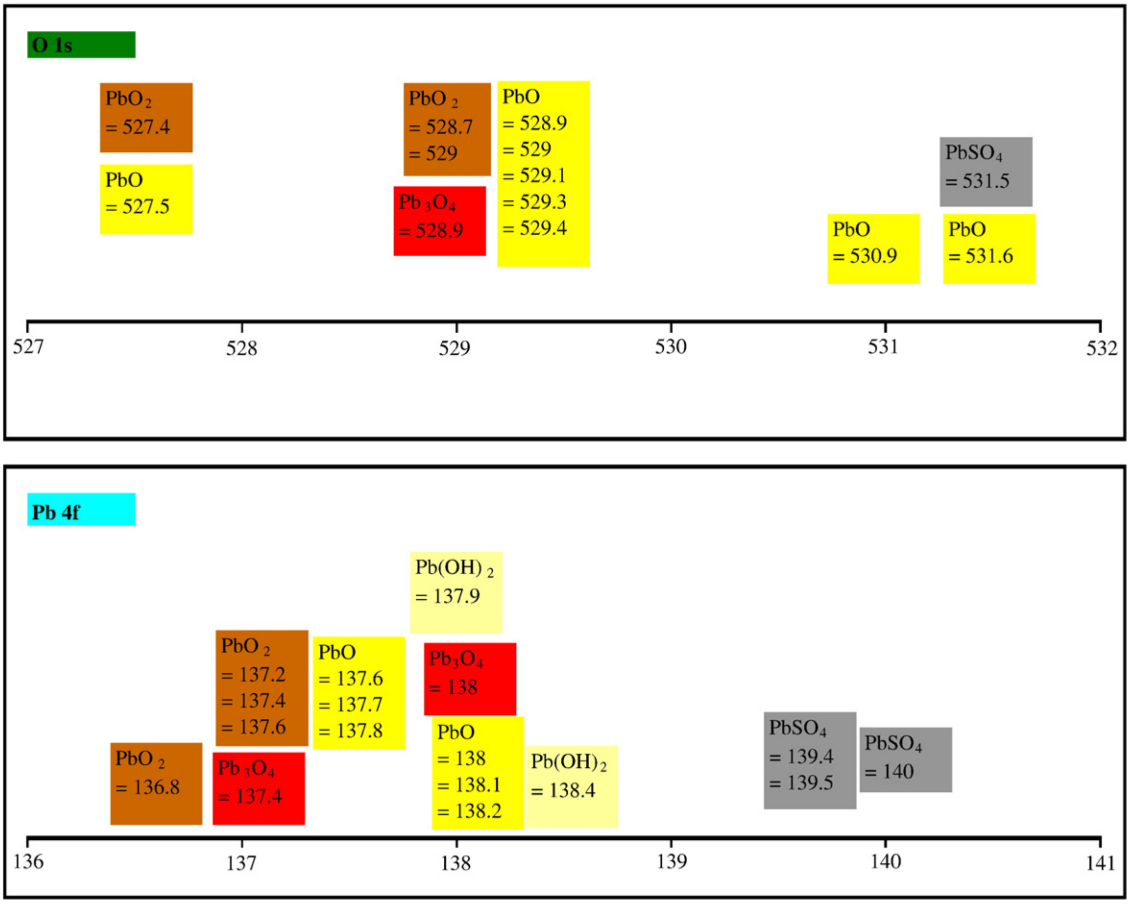

Fig. 1. Literature values for the binding energies (eV) for lead compounds (Kim et al., 1973).

nearest reaction site where they are oxidised to Pb^{4+} ions; these ions combine with water to form $Pb(OH)_4$ (because the Pb^{4+} ions are not thermodynamically stable in solution); and $Pb(OH)_4$ dehydrates to $PbO(OH)_2$ and to PbO_2. The process can be represented (Codaro and Vilche, 1997) as follows:

$$PbSO_4 \leftrightarrow Pb^{2+} + SO_4^{2-} \tag{4}$$

$$Pb^{2+} \rightarrow Pb^{4+} + 2e^- \tag{5}$$

$$Pb^{4+} + 4H_2O \rightarrow Pb(OH)_4 + 4H^+ \tag{6}$$

$$Pb(OH)_4 \rightarrow PbO(OH)_2 + H_2O \tag{7}$$

$$PbO(OH)_2 \rightarrow PbO_2 + H_2O \tag{8}$$

Prengaman and Siegmund (1999) suggested that oxygen, produced at the anode, directly oxidises lead by the formation of PbO, $PbSO_4$ and PbO_2 by the following reactions:

$$Pb + 1/2\ O_2 \rightarrow PbO \tag{9}$$

$$PbO + H_2SO_4 \rightarrow PbSO_4 + H_2O \tag{10}$$

$$PbO + H_2O \rightarrow Pb(OH)_2 \tag{11}$$

$$PbSO_4 + H_2O + 1/2\ O_2 \rightarrow PbO_2 + H_2SO_4 \tag{12}$$

$$Pb(OH)_2 + 1/2\ O_2 \rightarrow PbO_2 + H_2O \tag{13}$$

Prengaman and Siegmund (1999) postulated that some of the oxygen generated at the surface migrates through the β-PbO_2 film to oxidize the lead at the lead/oxidation product interface. As the oxidation product becomes thicker it develops cracks, these cracks become larger, the oxidation product flakes off the surface, fresh metal is exposed to the solution and allowing further oxidation.

1.2. Influence of cobalt ions on lead oxidation

The influence of cobalt ions in sulphuric acid solutions on lead oxidation has been investigated since the early 1930s (Rey et al., 1938) and it is well established that a small concentration of cobalt ions significantly reduces the lead oxidation rate (Antonov and Stepanenko, 1972; Bagshaw, 1997; Branzoi et al., 2001; Cachet et al., 1999; Gendron et al., 1975; Hrussanova et al., 2001, 2004a,b; Koch, 1959b; Koenig et al., 1941; Krivolapova and Kabanov, 1950; Nidola, 1989; Panda et al., 2004; Prengaman and Siegmund, 1999; Rashkov et al., 1999; Rey et al., 1938; Yu and O'Keefe 1999a). Moreover, in the presence of cobalt ions, the potential of the lead anode is lower (commonly assumed to indicate that the oxygen over-potential is lower) and the electro-winning cell produces high-quality fine-grain copper with minimal lead contamination (Panda et al., 2004). Yu and O'Keefe (1999a,b) proposed that the influence of cobalt ions on the oxygen evolution reaction was dependent on the type and quantity of active surface sites for the oxygen evolution reaction. In the presence of cobalt ions, the amount of PbO_2 on the lead anode surface was markedly decreased (Yu and O'Keefe, 1999a) and the oxidation product was found to be mainly lead sulphate (Pagliero et al., 1999). Rey et al. (1938) proposed that lead dissolves in sulfuric acid as lead persulfate, and that cobalt ions decrease the stability of lead persulfate so that it can no longer form, hence, inhibiting lead oxidation.