Electrodeposited PbO₂Anode For the Decomposition Of Low Concentrations of Cyanide

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Titanium anodes electroplated with lead dioxide in nitrate solutions containing a surfactant or an organic additive are more effective than the traditional graphite anode for decomposing cyanide in solutions containing a low cyanide concentration and sodium chloride. Data in this paper show that the efficiency of electrolytic decomposition is affected by the porosity of the PbO₂ surface layer and the electrode potential for the reaction: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$.

ecause of the high toxicity of cyanide compounds, most countries in the world have strict standards on the control of cyanide wastes. Metal finishing and metallurgical processes generate waste with cyanide in different forms and concentrations. Therefore, a variety of methods has been developed for their control. Common processes include thermal hydrolysis^{1,2}, chemical^{3,4} and electrolysis^{5,7}. Thermal hydrolysis is conducted at a high temperature, needs heating and cooling and thus is more costly than room temperature processes. Although chemical oxidation is operated at room temperature, it is low in efficiency and, therefore, costly. Moreover, it produces a large amount of sludge that requires further processing.

Electrolysis has mainly been used for the decomposition of high concentrations of cyanide. However, the method is not so effective for low cyanide concentrations because of its low efficiency. Addition of table salt has been proposed to increase the efficiency of electrolyzing solutions with low cyanide concentrations.[®]Unfortunately, sodium chloride accelerates the corrosion rate of graphite or stainless steel anodes and shortens their life.

Low-cost PbO₂-coated titanium anodes recently have become widely used as insoluble anodes to replace noble metal anodes for electrolysis purposes. ⁹⁻¹¹ Such anodes also have been used for the electrolysis of cyanide solutions. ⁶⁻¹⁰ Their effectiveness depends greatly on the surface properties of the PbO₂ coating, which can be modified by adding surfactants or organic additives to the coating solution. it has been reported that an adherent and porous PbO₂ anode could be prepared with addition of the surfactant Teepol to the solution.¹¹ Such an anode can significantly enhance the autocatalytic activity for the anodic oxidation of chlorate to perchlorate ions.

This paper discusses the preparation of new PbO₂/Ti anodes in nitrate solutions containing different surfactants or organic additives and the effectiveness of these anodes during the decomposition of low cyanide concentrations. The surface morphology and structure of the PbO₂ also was investigated in order to explain differences in the effectiveness of the anodes prepared in different solutions.

Experimental Procedure

A 2 x 5 cm titanium plate was first degreased with soap and water and then etched in 6N HCl solution at 80 to 90° C for 1 to 2 hr, followed by the formation of an inner layer of SnQ₂+ SbO₃. This inner layer was formed by baking the etched plate at 100° C for several min after it was dipped in a solution consisting of 20 g of SnCl₄.xH₂O, 2 g of SbCl₃, 20 mL of n-butanol and 1 mL of HCl. After three dip and bake cycles, the plate was baked at 450 to 500° C for 5 min under an airflow. Afterwards, PbO₂ was electrodeposited on the titanium anode in a solution containing 350 g/L of



Fig. 1—Cyanide concentration in low-cyanide solutions as a function of time of eleotrolysis at 3 A/dm² with a PbO₂/Ti anode obtained with Aerosol-AY addition to the lead nitrate solution.



Fig. 2—Cyanide concentration in a high-cyanide bath as a function of time of electrolysis at 3 A/din-.



Fig. 3-SEM photographs of PbO, electrodeposits with (a) Aerosol-OT, (b) Triton X-100, (c) gelatin, and (d) no additive.

Pb(NO₃)₂, 30g/L of Cu(NO₃)₂, 10 g/L of lead acetate, 10 g/L of cupric acetate and an additive. The temperature and current density were 70° C and 5 A/dm², respectively.

Two 4 x 6 cm stainless steel sheets were used as cathodes in cells used for the oxidation of cyanide ions. The backsides of the cathodes were stopped off by lacquering. Two PbO₂/Ti anodes were placed in the center of an acrylate cell that contained 500 mL of solution. The solution was prepared for initial studies with 10 g/L of KCN and 5.4 g/L of KOH and stirred during experiments at ambient temperature. Because both graphite and stainless steel corrode at current densities above 3 A/dm²in solutions containing NaCl, the PbO, anode current density was fixed at 3 A/dm² even though these anodes can be operated at much higher current densities. The cyanide solution was prepared with 10 g/L of KCN and 5.4 g/L of KOH. Cyanide concentration was determined by titration with a AgNO₃ standard solution and an indicator, 5-(4-dimethylaminobenzyliden)-rhoanin.

Results and Discussion

In the beginning, a comparison of cyanide decomposition efficiency during electrolysis of solutions containing a high concentration of cyanide (4 g/L) indicated better results for graphite anodes, by comparison with PbO₂/Ti anodes (Fig. 1), However, graphite corroded slightly, but the PbO₂coated anode showed no corrosion at all. Later, the PbO₂ anodes were tested in a solution containing 0.8 g/L of cyanide ions. NaCl was added to increase the conductivity of the solution and the current efficiency.

Cyanide can be destroyed by both direct and indirect oxidation. The reactions are described below.""":

Direct oxidation at the anode:

$$CN^{-} + 2OH^{-} \rightarrow CNO^{-} + H_2O + 2e^{-}$$
(1)

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Indirect oxidation at the anode: $2CI^{-} \rightarrow CI_2 + 2e^{-}$ (2)

At the cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ (3)

$$CI_2 + 2OH^- \rightarrow CIO^- + CI^- + H_2O$$
 (4)

$$CIO^- + CN^- \rightarrow CNO^- + CI^-$$
 (5)

Other CIO⁻ reactions:

 $6\text{CIO}^- + 3\text{H}_2\text{O} \rightarrow 2\text{CIO}_3^- + 4\text{CI}^- + 6\text{H}^+ + 1.5 \text{ O}_2 + 6\text{e}^-$ (6)

$$CIO^- + H_2O + 2e^- \rightarrow CI^- + 2OH^-$$
(7)

$$CIO^{-} \rightarrow CI^{-} + 0.5O_2 \tag{8}$$

Addition of NaCl enhances Reaction (2), which, in turn, increases the rates of equations (4), (5), (6), (7) and (8). With low Cl concentrations, the current efficiency is poor because of the low rates of indirect and direct oxidation. With high Cl concentrations, the loss of current efficiency due to Reactions (6), (7) and (8) makes operation economically unattractive. Thus, there should bean optimal Cl concentration for promoting the efficiency of CN destruction. Figure 2 shows that 10 g/L of NaCl gave better results than 6 or 14 g/L. Thus, 10 g/L of NaCl was added to solutions containing low concentrations of CN during subsequent cyanide decomposition experiments.

High chlorine and oxygen overpotentials of the anode are desirable to promote direct CN oxidation. Thus, electrodeposited PbO₂ on a titanium anode was selected for electrolyzing solutions containing a high concentration of CN ions,¹⁰ because the chlorine and oxygen overpotentials of the dimensionally stable (DSA) Ti/RuO₂, are



Fig. 4—Cyanide concentration as a function of time of electrolysis at 3 A/din' with a PbO₂ deposit obtained in solutions containing different additives.

lower. For enhancing the indirect oxidation of CN, the oxygen overpotential should still be as high as possible, but the chlorine overpotential should not be too high. During the study described in this paper, the chlorine overpotential of PbO₂ on Ti was lowered by using additives in the coating solution to increase the active sites in the PbO₂ coating.

The surface morphology and crystalline plane orientation are strongly affected by additives. Scanning electron microscopy (SEM) and X-ray diffraction have been used by the author and a colleague" to investigate the surface morphology and crystalline behavior of PbO, electrodeposits. The results of this study help explain discrepancies in the effectiveness of PbO,-coated anodes during the electrolysis of solutions containing low concentrations of cyanide. Electrodeposits from the lead nitrate solution were mainly β -PbO₂. Figure 3 shows some SEM photographs. Figure 3a displays a highly porous surface layer structure for the deposit obtained with the surfactant Aerosol-OT^a. Triton X-100^b exhibited a strong leveling effect (Fig. 3b). A gelatin addition increased the viscosity of the solution and resulted in the flat surface structure in Fig. 3c, which compares with Fig. 3d, a SEM photograph of the surface from a bath containing no additives.

Nine anodes were tested for the electrolysis of solutions containing 800 ppm of cyanide. Figure 4 shows that graphite had the lowest efficiency. All of the PbO₂ anodes were satisfactory for the decomposition of cyanide. The anode obtained with addition of Aerosol-OT had the best efficiency. Surfactants PE,^cAerosol-AY^d and Aerosol-MA were not as effective, but better than dextrin or gelatin.

The terminal voltage was about 3.7 V; thus, I x V x t could be used to calculate energy consumption, which was 0.017 kw-hr/g of CN for the best PbO₂/Ti anode. This value is in the range of data from the literature (0.007 to 0.025 kwhr/g)⁴⁶ for deposits obtained at a current density of 0.1 to 0.4 A/din', which is much lower than that used in this study (3 A/din').

Additive	mV vs SCE
None	272
Triton X-100	235
Gelatin	225
Aerosol-OT	238

*Deposits obtained with NaCl in solution.

Most of the PbO₂ deposits contained fractions of α -PbO₂, but exhibited different porosities. From SEM examinations, the sequence of porosities was in the following order: Aerosol-OT > gelatin > no additive> Triton X-100.

The redox potentials $(E_{CL/CL^2})^{15}$ of $2CL^2 - CL^2 + 2e$ for different PbO₂ deposits in a solution containing NaCl were measured by the polarization method with respect to a SCE reference electrode using an EG&G Model 273 potentiostat. The results are given in the table. This redox potential is the applied potential that equalizes the reaction rate on both sides of the equation: 2CI - CI, + 2e. Therefore, the electrode with a lower value of E_{CHCI2} can be considered to have more active sites than one with a higher value. The sequence of PbO₂electrodes with decreasing active sites was: gelatin > Triton X-100 > Aerosol-OT > no additive. However, Fig 4 showed that the order of decomposition efficiency was: Aerosol-OT>gelatin > no additive >Triton X-100. Thus, both porosity and active sites may be important factors affecting decomposition efficiency. The PbO₂ deposits prepared with no additive was more porous and had fewer active sites than that deposited with Triton X-100 in the solution. However, these electrodes were nearly equal in cyanide decomposition efficiency.

The surface layer of the PbO₂ deposited with addition of Aerosol-OT was considerably more porous than that of the electrode obtained with a gelatin addition, although active sites were greater for the deposit produced with gelatin. The Aerosol-OT addition was more effective for producing an electrode with a high current efficiency for cyanide decomposition. It enhances the electrocatalytic activity of the PbO₂ deposits in solutions containing sodium chloride and a low concentration of cyanide ions.

Conclusions

Lead dioxide has been deposited on titanium in nitrate solutions containing a surfactant or an organic additive. The PbO/Ti anodes are more effective than graphite for the electrolytic decomposition of cyanide in solutions containing a low cyanide concentration. Aerosol-OT in the nitrate solution produces a highly porous deposit with high electrolytic activity for low-cyanide solutions with addition of NaCI.

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