Electrolytic Oxidation of Cr(III) at Lead Dioxide

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Summary: Electrodeposition of pure and doped lead dioxide on titanium substrate are described from acid bath at room temperature, voltage 3.0 - 4.0 V and current density 0.007 - 0.013 A/cm^2. Prepared electrodes were tested for anodic oxidation of chromium(III) sulphate in sulphuric acid. UV-visible spectroscopy was used for the analysis of the oxidation product. Current efficiency and percentage conversion of Cr(III) to Cr(VI) at pure and different doped lead dioxide electrodes were determined. Results for pure and doped-lead dioxide electrodes were compared. Bi-PbO_2 electrode was found to have maximum electrocatalytic activity for chromium(III) oxidation.

Keywords: Lead dioxide anode, electrodeposition, chromium(III)

Introduction

Chromic acid bath is used in pickling and electropolishing. The dumping of such baths is harmful, so the recycling and restoration are preferable economically as well as environmentally. PbO_2 is generally used as the anode for electrooxidation of chromium(III) into chromium(VI). Plumbic oxide layers [1] were electrodeposited from acid bath. The electrocatalytic properties of plumbic oxides were studied in different conditions. It was concluded that catalytic properties of plumbic oxide were highly dependent on addition of dopant ions in the deposition bath. The effect of different dopant ions on the structure and catalytic activities of electrodes were studied [1]. Characteristics of doped lead dioxide layer deposited on titanium substrate were studied by X-ray photoelectron spectroscopy and secondary ion mass spectrometry. It was concluded that doped lead dioxide electrodes were more stable than pure lead dioxide electrodes [2]. Boron doped diamond, glassy carbon and gold electrodes were used for electrochemical oxidation of trivalent chromium in aqueous solution over the pH range (1.0 - 13). The mechanism of the reaction was studied and it was observed that a multistep mechanism was involved in the oxidation reaction in which first electron transfer was electrochemically irreversible and rate determining followed by two fast electron transfers. The presence of hydroxyl ion in the reaction mixture showed that oxidation can also take place through this ion [3]. Bi-doped lead dioxide anodes were fabricated by electrodeposition method and were used for electrolytic oxidation of chromium(III). It was observed that electrocatalytic properties of Bi-doped PbO_2 anodes were better than those of lead dioxide anodes. A mathematical equation was used to determine rate of oxidation of chromium(III) at different chromium concentrations [4]. Bi doped lead dioxide anode was used for electrocatalytic oxidation of Cr(III) to Cr(VI). The catalytic activity of thick Bi-PbO_2 layer increased during restoration of chromium(VI) with maximum current efficiency [5]. It was shown that lead anodes have good current efficiency in comparison to platinum electrodes. The best conditions for chromium(III) oxidation were current density 1.0 - 2.5 A/dm^2, temperature 30 - 40 ^{0}C and flow rate 300 cm^3 /min. It was observed that maximum rate of oxidation of chromium(III) was obtained by using bismuth doped lead dioxide electrodes [6]. Chromium sulphate was converted to chromic acid in sulphuric acid by using lead dioxide anodes containing 5% Sb. It was observed that antimony was added to lead dioxide deposition bath to increase the stability and surface area of lead dioxide layer [7]. Pt-Nafion and commercial Pt-C-Nafion air fuel cell electrodes were used for recycling of spent chromium plating bath. Sulphuric acid and chromic acid were used as electrolytes. Tafel plots for two electrodes were similar in H_2SO_4 but in chromic acid plots were not clearly defined. The polarization study showed that in chromic acid, cathodic potential of fuel cell cathode system increased as compared to that in sulphuric acid [8]. Photo Fenton process was applied for oxidation of chromium(III) to chromium(VI). Hydrogen peroxide, Fe(II) and Fe(III) were used as catalysts. Different parameters which affected the oxidation of Cr(III) to Cr(VI) such as Fe(II), Fe(III) catalyst, hydrogen peroxide concentration, pH, power of UV lamp and reactor size were also studied [9]. The oxidation of chromium(III) to chromium(VI) was reported in acidic media. Conditions such as composition of bath, 0.1 M chromic sulphate, 0.5 M Na_2SO_4, pH 2 - 4, temperature 333 K and current density 1 A/dm^2 were used to obtain maximum yield. The current efficiency of the reaction was 80% [10]. A new method was used for the conversion of Cr(III) to Cr(VI) by using bromate as oxidizing agent. It was observed that oxidation was favorable in less acid solution in the presence of cobalt as catalyst [11]. A gold single crystal (111) was used for electrolytic conversion of chromium(III) to chromium(VI) in basic solution. It was observed that rate of reaction was dependent on structure of crystal. The effect of electrolyte and hydroxyl ion on oxidation conditions and rate of the reaction were studied [12]. Cr(III) was oxidized to Cr(VI) by using $KMnO_4$ as oxidizing agent. The oxidized form of chromium formed the complex with diphenylcarbazide. UV-visible spectroscopy was used to examine the Cr(VI). It was observed that chromium was not completely oxidized by permanganate at high temperature but Cr(III) was totally converted into Cr(VI) by cerium(IV) at room temperature [13]. Chromium(III) was oxidized to chromium(VI) from biological samples with a combination of acids such as HNO_3, H_2SO_4 and $HClO_4$. Chromium(VI) was separated from solution with tributyl phosphate in methyl isobutyl ketone at 277 K. Acetylene flame was used for aspiration of extract. UV-Visible spectroscopy was used for quantitative analysis of chromium(VI) [14]. Persulphate oxidation method was reported for conversion of Cr(III) to Cr(VI) at room temperature. Anion exchange column was used for separation of Cr(VI) species from solution. Spectrophotometry was used for quantitative analysis of the product Cr(VI) [15]. Cr(III) was converted into Cr(VI) on gold ring electrode. Two anodic Tafel plots were obtained. A new mechanism was developed to study experimental results comparable to Bockris mechanism [16]. A titanium-platinum anode was used for electrochemical oxidation of Cr(III) to Cr(VI). Different factors which affected the reaction were studied by using Doehlert design. Nemrod software was used to study Faradic (R_F) yields of the reaction. The results showed that oxidation of Cr(III) was highly dependent on current intensity and electrolysis time [17]. A new method to reduce industrial hazardous wastes was reported. Chromium plating industries released chromium waste in the form of Cr(III). Chromium sludges were removed by oxidation of chromium(III) to chromium(VI) in air at 850 - 900 ^{0}C. It was observed that regeneration of chromium(VI) from spent chromium bath was environmentally as well as economically favorable [18]. Pure and Cu doped lead dioxide electrodes were used for anodic oxidation of chromium sulphate in divided and undivided electrochemical cell. The results showed that 74% chromium(III) was converted into chromium(VI) for 85.5 hours electrolysis by using lead dioxide anode and 84% chromium(III) was converted into chromium(VI) for 90 hours electrolysis at Cu-doped lead dioxide anode [19]. The results compared with the electrolysis result of Bi doped lead dioxide anode and it was concluded that Bi doped lead dioxide anode had greater electrocatalytic activities for electrolysis of chromium(III) solution than Cu-doped lead dioxide anode. A concentrator cell technology was used for oxidation of chromium(III) to chromium(VI). In this cell electrolysis and electrodialysis processes were combined. The percentage of chromium conversion was 92% along with 90% copper recovery [20]. But due to complication of experimental set-up and energy consumption of this cell, divided cell with with doped electrodes was better. The reactor with membranes sintered at 1300°C was for restoration of chromium(VI). The conversion of chromium(VI) was 90% but current efficiency of the reaction was only 25% [21]. Other related recent work can be found in literature [22-26].

In this work, pure and doped lead dioxide layers were electrodeposited on titanium base material. The prepared electrodes were used for electrooxidation of chromium(III) sulphate solution in H_2SO_4 at room temperature. The electrocatalytic behavior of lead dioxide and doped lead dioxide electrodes were compared.

Results and Discussion:

Titanium based lead dioxide and doped lead dioxide electrodes were prepared from acidic bath by electrodeposition method at room temperature, 3 - 4 V deposition potential and 0.007 - 0.013 A/cm^2 current density. The prepared electrodes were used as anodes and lead as cathode for electrolysis of chromium(III) solution in electrolytic cell. 2.0 mM solution of chromium(III) in distilled water was used as anolyte in anodic compartment of the cell and pH of the anolyte was maintained at 3 - 4 by 1.0 M sulphuric acid. 1.0 M sulphuric acid was used as catholyte (Table 1). Two portions of cell were connected with salt bridge filled with 1.0 M sulphuric acid. Electrolysis was done for 60 hours by using lead dioxide as anode at 3.2 V and 0.47 mA current. The electrode area used for electrolysis was 4.5x2.2 cm^2. Similarly for iron doped lead dioxide, electrolysis was done at 4.5 V and 0.45 mA, for bismuth iron doped lead dioxide voltage was 2.8 V and current 0.40 mA and for bismuth doped lead dioxide chromium(III) solution was oxidized at potential 3.3 V and current 0.36 mA. The electrode area was kept constant to compare the results. A double beam spectrophotometer, UV-1650 PC, Shimadzu, Japan, was used for analysis of oxidized solution after electrolysis. Chromium(VI) solutions of different concentrations were prepared in distilled water. The absorbance at each concentration was determined at 350 nm by UV-visible spectrophotometer and calibration curve for Cr(VI) was drawn (Fig. 1).

The percentage conversion of Cr(III) to Cr(VI) and current efficiency for each anode were measured. The results of electrolysis of chromium(III) at same temperature, same anode area, same concentration of Cr(III), and same electrolysis time by using different electrodes are summarized in Table 1. The results showed that bismuth-doped lead dioxide electrode had the highest electrocatalytic activity of all the prepared electrodes. After 60 hours electrolysis, the surface of each electrode was studied. The shine, corrosion resistance and appearance of each electrode were observed to be very good. So these electrodes can be scaled up for industrial purpose, however, best results were obtained with Bi doped lead dioxide anode. This study was designed for preparation of titanium based anodes as well as for the electrolysis of chromium(III) solution. This method can be widely used due to simple apparatus, good current efficiency and better percentage conversion of chromium(III) to chromium(VI). Titanium based lead dioxide electrodes can be used for industrial purposes due to long life and good electrocatalytic activity shown by these electrodes.

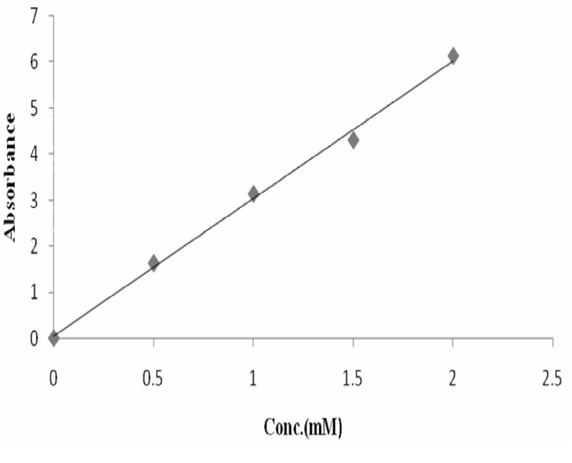

Fig. 1: Calibration curve for Cr(VI) at wavelength 350 nm

Experimental

Chemicals used

Lead nitrate, BDH, England; nitric acid (65 % pure), E Merck, Germany; sodium fluoride, Riedal de-Haen, Germany; oxalic acid, Riedal de-Haen, Germany; bismuth nitrate, BDH, England; ferric nitrate, BDH, England; sulphuric acid, BDH, England; potassium dichromate, Riedal de-Haen, Germany and chromium(III) sulphate, commercial grade purchased from local market.

Preparation of electrodes

Four types of lead dioxide coatings were electrodeposited on Ti to obtain:

1. lead dioxide electrode
2. iron doped lead dioxide electrode
3. bismuth doped lead dioxide electrode
4. bismuth iron doped lead dioxide electrode

Titanium sheet as anode and stainless steel rod as cathode were used for electrodeposition process. Acidic baths of lead nitrate with different dopants were prepared for electrodeposition [22-25]. The preparation of bath was dependent on the nature of dopants. Addition of fluoride ion to nitrate plating bath improved the adhesion of lead dioxide deposits and reduced the formation of titanium dioxide layer.

Electrodeposition procedure

Titanium sheet was first roughened with emery papers of different grade for removal of titanium dioxide layer. Cleaned Ti substrate was etched in 1.6 M boiling oxalic acid before coating for three hours. Dark purple color of the solution during etching indicated completion of the etching. After etching, the Ti substrate was washed with distilled water and instantly put into baths for electrodeposition. Direct current was applied for electrodeposition by using a DC power supply.

Electrode 1

Lead dioxide layer was electrodeposited on titanium substrate from acid bath having composition 1.0 M $Pb(NO_3)_2$+1.0 M HNO_3+0.04 M NaF. Electrode deposition was carried out at room temperature, voltage 3 - 4 V and current density 0.012 - 0.013 A/cm^2 for five hours. Area of prepared electrode was 6×2.2 cm^2.

Table 1. Electrolysis of chromium(III) solution

Anode (coating on Ti)	Anode area, cm^2	Cathode	Cr^{+3} (mM)	Time, hrs	% Conversion	C. E.
PbO_2	**4.5×2.2**	**lead**	**2.0**	**60**	**64**	**57.03 %**
Iron-doped PbO_2	**4.9×2**	**lead**	**2.0**	**60**	**68**	**59.56 %**
Bismuth-iron-doped PbO_2	**4.9×2**	**lead**	**2.0**	**60**	**74**	**67.0 %**
Bismuth-doped PbO_2	**4.9×2**	**lead**	**2.0**	**60**	**80**	**74.0 %**

Electrode 2

Iron doped lead dioxide layer was coated on Ti substrate. Iron doped lead dioxide electrode was prepared by electrodeposition from bath, 0.5 M $Pb(NO_3)_2$+0.5 M HNO_3+0.04 M NaF+0.01 M $Fe(NO_3)_3$ at room temperature, voltage 3.6 - 3.80 V and current density 0.01 A/cm^2 for 4 hours. Area was 5.3×1.9 cm^2.

Electrode 3

Bismuth doped lead dioxide film was electrodeposited on Ti from 0.5 M $Pb(NO_3)_2$+0.5 M HNO_3+0.01 M $Bi(NO_3)_3$ bath. Electrodedeposition was carried out at room temperature, voltage 3.4 - 3.60 V at current density 0.008 A/cm^2 for 4 hours. Electrode with area 5.0× 2.0 cm^2 was prepared.

Electrode 4

Double layer electrode was prepared by using titanium substrate. First a layer of Fe doped-PbO_2 was deposited onto etched titanium sheet from the bath having composition 0.5 M $Pb(NO_3)_2$+0.1 M HNO_3+0.04 M NaF+0.01 M $Fe(NO_3)_3$ at current density 0.01A/cm^2 for one hour. Secondly, Bi doped-PbO_2 layer was deposited from bath having composition 1.0 M $Pb(NO_3)_2$+1.0 M HNO_3 +0.01 M $Bi(NO_3)_3$. First layer was deposited at room temperature, voltage 3.5 V and current density 0.01 A/cm^2 for one hour and second layer was deposited at room temperature, voltage 3.2 V and current density 0.008 - 0.01A/cm^2 for two hours. Area of the finished electrode was 7.2×2 cm^2.

Electrolysis of Chromium(III) Sulphate Solution

Chromium sulphate solution was oxidized in divided cell. The prepared electrodes were used as anode and lead as cathode. Acidified 2.0 mM chromium sulphate solution was used as anolyte and 1.0 M sulphuric acid as catholyte. Two portions of the cell were connected by salt bridge containing 1.0 M sulphuric acid. The electrolysis was carried out for 60 hours and oxidized solution was examined by UV-visible spectrophotometry.

Conclusions

The results showed that titanium based electrodes were chemically stable and had good catalytic properties for anodic oxidation of chromium (III) species in sulphuric acid. It was concluded that electrocatalytic activities of electrodes were in the order Bi doped PbO_2 > bismuth iron doped PbO_2 > iron doped PbO_2 > PbO_2. Extended electrolyses showed that precious metal anodes can be replaced by these electrodes for industrial use.

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