Regeneration of Spent Chromium Solutions

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Abstract. Regeneration of spent Cr^{+6} solutions using lead dioxide anodes was investigated. Pure and Cu^{+2} doped lead dioxide electrodes were prepared by electrodeposition of lead dioxide on carbon-based substrates using Pb^{+2} nitrate bath at 1.5-1.75 V, pH 4-4.5, temperature 60-70 °C and current density 0.0125-0.0175 A/cm². Electrolyses of prepared Cr^{+3} solutions, both in divided and undivided cells, were used to investigate the electrocatalytic activity, adhesion and stability of lead dioxide electrodes, which can serve as industrial electrodes. UV-visible spectrophotometry was used for estimating conversion of Cr^{+3} to Cr^{+6}. The electrocatalytic activity of lead dioxide was increased by doping of Cu^{+2} ions.

Keywords. regeneration, chromium+6, lead dioxide electrode

Introduction

Chromium used in the electroplating and tanning industries causes environmental pollution through the generation of effluent. Processes based on "recovery-reuse" are now being increasingly projected and used.

Earlier, Van Andel and Janssen (2002) used a new anode material, namely boron-doped diamond, to investigate the oxidation of Cr^{+3} to Cr^{+6}. It was found that the current efficiency for Cr^{+3} oxidation decreases with increasing total current density. The current density of Cr^{+3} oxidation increases linearly with increasing its Cr^{+3} concentration and is practically independent of the Cr^{+6} concentration. It was concluded that the diffusion of Cr^{+3} is the rate-determining step for its oxidation at Cr^{+6} concentrations from 40 to 160 mol/m³. A filter-press type cell divided into two compartments by a cation exchange membrane was proposed.

For regeneration of spent hard chrome plating solution, Ahmed *et al.* (2001) carried out work on an electrolysis cell with an ion exchange membrane (Nafion-117), used as a simulated plating bath containing Cu^{+2}, Fe^{+2}, Ni^{+2}, and Cr^{+3} as contaminants, with a lead anode and a gas diffusion cathode, for different experimental conditions at room temperature. The results indicated the possibility of decreased energy consumption and better removal rates over traditional methods.

The regeneration of Cr^{+6} and the recovery of etched copper from chromium etching solutions by electrodialysis was improved by the addition of a concentrator cell in the catholyte chamber containing ion-exchange resins or activated carbon

cloth (Chaudhary *et al.*, 2006). The maximum regeneration of chromium and recovery of copper were however less than 80% and 90% respectively. A novel combination of electrolysis with electrodialysis and concentrator cell technology was developed that achieved 92% chromium regeneration and 90% copper recovery.

Welch *et al.* (2004) examined the electrochemical oxidation of Cr^{+3} to Cr^{+6} species in aqueous solution. The responses of boron-doped diamond glassy carbon and gold electrodes were probed towards the oxidation of trivalent chromium over a wide pH range (1.0-13.0). High quality voltametric profiles were found to appear only at a gold electrode and in solution of pH greater than 12. The oxidation reaction proceeded via multi-step mechanism.

Devilliers *et al.* (2003) proposed a procedure for preparing lead dioxide-based electrodes with a platinum under-layer deposited on titanium. The current efficiency of the prepared electrodes was compared with that of lead/lead dioxide and Ebonex®/lead dioxide electrodes with different pH conditions. The titanium/platinum/lead dioxide were found to have a very good electrochemical behavior (current efficiency: Φ=0.93 for pH 2), and may be used as dimensionally stable anodes for the oxidation of Cr^{+3}.

Recently, streams/wastes containing chromium suitable for electroplating have been identified and the applicability of conventional and promising techniques to treat such substances have been reviewed (Agarwal *et al.*, 2006). Membrane electrochemical reactor was developed for continuous regeneration of spent chromium baths (Sanchez *et al.*, 2006). Electrooxidation of Cr^{+3} to Cr^{+6} species was investigated on the (111) plan of a gold single crystal in a highly alkaline

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solution (Skoluda, 2007). Recently, electrolytic processes using lead dioxide anodes have been reviewed (Haque *et al.*, 2005). Considering all options, in the present study, lead dioxide anodes were used for regeneration of spent Cr^{+6} solution.

Materials and Methods

Chemicals. Nitric acid (65% pure), HNO_3, E-Merck, Germany; Sulfuric acid, H_2SO_4, BDH, England; Potassium dichromate, $K_2Cr_2O_7$, Riedal-de-Haen, Germany. Other chemicals, lead nitrate, chromium sulphate anhydrous, sodium hydroxide, lead sulphate, copper sulphate and sodium bicarbonate, were from Aldrich and were used as received. Copper nitrate was prepared in the laboratory. For this purpose, pure copper sheet was cleaned and dissolved in nitric acid. The excess of nitric acid was removed, and the blue-green (Budavari, 1996) crystals of copper nitrate were washed, dried and used.

Preparation of the lead dioxide electrodes. Two types of lead dioxide electrodes were prepared:

1- Cu^{+2}-doped lead dioxide electrode
2- Pure lead dioxide electrode

Anode. Carbon-based substrate of different dimensions was used as base material for depositing both pure and Cu^{+2}-doped lead dioxide.

Cathode. Stainless steel sheet, 12.5x3.75 cm², was employed as cathode for the anodic deposition of lead dioxide.

Preparation of the bath. For the electrodeposition of the lead dioxide, lead nitrate bath was used (Narasimham and Udupa, 1976). Lead nitrate, 300 g, was weighed and dissolved in 700 ml of distilled water. Copper nitrate, 25-30 g/l, was added to the solution. The solution was made 1000 ml with distilled water, heated at 70 °C for a few minutes, allowed to cool slowly, and then filtered. pH of the bath was adjusted at 4-4.5 by the addition of sodium bicarbonate. Copper nitrate was not added in the bath when only lead dioxide was deposited.

Electrodeposition of lead dioxide. Pre-cleaned carbon-based anode was immersed in the bath and direct current was

Table 1. Conditions for anodic deposition of lead dioxide

Parameters	Conditions
Voltage	1.5-1.75 V
pH	4-4.5 (adjusted by addition of sodium bicarbonate)
Temperature	60-70 °C
Current density	0.0125-0.0175 A/cm²

applied using home-built direct current power-supply. The electrodeposition conditions are given in Table 1. The current was measured using multimeter, DT-830B whereas the voltage was measured with digital voltmeter, connected parallel in the circuit of direct current power-supply.

Details of different electrodes prepared. Three electrodes of different areas were prepared for the electrolysis of Cr^{+3} sulphate solutions of different concentrations to check the durability of the electrodeposit.

Electrode 1. The area of the carbon-based substrate taken for electrodeposition of Cr^{+2}-doped lead dioxide was 7 x 3.5 cm². Electro-deposition was carried out at temperature 60-70 °C, pH 4-4.5, voltage 1.6-1.75 V, and current density 0.0061-0.0078 A/cm² for five hours. The electrode thus prepared was used for the electrolysis of 0.0625 mM Cr^{+3} sulphate solution and background electrolyte in undivided cell, and for the electrolysis of 1.0 mM Cr^{+3} sulphate solution in divided cell.

Electrode 2. The area of the carbon-based substrate taken for electrodeposition of Cr^{+2}-doped lead dioxide was 6 x 3.5 cm². Electrodeposition was carried out at temperature 60-70 °C, pH 4-4.5, voltage 1.40-1.60 V, and current density 0.0071-0.0114 A/cm² for three hours. The electrode thus prepared was used for the electrolysis of Cr^{+3} sulphate solutions of different concentrations to check the durability of the electrodeposit.

Electrode 3. The area of the carbon-based substrate taken for electrodeposition of pure lead dioxide was 7 x 2.9 cm². Electro-deposition was carried out at temperature 60-70 °C, pH 4-4.5, voltage 1.35-1.55 V, and current density 0.0054-0.0108 A/cm² for three hours.

Electrolysis of chromium sulphate solution. Electrolysis of chromium sulphate solution was run both in divided and undivided cells. In undivided cell, electrolysis was run by using Cu^{+2}-doped lead dioxide electrode as anode and a platinum wire as cathode. In divided cell, electrolysis was run using both pure and Cu^{+2}-doped lead dioxide electrodes as anodes. Nickel rod, 15 x 2.5 cm², was employed as cathode. The salt bridge, connecting two compartments, was filled with 1.0 M sulphuric acid. The two ends of the salt bridge were terminated by glass wool and agar.

Analysis of the solutions. The electrolyzed and other solutions were analyzed by UV-visible spectroscopy. The double-beam spectrophotometer, UV-1601 PC, Shimadzu, Japan, was used for the purpose.

Results and Discussion

Pure and Cu^{+2}-doped lead dioxide electrodes were prepared from lead nitrate bath (Narasimham and Udupa, 1976).

The electrodes prepared were employed as anodes for the oxidation of Cr^{+3} to Cr^{+6}. Electrolysis of Cr^{+3} sulphate solution was run both in divided and undivided cells.

In undivided cell, the platinum wire was used as cathode. Cr^{+3} sulphate solution, 0.625 mM, was prepared in the 1.0 M sulphuric acid. The electrolysis was run for five hours. The potential was 1.64-2.50 V. Electrolysis of background electrolyte, 1.0 M sulphuric acid, was run in undivided cell using Cu^{+2}-doped lead dioxide electrode for five hours. The potential was 2.50 V. The current was measured with multi-meter (TES-2201). Only Cu^{+2}-doped lead dioxide electrode (electrode no.1) was used as anode in undivided cell.

In divided cell, nickle electrode was employed as cathode and lead dioxide, as anode. The catholyte was 1.0 M sulphuric acid and the anolyte was 1.0 mM Cr^{+3} sulphate solution in distilled water. The pH of the anolyte was adjusted to 3.5-4.0 by addition of sulphuric acid. The two compartments were connected through salt bridge, containing 1.0 M sulphuric acid. The electrolysis was run for three and half hours. The potential was 14.0 V, necessitated by the presence of wide salt bridge and large separation between containers. In an optimized configuration, the operating potential is expected to be considerably less than this value, and the current density 1.62-2.25 mA/cm^2. The potential was measured using multimeter (DT-830B) and current was measured with multimeter (TES-2201).

Analysis of the solutions. UV-visible spectrophotometer was used to analyze the solution. Analyses of 1.0 M sulphuric acid, Pb^{+2} solution, Cu^{+2} solution and electrolyzed Cr^{+3} sulphate solution were also carried out. UV-visible spectrum for Cr^{+6} solution is given in Fig. 1. The spectra of Cr^{+6} solutions of different concentrations were also taken in order to get the calibration curve (Fig. 2).

At wavelength of 345-350 nm, no other ions interfered, as shown in Fig. 1. It was found that in undivided cell, Cr^{+3} was not oxidized to Cr^{+6} on Cu^{+2}-doped lead dioxide electrode. However, in divided cell, the Cr^{+3} was oxidized to Cr^{+6} on Cu^{+2}-doped lead dioxide electrode at pH 0-1, and concentration 1.0 mM in 1.0 M sulphuric acid. Conversion from Cr^{+3} to Cr^{+6} was 14-15 %. Under the same conditions, conversion of Cr^{+3} to Cr^{+6} at pure lead dioxide electrode, was 10%. The influence of concentration of Cr^{+3} sulphate and time of electrolysis on conversion of Cr^{+3} to Cr^{+6} is shown in Table 2.

Concentration of Cr^{+3} sulphate was varied and the time for total conversion was noted. In case of pure lead dioxide anode at 10 mM chromium sulphate, conversion of Cr^{+3} to Cr^{+6} was maximum 75.6%, and in case of Cu^{+2}-doped lead dioxide anode at 10 mM Cr^{+3} sulphate, conversions of Cr^{+3} to Cr^{+6} was maximum 84%. Life of both the electrodes was studied.

The appearance, abrasion resistance and adhesion of the deposits were very good. The electrodeposits had good metal like shine. The Cu^{+2}-doped lead dioxide electrodes had grayish color. Furthermore, electrocatalytic activity of Cu^{+2}-doped lead dioxide anode was more than pure lead dioxide anode.
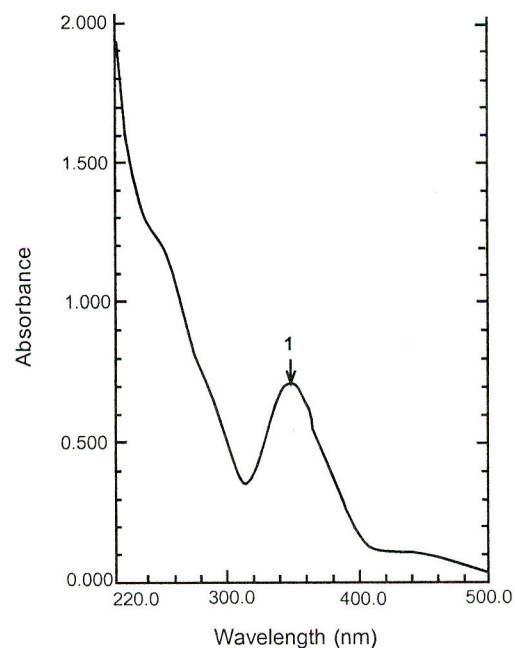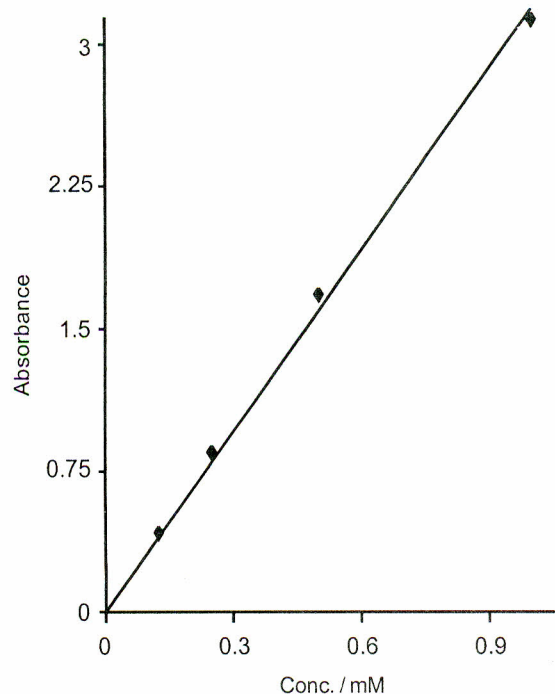

Fig. 1. UV-visible spectrum of Cr^{+6}.

Fig. 2. Calibration curve of Cr^{+6} at wavelength 350 nm.

Table 2. Influence of Cr^{+3} sulphate and time on conversion rate of Cr^{+3} to Cr^{+6}

Cell	Electrode	Cr^{+3} (mM)	Electrolysis duration (h)	Conversion to Cr^{+6} (%)
Divided	Lead dioxide anode	1	3.5	10
			45.5	60
		10	85.5	74
			122	75.6
Divided	Cu^{+2}-doped lead dioxide anode	1	3.5	14
			45.5	60
		10	90	84
			117	84

Conclusion

Synthetic Cr^{+3} solutions were electrolyzed using self-electro-deposited pure and Cu^{+2}-doped lead dioxide electrodes. The regeneration of Cr^{+6} was conducted at different concentrations of trivalent chromium in both divided and undivided cells. In undivided cell, trivalent chromium was not oxidized. Electrocatalytic activity of Cu^{+2}-doped lead dioxide was found to be more than that of pure lead dioxide electrode. The electrodeposits had good adherence, stability and lifetime. In case of pure lead dioxide electrode, electrodeposit was of black colour, and in case of Cu^{+2}-doped lead dioxide electrode, electrodeposit was grayish black in colour. Continuous electrolyses for several hours ($\geq$ 72 h.) showed that these electrodes are prototypes for industrial anodes for the regeneration of spent Cr^{+6} solutions.

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