THE ELECTROCHEMICAL REGENERATION OF Cr(VI) IN SULPHURIC ACID

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The oxometal ions of transition metals are excellent oxidants for organic compounds. The Cr(VI), in presence of proton has been used extensively in the synthesis of organic compounds in research laboratories as well as in industries [1-2]. The problem associated with this versatile reagent is its toxicity. The disposal of spent Cr(VI) creates the environmental hazard. There are industrial practices to reduce the spent Cr(VI) by SO_2 and convert them into insoluble metal hydroxide sludges for disposal. Alternatively chemical oxidants like peroxides and persulphate-reoxidise Cr(III) to Cr(VI) for reuse. However, chemical oxidation results in large volume expansion and interference from added cation may also arise; in addition this method is not economical.

The problem of electrochemical regeneration has been addressed by many investigators [3-8]. The most of the earlier workers have made use of a divided cell. This results in increase of the cell voltage and hence power consumption . So scale up becomes difficult. There is only one reference [8] where an undivided cell is used but current efficiency reported is quite low even at high proton concentration. Therefore, the problem of regeneration has been reinvestigated thoroughly. The study includes the effect of : (1) proton concentration (11) concentration of Cr(III) in electrolyte (iii) temperature (iv) preparation of anode surface (v) effect of separator (vi) duration of electrolysis (vii) current density and (viii) addition agents.

The experiments on regeneration were carried at a laboratory scale as well as on 80A cell and the results have been discussed.

EXPERIMENTAL

The laboratory scale experiments were carried out in one litre pyrex glass beaker which served as an electrolytic cell. In all the experiments,a lead strip (30cm^2) was pre-polarised in 2 N H_2SO_4 at c.d. of 25 mA/cm^2 for 30 minutes and was used as an anode. A blue asbestos covered strip of lead (7.5 cm^2) was used as a cathode.

The electrolyte is agitated using a stirrer motor. The potential of the anode was monitored using V.T.V.M. against Hg/Hg_2SO_4 reference electrode. During the evaluation of the regeneration system,the regenerated solution was monitored for Cr(VI) at regular intervals iodometrically.

The 80A electrolytic cell was a rectangular PVC box of 20 l capacity. The experiments were also tried in lead claded M.S. tank. But it was found that lead claded M.S.tanks were not suitable for the reaction because of the formation of lead sulphate which makes the cell operation uneconomic. In these experiments the lead anode having 3 mm perforation with an apparent area of 16 dm^2 was used and asbestos wrapped lead (4 dm^2) was used as cathode.

RESULTS AND DISCUSSION

Regeneration of Cr(III)

The formation of PbO_2 on anode surface is of critical importance. The parameters which affects the formation of PbO_2 during pre polarization on vergin anode surface are temperature, acid concentration and impurities present in the anode material. It was observed that it is economical to use blue asbestos wrapped cathode. Different cell configurations have been tried.

It has been observed that it is possible to oxidize Cr(III) quantitatively if the duration of electrolysis is prolonged, and extra 50% current was passed than required theoretically. In the presence of small quantities of ClO_4^-/ Ag^+/ $S_2O_8^{2-}$ (not more than 1 m mol/l.) the current efficiency of the system increases to 88% (Table 1). In presence of catalyst extra current required was only 35 - 40%.

TABLE 1

EFFECT OF FOREIGN IONS ON CURRENT EFFICIENCY-ELECTROLYTE 10% H_2SO_4 - 55.47 mg Cr III/ml

Temp. 52°C	Cell Voltage 3.4 V			
Add Agent (1 mM)	-	ClO_4^-	$S_2O_8^{2-}$	Ag^+
Curr eff %	74.16	79.3	82.0	88.0

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The current density is one of the critical parameters for the regeneration. Higher current density (more than 5A/dm^2) leads to the side reaction of oxygen evolution.

The anodic and cathodic reaction in electrolytic regeneration can be represented by equations (1) and (2).

$$Cr^{3+} \longrightarrow Cr^{6+} + 3e^- \quad ...(1)$$

$$3H^+ + 3e^- \longrightarrow 3/2\ H_2 \quad ...(2)$$

The stoichiometric reaction as given in equations (1) and (2) indicates that this is the ideal system for electrochemical regeneration of oxidant in a homogeneous redox system. The overall reaction can be given by equation (3).

$$Cr_2(SO_4)_3 + 8\ H_2O \rightarrow 2\ CrO_4^{2-} + 10H^+ + 3SO_4^{2-} + 3H_2 \quad ....(3)$$

At the anode a competiting reaction

$$H_2O \longrightarrow 2H^+ + 2e^- + {}^1/_2\ O_2 \quad ....(4)$$

is possible. This reaction would reduce the current efficiency of reaction (1).

It was observed that proton concentration has considerable effect on regeneration efficiency. This is so because it directly affects the redox potential of Cr(VI) Cr(III). The effect of H_2SO_4 on the oxidation efficiency is given in Table 2.

It is also observed that concentrations of Cr(III) in the electrolyte affects the regeneration of Cr(VI). It is likely that Cr(III) when present in large concentration may combine with Cr(VI) formed and give reactive Cr(IV)/ Cr(V) species and these are not further oxidized. The effect of Cr(III) on the oxidation is given in Table 3.

TABLE 2

EFFECT OF CONCENTRATION OF H_2SO_4 ON OXIDATION of Cr III; CURRENT DENSITY 5 A/dm^2

H_2SO_4 (%)	6.5	10.0	15.0
Cell Voltage (v)	5.0	4.0	3.0
Current efficiency (%)	62.5	74.16	76.6

TABLE 3

EFFECT OF Cr(III) CONCENTRATION ON OXIDATION CURRENT EFFICIENCY; SYSTEM 10% H_2SO_4

Cr(III) (Mg/ml)	13.87	27.73	41.60	55.47
Current efficiency (%)	44.5	62.5	66.0	74.16

Thus it is found that concentration of Cr(III) and H^+ greatly influences the regeneration of Cr(VI). The maximum current efficiency of the system in absence of any catalyst was found to be 76.6% in presence of 15% H_2SO_4 containing 55.47 mg/ml of Cr(III) at an anode current density of 5A/dm^{2}at 52°C. The temperature of the electrolyte affects the O_2 evolution on PbO_2anode. If the temperature of electrolyte is maintained at 30 to 40°C, the current efficiency of the system comes down to 65 to 70%.

The presence of organic impurities affects the regeneration efficiency as seen in Table 4. Therefore it is better to remove the organic impurities present in the spent electrolyte by charcoal treatment or by boiling off under vacuum.

The regenerated Cr(VI) has been used for the oxidation of aranic compounds. The results are given in Table 4.

Oxidation Studies of Organic Compounds

The mechanism for the chromic acid oxidation of an alcohol involves a rapid reversible formation of the chromate ester, either as the mono-or di-ester followed by a cleavage of the C-H bond as the rate determining step. If the OH group of alcohol is considerably hindered, the chromate ester cannot be formed. As a

TABLE 4

EFFECT OF ORGANIC MATTER IN ELECTROLYTE; CURRENT EFFICIENCY AFTER REUSE

Number of reuser	First	Second	Third	Fourth
Without removing the organic impurities (%)	65.4	64.0	64.0	63.0
After removing the organic impurities (%)	79.3	78.0	78.0	77.5

result, oxidation does not occur even though the C-H bond is susceptible to cleavage. In highly hindered alcohols, formation of the chromate ester becomes the rate determining step. During studies on oxidation of secondary terpine alcohols, it was found that the oxidation of axial-OH group requires more time than the equitorial group. The oxidation studies of these secondary alcohols were carried out in an organic solvent like benzene, methylene chloride and ether. Reason for this delayed oxidation is due to the formation of chromate ester at liquid-liquid interface. For this liquid-liquid interface reaction the equitorial-OH group has the right stereo electronic arrangement for the formation of intermediate ester which becomes the rate determining step in systems studied by us.

Oxidation reactions can be written as

$$R_2CHOH + Cr^{+6} \rightarrow R_2C = O + Cr^{+4} + 2H^+ \quad ..(6)$$

$$Cr^{+4} + Cr^{+6} \longrightarrow 2\,Cr^{+5} \quad ..(7)$$

$$2Cr^{+5} + R_2CHOH \longrightarrow R_2C = O + Cr^{+3} + 2H^+ \quad ... (8)$$

Overall reaction can be written as

$$3\,R_2CH\text{-}OH + 2Cr^{+6} \rightarrow 3\,R_2CO + 2\,Cr^{3+} + 6H^+ \quad .... (9)$$

$$R_2CHOH + Cr^{+6} \longrightarrow R_2CO + Cr^{+4} + 2H^+$$

To avoid the formation of Cr^{+4}, the proper concentration of acid and organic substrates become essential.

Based on the results on laboratory scale, a 80A cell was operated with 16 litres of electrolytes containing 2 N H_2SO_4 and 55.47 mg/ml of Cr(III). The conversion of Cr(III) to Cr(VI) in this cell was found to be 40 gm per hour. The life time of lead anode is quite high in our system.

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REFERENCES

1. K.B. Wiberg, (Ed) *Oxidation by chromic acid and chromyl compounds in oxidation in Organic Chemistry Part A*, **Academic Press, New York** (1965).

2. R.A. Sheldon and J.K. Kochi, *Metal catalysed oxidations of organic compounds*, **Academic Press, New York** (1981).

3. Regelsherge Z., *Angew. Chem.* **12** (1899) 1123.

4. R.F.J. Gross, and A. Hickling, *J. Chem. Soc* (1937) 325.

5. S.G. Digbe, *J. Ind. Chem. Soc.*, **23** (1946) 291.

6. A.W. Wylie, *Aust. J. Appl. Sc.*, **1** (1950) 376.

7. B.I. Tomilov, *Zhar. Prackol Khim*, **30** (1957) 1785.

8. S. Chidambaram, M.S.V. Pathy and H.V.K. Udupa, *Indian J. Technol.* **6** (1968) 12.

READERS' COLUMN

Question: We have a problem in Nickel plating of small components in a barrel. The plating is non uniform and a few are only partially plated. We use propritary bright metal plating solution. How can one get uniform coating?

Answer: When barrel plating small components, very often there is the possibility of interlocking or stacking of the components resulting in uneven distribution of current and partial shielding of the surfaces. This can be eliminated by introducing small amount of beads of glass or ceramic material which prevent interlocking and stacking and keep the surfaces fully exposed to the solution.

Question: We are anodising small items holding them in a perforated basket in a sulphuric acid bath. We find the anodising is non-uniform resulting in a large amount of rejects. What is the solution?

Answer: Two factors are involved. Firstly the items should have good electrical contact for the anodic reaction to proceed. Secondly if they shield each other, again the result will be poor. To ensure good electrical contact, they are to be fairly tightly packed with a closure lid. This might result in poor circulation of the solution, To avoid this there should be an inlet at the top of the closure to force the solution into the basket and this ensures uniform circulation and exposure of the items to the solution. For this purpose a solution circulating pump has to be used.