

# The electrochemical production of cobaltic sulphate

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The electrochemical preparation of cobaltic sulphate has been studied and we have found that the reaction is best effected in 40 wt% H<sub>2</sub>SO<sub>4</sub> in the presence of silver ions as the catalyst, using PbO<sub>2</sub> as the anode, with a low current density and a low conversion.

## 1. Introduction

Uncomplexed cobaltic salts can be prepared by oxidation of cobaltous salts with strong oxidizing agents such as fluorine [1], ozone [2] and sodium persulphate [3].

The electrolytic method was first described by Swann and Xanthakos [4]. The oxidation of cobaltous sulphate in 10 N sulphuric acid at a platinum anode is certainly a simple way to obtain cobaltic salts, but the current efficiency of the reaction was low (30%).

The cobaltic sulphate can be used as an oxygen carrier in the oxidation of organic compounds [5, 6] and after regeneration by the electrolytic method, as a catalyst in the oxidation of some aromatic hydrocarbons [7].

A study was therefore undertaken to determine the optimum conditions for the electrolytic preparation of cobaltic sulphate.

## 2. Experimental

The experiments were carried out in an electrolytic cell (150 cm<sup>3</sup> volume); the anode was made of platinum or lead dioxide electrodeposited onto platinum (16 cm<sup>2</sup> area) (platinized titanium and graphite were also used) and the cathode was a platinum wire (1.4 cm<sup>2</sup> area). For experiments with a diaphragm it was enclosed in a 2 cm<sup>3</sup> porous porcelain pot. Stirring was provided by a magnetic bar.

Some preliminary experiments at higher and lower temperatures showed that 11-12°C was the most suitable temperature. This temperature was

maintained throughout the whole investigation. The cobaltic sulphate was determined by iodometric titration and the oxygen evolved was measured using a gas burette.

The experiments were carried out at different current densities, sulphuric acid concentrations, conversions, electrode materials, using a divided and an undivided cell and in the presence and absence of a catalyst (Ag<sub>2</sub>SO<sub>4</sub>).

## 3. Results

### 3.1. *Electrolysis without catalyst in a divided cell using a platinum anode*

**3.1.1. Influence of current density.** The current efficiencies for cobaltic sulphate formation as a function of current density at four different quantities of electricity passed (expressed in percentages of the theoretical charge needed for complete conversion of cobaltous sulphate to cobaltic sulphate) are shown in Fig. 1.

At high current density and charge the current efficiency for cobaltic sulphate formation is decreased. This decrease is especially rapid when the current density increases from 10 to 50 mA cm<sup>-2</sup>; at higher current density the current efficiency is lower but much less affected by the current density and the charge passed.

### 3.2. *Electrolysis in the presence of Ag<sub>2</sub>SO<sub>4</sub> in a divided cell, using a platinum anode*

**3.2.1. Influence of conversion.** Fig. 2 shows the dependence of the current efficiency for cobaltic

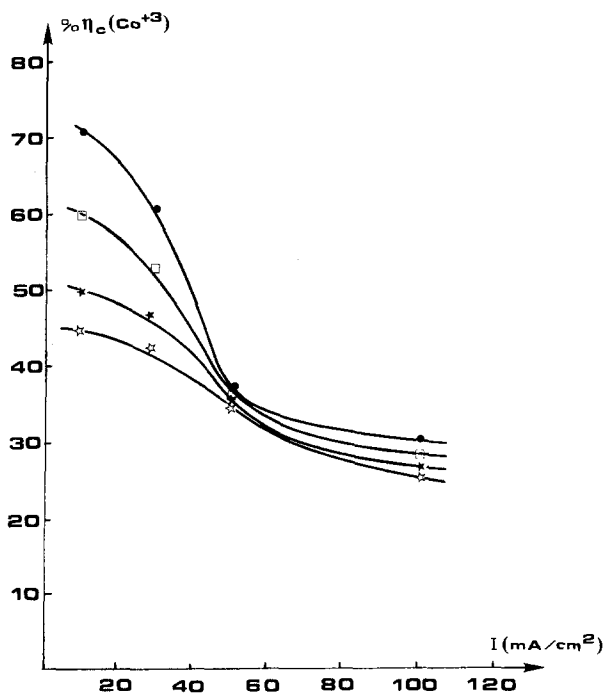


Fig. 1. Variation of the current efficiencies of cobaltic sulphate formation with current density in a divided cell. • 50%, □ 100%, ★ 150%, ☆ 200% of the theoretical charge for complete conversion.  $\text{H}_2\text{SO}_4$  concentration, 40 wt%;  $\text{CoSO}_4$  concentration, 0.49 M; Pt anode.

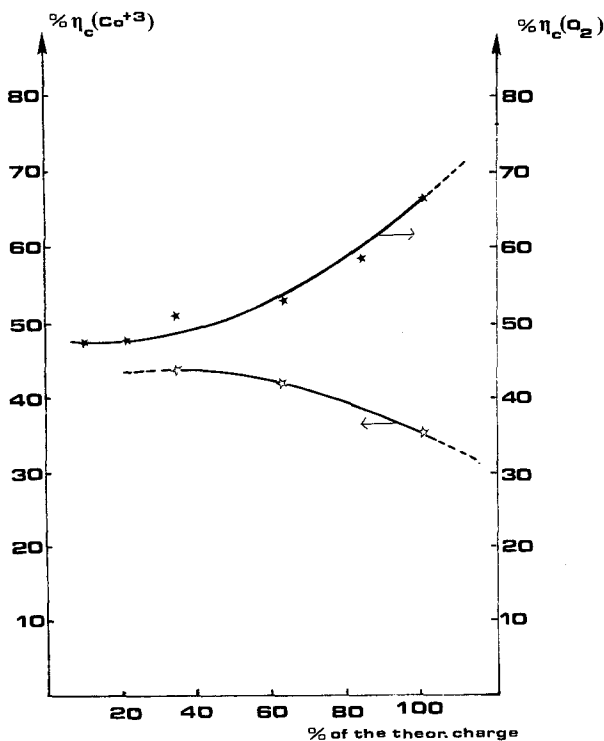


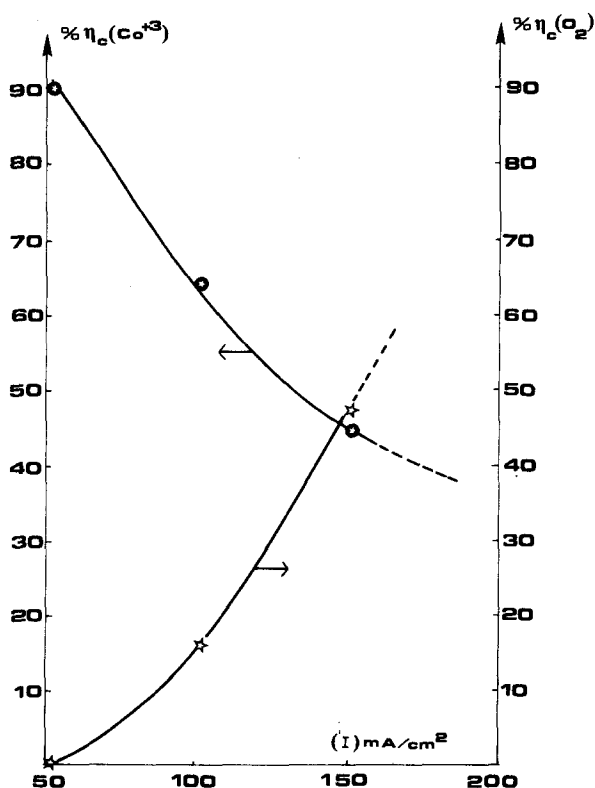
Fig. 2. Variation of the current efficiency for ★ oxygen evolution and ☆ cobaltic sulphate formation with the quantity of electricity passed expressed in a percentage of that theoretically needed for complete conversion in a divided cell.  $\text{H}_2\text{SO}_4$  concentration, 40 wt%;  $\text{CoSO}_4$  concentration, 0.49 M;  $\text{Ag}_2\text{SO}_4$  concentration,  $10^{-2}$  M; current density,  $150 \text{ mA cm}^{-2}$ ; Pt anode.

sulphate and oxygen formation on the charge passed (percentage of the theoretical) for one current density ( $150 \text{ mA cm}^{-2}$ ) and  $\text{H}_2\text{SO}_4$  concentration (40 wt%) in the presence of a catalytic amount of  $\text{Ag}_2\text{SO}_4$  ( $10^{-2} \text{ M}$ ).

An increase in the amount of electricity passed results in a decrease of current efficiency for cobaltic sulphate formation and an increase in oxygen evolution.

**3.2.2. Influence of current density.** The effect of current density was typically as shown in Fig. 3 for experiments conducted in 40 wt%  $\text{H}_2\text{SO}_4$  and in the presence of a catalytic amount of  $\text{Ag}_2\text{SO}_4$  ( $10^{-2} \text{ M}$ ). An increase in the current density results in a rapid decrease in the current efficiency for cobaltic sulphate formation and a rapid increase in the current efficiency for oxygen evolution.

The fact that the total current efficiency was always 80–90% is probably due to the fact that a fraction of the product reacts with the metallic powdery silver formed at the cathode.



### 3.3. Electrolysis without catalyst in an undivided cell using a platinum anode

**3.3.1. Influence of  $\text{H}_2\text{SO}_4$  concentration.** Fig. 4 shows the dependence of the current efficiency for cobaltic sulphate formation on the charge passed for one constant current density ( $50 \text{ mA cm}^{-2}$ ) and for four different  $\text{H}_2\text{SO}_4$  concentrations.

An increase in  $\text{H}_2\text{SO}_4$  concentration or the charge passed results in a decrease of the current efficiency for cobaltic sulphate formation. Comparison of Fig. 1 with Fig. 4 shows that a divided and an undivided cell give approximately the same results.

### 3.4. Electrolysis without catalyst in an undivided cell

**3.4.1. Influence of anode material.** The current efficiency for cobaltic sulphate formation using four different anodes (Pt,  $\text{PbO}_2$ , platinized

Fig. 3. Variation of the current efficiency for  $\bullet$  cobaltic sulphate and  $\star$  oxygen formation with the current density in a divided cell.  $\text{H}_2\text{SO}_4$  concentration, 40 wt%;  $\text{CoSO}_4$  concentration, 0.49 M;  $\text{Ag}_2\text{SO}_4$  concentration,  $10^{-2} \text{ M}$ ; quantity of electricity, 20% of the theoretical charge needed for complete conversion; Pt anode.

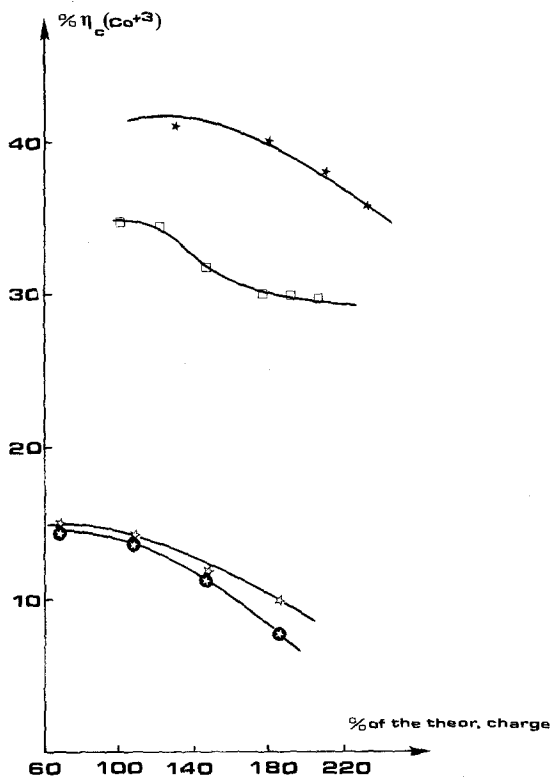


Fig. 4. Variation of the current efficiency for cobaltic sulphate formation with the amount of electricity passed (percentage of the theoretical) in an undivided cell.  $\star$  40% H<sub>2</sub>SO<sub>4</sub>,  $\square$  46.5% H<sub>2</sub>SO<sub>4</sub>,  $\ast$  50% H<sub>2</sub>SO<sub>4</sub>,  $\bullet$  52% H<sub>2</sub>SO<sub>4</sub>. Current density, 50 mA cm<sup>-2</sup>; CoSO<sub>4</sub> concentration, 0.49 M; Pt anode.

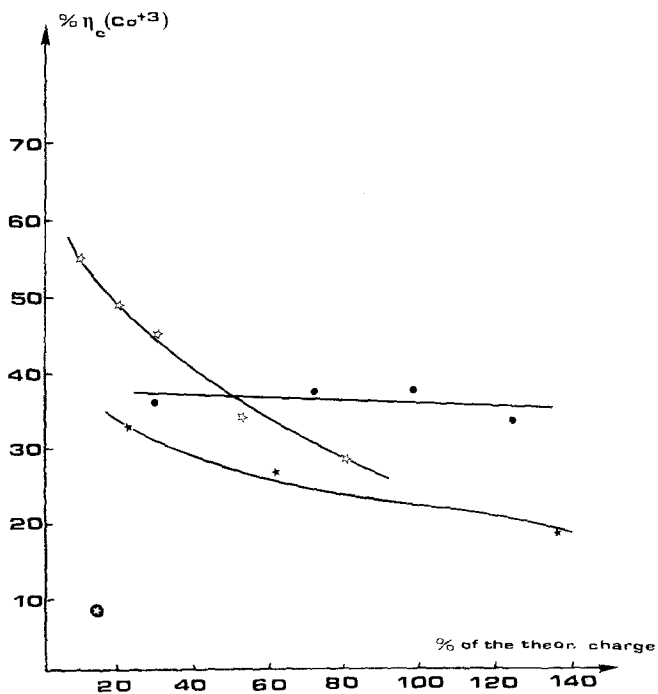


Fig. 5. Variation of the current efficiency for cobaltic sulphate formation with the amount of electricity passed (percentage of the theoretical) in an undivided cell.  $\ast$  PbO<sub>2</sub>,  $\bullet$  Pt,  $\ast$  platinumized titanium,  $\bullet$  graphite. H<sub>2</sub>SO<sub>4</sub> concentration, 40 wt%; CoSO<sub>4</sub> concentration, 0.49 M; current density, 50 mA cm<sup>-2</sup>.

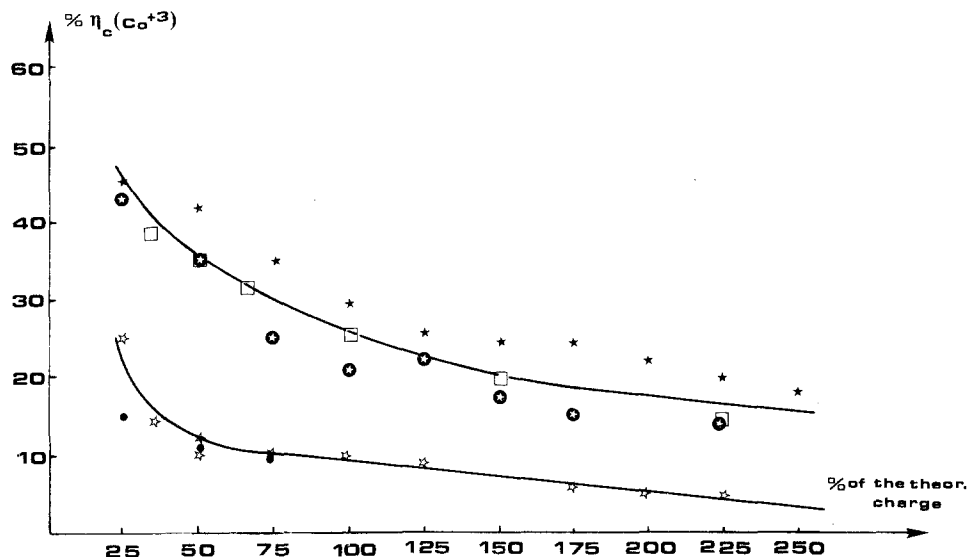


Fig. 6. Variation of the current efficiency for cobaltic sulphate formation with the quantity of electricity passed (percentage of the theoretical) in an undivided cell at different  $\text{Ag}_2\text{SO}_4$  concentrations.  $\bullet$   $1.8 \times 10^{-2}$  M,  $\star$   $9 \times 10^{-3}$  M,  $\square$   $1.8 \times 10^{-3}$  M,  $\circ$   $1.8 \times 10^{-4}$  M,  $\ast$  0.0 M.  $\text{H}_2\text{SO}_4$  concentration, 55.7 wt%;  $\text{CoSO}_4$  concentration, 0.55 M; current density,  $125 \text{ mA cm}^{-2}$ ;  $\text{PbO}_2$  anode.

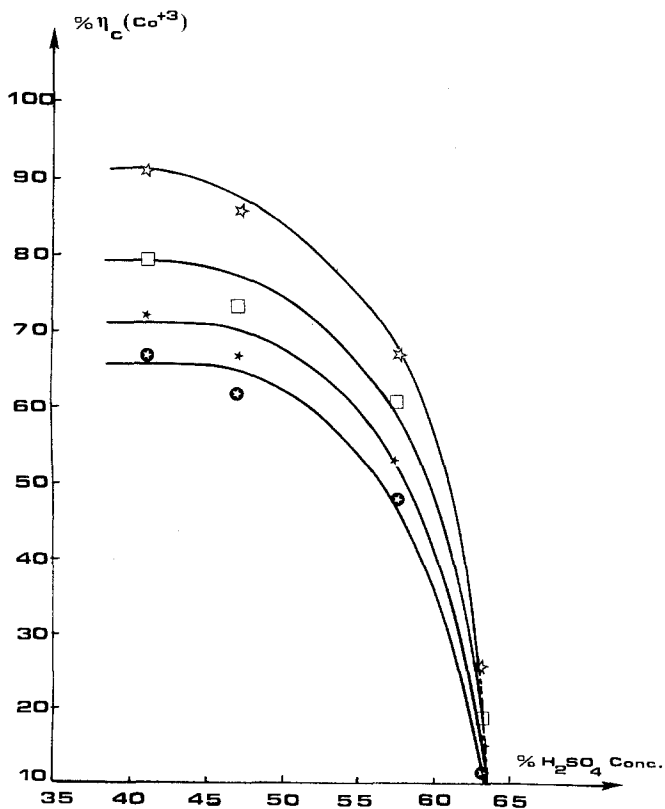


Fig. 7. Variation of the current efficiency for cobaltic sulphate formation with the  $\text{H}_2\text{SO}_4$  concentration in an undivided cell after the passage of:  $\ast$  10%,  $\square$  20%,  $\star$  30%,  $\bullet$  40% of the theoretical charge.  $\text{Ag}_2\text{SO}_4$  concentration,  $1.8 \times 10^{-3}$  M,  $\text{CoSO}_4$  concentration, 0.55 M; current density,  $50 \text{ mA cm}^{-2}$ ;  $\text{PbO}_2$  anode.

titanium, graphite) is shown in Fig. 5. Lead dioxide gives the best results at low conversion, platinum at high conversions and the graphite corroded.

### 3.5. *Electrolysis in the presence of $Ag_2SO_4$ in an undivided cell using a $PbO_2$ anode*

3.5.1. *Influence of catalyst concentration.* In Fig. 6 the current efficiencies for cobaltic sulphate formation as a function of catalyst concentration is shown. The concentration of  $Ag_2SO_4$  must lie between  $1.8 \times 10^{-2}$  and  $1.8 \times 10^{-3}$  M.

With increasing charge passed, the current efficiency of cobaltic sulphate formation gets worse. This decrease in the current efficiency was especially rapid at low charge passed.

3.5.2. *Influence of  $H_2SO_4$  concentration.* The variation of the current efficiency for cobaltic sulphate formation with  $H_2SO_4$  concentration is shown in Fig. 7. An increase in the  $H_2SO_4$  concentration results in a rapid decrease of current efficiency for cobaltic sulphate formation.

## 4. Discussion

During the electrolysis of cobaltous sulphate in concentrated  $H_2SO_4$  solution two simultaneous processes occur at the anode: (a) The oxidation of water to oxygen; (b) the oxidation of cobaltous to cobaltic sulphate. The operating conditions influence the mechanism and the kinetics of these anodic reactions.

### 4.1. *Anode material*

The materials tested can be divided in three groups:

(a)  $PbO_2$  and Pt: cobaltous sulphate is oxidized with high current efficiency.

(b) Platinized titanium: cobaltous sulphate is oxidized with low current efficiency.

(c) Graphite: corrosion is rapid.

At low conversion there appears to be a relationship between the oxygen overvoltage and the current efficiency for cobaltous sulphate oxidation. Lead dioxide has a higher overpotential for oxygen evolution [8] and therefore gives

higher current efficiency for  $Co^{3+}$  formation. At high conversion a contrary effect is observed.

### 4.2. *Conversion*

The current efficiency for cobaltic sulphate formation decreases with conversion. This might be due to a variation of the overpotential either of the oxygen evolution or of the cobaltous oxidation. This overpotential shift can be attributed either to the increase of the cobaltic ion concentration, or to the decrease of the cobaltous ion concentration.

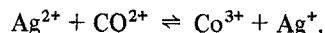
Borisova [9] has studied the electrochemical production of cobaltic perchlorate with a platinum anode and found that the cobaltous concentration does not influence the oxygen overpotential but the cobaltous/cobaltic overpotential is shifted to more positive values by a decrease in the cobaltous concentration. The model proposed by the above authors is sufficient to explain our experimental results.

### 4.3. *Diaphragm*

A divided and an undivided cell gave the same current efficiency for cobaltic sulphate formation. This is due to the high ratio of the anode to the cathode surface (11.4) used in these experiments. Under these conditions the current efficiency at the cathode of cobaltic sulphate reduction is negligible compared to the current efficiency for hydrogen evolution.

### 4.4. *Catalyst*

Argentous ions formed at the anode probably act as charge carriers in the oxidation of cobaltous ions



The mechanism for this catalysis and increase in the current efficiency of cobaltic sulphate formation has not been investigated in the present work.

### 4.5. *$H_2SO_4$ concentration*

The current efficiency of cobaltic sulphate formation decreases sharply at concentrations greater than 60 wt%  $H_2SO_4$ . It has been found [10] that

at about 60 wt% H<sub>2</sub>SO<sub>4</sub> concentration the yield and the rate of oxidation of *o*-nitrotoluene to *o*-nitroaldehyde increases brusquely.

From these data it follows that at 60 wt% H<sub>2</sub>SO<sub>4</sub> concentration the structure of cobaltous (and/or cobaltic) sulphate is modified.

#### 4.6. Current density

The fact that the current efficiency of cobaltic sulphate formation decreases with the current density and that that of oxygen evolution increases indicates that the Tafel slope for cobaltic sulphate formation is higher than that of oxygen evolution.

#### 5. Conclusion

The electrolytic oxidation of cobaltous sulphate to cobaltic sulphate must be effected under the following conditions:

- (a) using PbO<sub>2</sub> anode;
- (b) in the presence of Ag<sub>2</sub>SO<sub>4</sub> ( $1.8 \times 10^{-2}$ – $1.8 \times 10^{-3}$  M);
- (c) at low current density (20–50 mA cm<sup>-2</sup>);

(d) at low H<sub>2</sub>SO<sub>4</sub> concentration (~ 40 wt% H<sub>2</sub>SO<sub>4</sub>);

(e) at low conversion.

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