JOURNAL OF APPLIED ELECTROCHEMISTRY **13** (1983) 117–120

Electrochemical production of ceric sulphate in concentrated H_2SO_4

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Received 25 June 1982

The electrochemical preparation of ceric sulphate has been studied in concentrated H_2SO_4 (10 mol dm^{-3}) and we have found that the current efficiency of the reaction increases considerably if a mixed catalyst is used (Ag_2SO_4 + $MnSO_4$).

1. Introduction

The electrochemical oxidation of cerous sulphate to ceric sulphate can be effected with high current efficiency (80–90%) in dilute H_2SO_4 (1–2 mol dm^{-3}) [1].

The ceric sulphate thus obtained can be used as an oxygen carrier in the oxidation of some aromatic hydrocarbons [2].

The main problem to be overcome in this system is the opposing requirement of the electrochemical and chemical reaction. High chemical conversions are obtained at high acid concentration, whereas the current efficiency of the electrochemical reaction falls with increasing acid concentration [3].

Previously it has been found [4, 5] that the presence of catalytic amount of Ag_2SO_4 increases the current efficiency of cobaltous and manganous sulphate oxidation in concentrated H_2SO_4.

Recently Oehr [6] has reported that the current efficiency of ceric sulphate formation increases if $CoSO_4$ and Ag_2SO_4 are present in the electrolyte.

In this work we have studied the influence of the catalyst on the current efficiency of cerous sulphate oxidation in 10 mol dm^{-3} H_2SO_4.

2. Experimental procedure

The experiments were carried out in an electrolytic cell (150 cm^3 volume). The anode was a cylinder of platinum (28 cm^2 area) and the cathode was a lead sheet (4 cm^2 area) enclosed in a 10 cm^3 porous porcelain pot, stirring was provided by a magnetic bar.

The amount of ceric sulphate formed in the cell was determined by iodometric titration and the oxygen formed during electrolysis was measured by a gas burette.

Preparative electrolysis has been effected at constant current density using a slurry of $Ce_2(SO_4)_3$ in the presence of Ag_2SO_4 and/or $MnSO_4$ as the catalyst.

3. Results

3.1. *Electrolysis in the presence of $MnSO_4$ as a catalyst*

The instantaneous current efficiency for ceric sulphate and oxygen formation as a function of conversion is shown in Fig. 1 in the presence of different amounts of $MnSO_4$.

Increasing the $MnSO_4$ concentration results in an increase in the instantaneous current efficiencies (ICE) of ceric sulphate formation and decreases the ICE for oxygen formation.

3.2. *Electrolysis in the presence of Ag_2SO_4 as a catalyst*

Figure 2 shows the ICE for ceric sulphate and oxygen formation as a function of conversion in the presence of different amounts of Ag_2SO_4. The presence of Ag_2SO_4 in the electrolyte does not influence the selectivity of the reaction.

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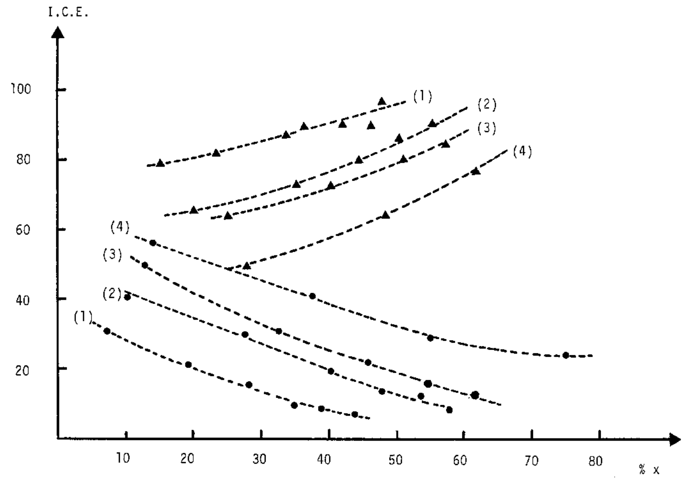

Fig. 1. Instantaneous current efficiency (ICE) for ● ceric sulphate formation; ▲ oxygen formation; as a function of conversion. Concentration H_2SO_4, 10 mol dm^{-3}; temperature, 85° C; i, 100 mA cm^{-2}; $Ce_2(SO_4)_3$, 0.12 mol dm^{-3}. (1). in absence of $MnSO_4$, (2). 1.2 10^{-2} mol dm^{-3} $MnSO_4$, (3). 1.9 10^{-2} mol dm^{-3} $MnSO_4$, (4). 3.9 10^{-2} mol dm^{-3} $MnSO_4$.

3.3. *Electrolysis in the presence of Ag_2SO_4 and $MnSO_4$ as catalysts*

The variation of ICE for ceric sulphate formation as a function of conversion without catalyst and in the presence of $MnSO_4$, Ag_2SO_4 and $MnSO_4 + Ag_2SO_4$ as catalyst is shown in Fig. 3. The catalytic effect of Ag_2SO_4 is observed only if $MnSO_4$ is also present in the electrolyte.

Figure 4 shows the ICE for ceric sulphate and oxygen formation as a function of conversion in the presence of Ag_2SO_4 (0.53 10^{-2} mole dm^{-3}) and different amounts of $MnSO_4$.

Increasing the $MnSO_4$ concentration results in an increase of the ICE for ceric sulphate formation and decreases the ICE for oxygen formation.

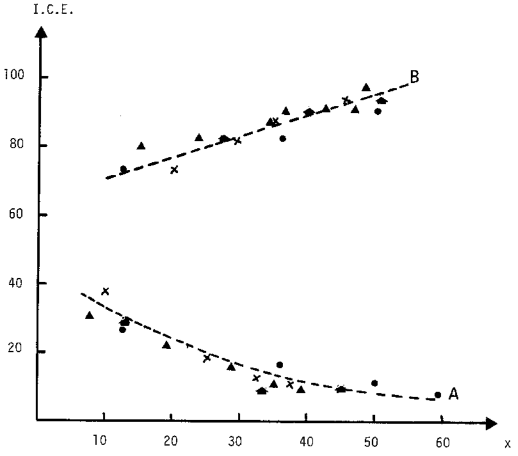

Fig. 2. Instantaneous current efficiency (ICE) for A, ceric sulphate formation; B. oxygen formation; as a function of conversion. Concentration H_2SO_4, 10 mol dm^{-3}; temperature, 85° C; i, 100 mA cm^{-2}; $Ce_2(SO_4)_3$, 0.12 mol dm^{-3}. ▲, in absence of Ag_2SO_4; x, 0.53 10^{-2} mol dm^{-3} Ag_2SO_4; ●, 2.14 10^{-2} mol dm^{-3} Ag_2SO_4; ✦, 4.28 10^{-2} mol dm^{-3} Ag_2SO_4.

4. Discussion

The low current efficiency of cerous sulphate oxidation in concentrated H_2SO_4 is due to the low solubility of the cerous salt in concentrated H_2SO_4 (Table 1) which effects the mass transfer and hence the limiting anodic current.

4.1. *Influence of Mn^{2+}*

In the presence of Mn^{2+} the oxidation of the cerous ion to ceric ion can proceed by two parallel pathways.

Direct oxidation at the anode

$$Ce^{3+} \rightarrow Ce^{4+} + e \qquad (1)$$

oxidation by Mn^{3+} formed at the anode

$$Mn^{2+} \rightarrow Mn^{3+} + e \qquad (2)$$

$$Ce^{3+} + Mn^{3+} \rightarrow Ce^{4+} + Mn^{2+} \qquad (3)$$

The anodic oxidation of cerous and manganous ion is reversible and occurs in the limiting current at the working current density (50–100 mA cm^{-2}).

Table 1. Solubility in 10 mol dm^{-3} H_2SO_4. Temperature = 85° C.

Compound	*Solubility* (m mol dm^{-3})
$Ce_2(SO_4)_3$	23
$MnSO_4$	80
Ag_2SO_4	70

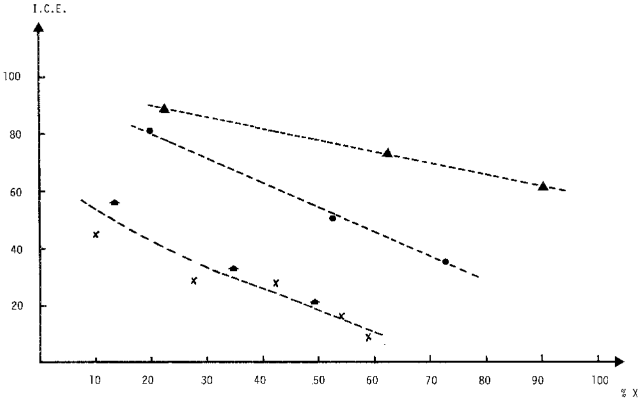

Fig. 3. Instantaneous current efficiency for ceric sulphate formation as a function of conversion. Concentration H_2SO_4, 10 mol dm^{-3}; temperature, 85° C; i, 50 mA cm^{-2}; $Ce_2(SO_4)_3$, 0.06 mol dm^{-3}. x, in absence of catalyst; ⬆, 0.53 10^{-2} mol dm^{-3} Ag_2SO_4; ●, 1.9 10^{-2} mol dm^{-3} $MnSO_4$; ▲, 0.53 10^{-2} mol dm^{-3} Ag_2SO_4 + 1.9 10^{-2} mol dm^{-3} $MnSO_4$.

The electrolysis of water to produce oxygen occurs also under these conditions

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (4)$$

the maximum current density (i_m) where reaction 4 does not occur can be obtained from the relation

$$i_m = i_{l(Ce^{3+})} + i_{l(Mn^{2+})}$$

$i_{l(Ce^{3+})}$ = limiting current of cerous ion oxidation,
$i_{l(Mn^{2+})}$ = limiting current of manganous ion oxidation in the presence of cerous ion.

If the working current density is i ($i > i_m$) the current efficiency of cerous sulphate oxidation can be given by the relation:

$$\eta_c = \eta_0 \frac{i_{l(Mn^{2+})}}{i}$$

η_c = current efficiency in the presence of Mn^{2+},
η_0 = current efficiency in absence of Mn^{2+}.

Neglecting the influence of oxygen evolution on the rate of mass transfer this relation can be written as

$$\eta_c = \eta_0 + \frac{ZFD_{Mn^{2+}}}{i\,\delta_R}\,[Mn^{2+}]$$

$D_{Mn^{2+}}$ = diffusion coefficient of Mn^{2+} (0.5 10^{-5} cm^2 sec^{-1}),
F = Faraday,
Z = equivalent per mole (Z = 1),
δ_R = thickness where the reaction 3 occurs (reaction layer)
$[Mn^{2+}]$ = concentration of manganous sulphate (mol cm^{-3}).

The linear relation obtained between the current efficiency of cerous sulphate oxidation and the concentration of manganous sulphate (Fig. 5a) verifies this model, from the slope of this straight line the thickness of the reaction layer can be determined (δ_R = 6.5 10^{-4} cm).

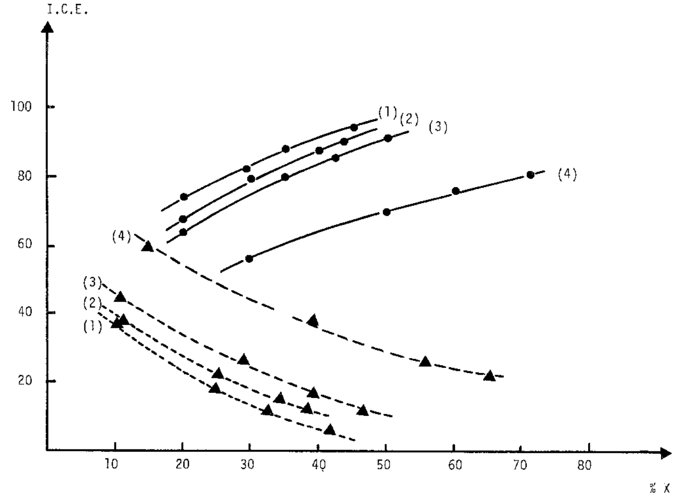

Fig. 4. Instantaneous current efficiency (ICE) for ▲ ceric sulphate formation, ● oxygen formation, as a function of conversion. Concentration H_2SO_4, 10 mol dm^{-3}; temperature, 85° C; i, 100 mA cm^{-2}; $Ce_2(SO_4)_3$, 0.12 mol dm^{-3}; Ag_2SO_4, 0.53 10^{-2} mol dm^{-3}. (1) in absence of $MnSO_4$, (2) 0.2 10^{-2} mol dm^{-3} $MnSO_4$, (3) 0.4 10^{-2} mol dm^{-3} $MnSO_4$; (4) 1.2 10^{-2} mol dm^{-3} $MnSO_4$.

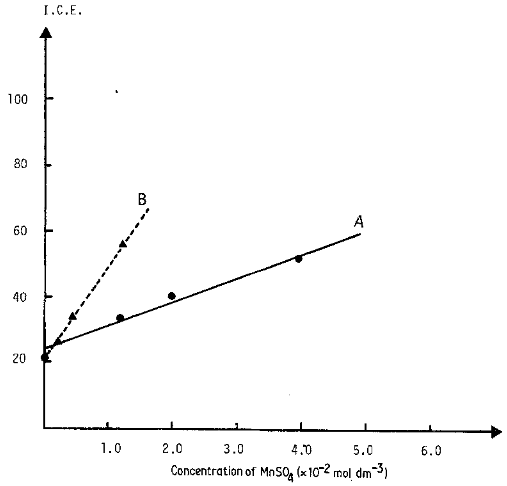

Fig. 5. Instantaneous current efficiency for ceric sulphate formation as a function of $MnSO_4$ concentration. A, in absence of Ag_2SO_4; B, 0.53 10^{-2} mol dm^{-3} Ag_2SO_4. Concentration H_2SO_4, 10 mol dm^{-3}, temperature, 85° C; i, 100 mA cm^{-2}; $Ce_2(SO_4)_3$, 0.12 mol dm^{-3}. conversion Ce^{+3} = 20%.

4.2. *Influence of Ag^+*

The oxidation of Ag^+ at the anode is a fast reaction [5]

$$Ag^+ \rightarrow Ag^{2+} + e.$$

The argentic ion formed can react in two different ways:

i) oxidation of Ce^{3+}

$$Ag^{2+} + Ce^{3+} \rightarrow Ag^+ + Ce^{4+}$$

ii) decomposition of water

$$4\ Ag^{2+} + 2\ H_2O \rightarrow 4\ Ag^+ + O_2 + 4\ H^+$$

This second reaction is probably a much faster reaction. This can explain the fact that Ag^+ does not act as a catalyst in the oxidation of cerous sulphate.

4.3. *Influence of $Ag^+ + Mn^{2+}$*

The catalytic effect of Ag^+ is observed only if Mn^{2+} is present in the electrolyte. This can be explained by the fact that the reaction

$$Ag^{2+} + Mn^{2+} \rightarrow Ag^+ + Mn^{3+}$$

is faster than the side reaction

$$4\ Ag^{2+} + 2\ H_2O \rightarrow 4\ Ag^+ + O_2 + 4\ H^+$$

and much faster than the reaction

$$Ag^{2+} + Ce^{3+} \rightarrow Ag^+ + Ce^{4+}$$

The reactions which occur in the reaction layer are:

$$Ag^{2+} + Mn^{2+} \rightarrow Ag^+ + Mn^{3+}$$

$$Mn^{3+} + Ce^{3+} \rightarrow Mn^{2+} + Ce^{4+}$$

The thickness of the reaction layer in this case can be evaluated from Fig. 5b ($\delta_R = 1.6\ 10^{-4}$ cm).

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