

# Cupric oxalate – magnesium seawater cells

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Cells with cupric oxalate cathodes bonded with polystyrene and magnesium alloy AZ61 anodes were discharged at room temperature. The cathode current efficiency was approximately 75% to a 0.8 V cut-off at an apparent current density of  $10 \text{ mA cm}^{-2}$ . Cells with sulphur–cupric oxalate cathodes showed discharge performance at higher voltages with higher efficiencies than those without sulphur. The use of different oxalate samples appeared to result in no significant difference in performance. The samples were either obtained commercially or prepared by precipitation. The cathodic behaviour of cupric oxalate was also investigated by potential sweep voltammetry with a slow sweep rate. In sodium chloride solutions a double peak was obtained on the voltammogram. When the stoichiometric quantity of sulphur was added to the cupric oxalate active material, it gave a main and two smaller peaks. The possible reactions are discussed.

## 1. Introduction

It has been reported that cupric oxalate is an effective cathode material in a seawater battery [1, 2]. The effect of the addition of sulphur to the cathode has also been reported [3]. Wales [4] reported the discharge behaviour of cells with neoprene-bonded cathodes which were made from nearly anhydrous cupric oxalate. He also discussed the electrode reactions on the basis of the observed potentials and the results of X-ray diffraction analysis.

The present work was undertaken to examine if water content affects discharge characteristics and if the cupric oxalate cathode bonded with polystyrene is practical. The second objective was to study in detail the electrode reactions.

## 2. Experimental

### 2.1. Cupric oxalate

Five samples of cupric oxalate were tested:

(a) A commercial sample from Mitsuwa's Pure Chemicals Co., Japan.

(b) A sample precipitated from aqueous solution of 0.2 M cupric sulphate by adding 0.22 M oxalic acid at  $80\text{--}90^\circ \text{C}$ . The precipitate was digested for 3 h at about  $80^\circ \text{C}$ .

(c) One precipitated from the same solutions as (b) at room temperature ( $24^\circ \text{C}$ ).

(d) One precipitated from a solution containing 0.1 M cupric sulphate and 0.1 M dimethyl oxalate by heating to  $50\text{--}60^\circ \text{C}$  for 3 h.

(e) One precipitated from the same solution as (d) at room temperature. The solution was allowed to stand overnight.

The precipitates were filtered, washed thoroughly and air-dried at room temperature for a week. The samples of cupric oxalate were then examined by X-ray analysis and thermogravimetry. The sizes of the precipitates were also measured with a microscope. All samples gave nearly identical X-ray diffraction patterns, with the exception of sample (a) which gave two extra lines in the diffraction pattern. These lines were those of  $\text{CuSO}_4$  which was a starting material in the production of cupric oxalate.

Cupric oxalate loses weight by dehydration when heated from room temperature and completely decomposes at about  $255^\circ \text{C}$  [5–8]. The water of crystallization was calculated from the total weight loss up to  $255^\circ \text{C}$ . Samples (a), (b), (c), (d) and (e) lost 1.2%, 2.4%, 3.2%, 1.8% and 3.3% of their weight, respectively, corresponding to the forms  $\text{CuC}_2\text{O}_4 \cdot 0.1\text{H}_2\text{O}$ ,  $\text{CuC}_2\text{O}_4 \cdot 0.21\text{H}_2\text{O}$ ,  $\text{CuC}_2\text{O}_4 \cdot 0.28\text{H}_2\text{O}$ ,  $\text{CuC}_2\text{O}_4 \cdot 0.15\text{H}_2\text{O}$  and  $\text{CuC}_2\text{O}_4 \cdot 0.29\text{H}_2\text{O}$ , respectively.

Dollimore *et al.* [7] have reported a weight loss of 3.5% for the dehydration of cupric oxalate, giving a formula  $\text{CuC}_2\text{O}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , which contains

5.6% water. The remainder of the water is probably released on decomposition.

The size of the particles was 2–8  $\mu\text{m}$  in diameter and large cubic or rectangular particles were observed among the spherical particles when cupric oxalate was precipitated at higher temperatures [samples (b) and (d)]. The diameter of samples (a), (c) and (e) was in the range of 0.8–3  $\mu\text{m}$ .

The discharge behaviour of these samples was examined with potential sweep voltammetry. It was found that there were no significant differences in the potentiodynamic current–voltage curves obtained for the different samples in 3% sodium chloride solution (cf. Fig. 6). Therefore, sample (b) was used for the later work.

## 2.2. Test cell

The cathodes tested were prepared from a blend of cupric oxalate (78 wt%), graphite (5%), acetylene black (5%) and polystyrene (12%). Cathodes containing sulphur were also made. The mole ratios of cupric oxalate to sulphur ranged from 1:0.1 to 1:1. Polystyrene was added in a toluene solution. After removing toluene by evaporation, 4 g of the cathode mix was pressed on to a copper mesh at a pressure of 2 kg mm<sup>-2</sup> to make a cathode plate of 20 mm × 30 mm in size. The average thickness of the plates after pressing and drying was 3.8 mm with approximately half on each side of the grid. The positive electrode was allowed to air-dry for at least one week before use in a cell.

Mg AZ61 alloy (6% Al, 1% Zn, 0.9 mm thick), of equal size to that of the cathode, was used as the anode. Each cell contained one cupric oxalate cathode and two anodes of the Mg alloy, one on each side of the cathode with an anode–cathode separation of 1 mm. Six 1 mm<sup>3</sup> separators were used on each side of the cathode. The test cell was activated in a beaker by adding 100 cm<sup>3</sup> of 3% sodium chloride solution saturated with Mg(OH)<sub>2</sub>. Cells were discharged at room temperature (22–26°C) using constant current without any circulatory system of the electrolyte. The discharge was begun after the open-circuit voltage had been measured for 10 min.

Discharges were limited by the capacity of the cupric oxalate cathodes. Sample (b) cupric oxalate was used as the active material. A capacity of 0.345 Ahg<sup>-1</sup> was used in computing electrode efficiencies.

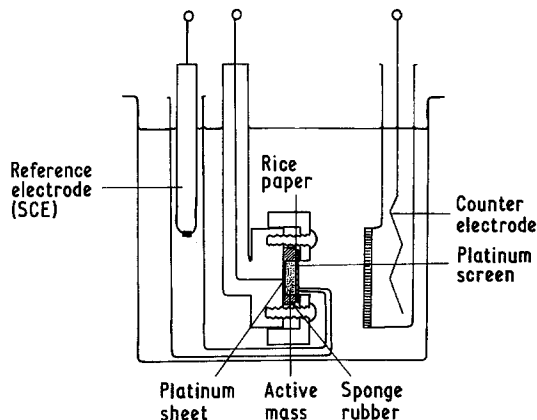


Fig. 1. Cell arrangement for sweep voltammetric measurement.

## 2.3. Linear sweep voltammetry

Potential sweep voltammetry was used to study the reactions for the cupric oxalate electrodes with or without sulphur. The half-cell arrangement is shown in Fig. 1, which is a modification of the arrangement previously used by Alt *et al.* [9]. A holding device incorporated a platinum plate as a collector; the active material was placed on this and covered with two sheets of rice paper for retention. The layers were then pressed together using a platinum mesh and plastic screws. The potential sweep was made by using a potentiostat (PS-1000, Hokuto Denko) and a function generator (HB-102, Hokuto Denko). The sweep rate used was 3.64 mV min<sup>-1</sup> (0.06 mV s<sup>-1</sup>).

## 3. Results and discussion

### 3.1. Single-cell discharges

Fig. 2 shows some typical discharges of the cupric oxalate cell and a few of the results with single cells are listed in Table 1. The discharge voltage generally increased at the initial stage of discharge and then decreased to a stable potential. The results show that these cells can be discharged up to a current density of 20 mA cm<sup>-2</sup>. The figures for specific energy in Wh kg<sup>-1</sup> listed in Table 1 are based on the weight of cathodes, anodes, grids and spacers, excluding the weight of the casing, electrolyte and leads. They were calculated for the average cell voltage to a cut-off voltage of 0.8 V.

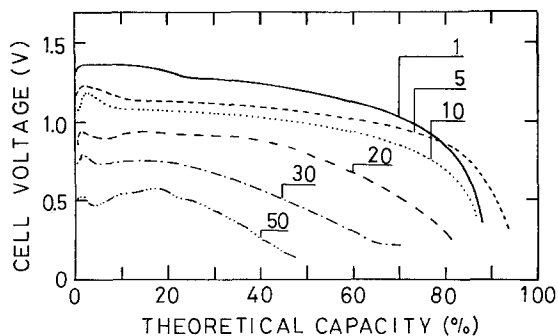


Fig. 2. Constant current discharges of seawater cells containing cupric oxalate cathodes (78 wt% cupric oxalate, 5% graphite, 5% acetylene black and 12% polystyrene) and Mg AZ61 anodes. Numbers give discharge current densities in  $\text{mA cm}^{-2}$ .

When the specific energy is calculated based on the weight of the complete cell, the value decreases to about half of that shown in the table.

Discharge curves for cells containing cathodes with different mole ratios of cupric oxalate and sulphur are shown in Figs. 3, 4 and 5. The characteristics of cells containing cathodes with a mole ratio of 1:1 are listed in Table 2. The cathode gave a higher potential when sulphur was added. Cells with sulphur-cupric oxalate cathodes usually showed 0.2–0.3 V higher discharge than those

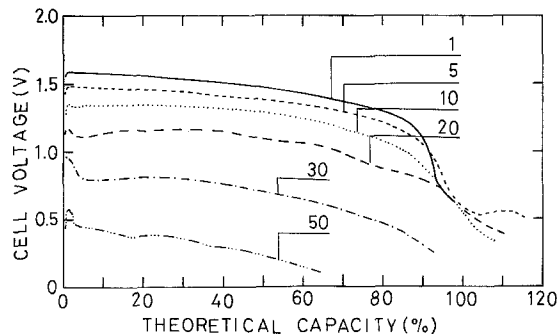


Fig. 3. Discharges of seawater cells with cupric oxalate-sulphur cathodes (64.7 wt% cupric oxalate, 13.3% sulphur, 5% graphite, 5% acetylene black and 12% polystyrene). The mole ratio for cupric oxalate:sulphur was 1:1.

without sulphur. At high discharge rates ( $> 50 \text{ mA cm}^{-2}$ ), the effect of added sulphur appeared to be small, if not negative, probably because of high resistance between the copper grid and the cathode mix due to formation of copper sulphide on the collector. The capacity of the cathodes containing sulphur often exceeded 100% when cells were discharged at low current densities and when the capacity was calculated on the basis of cupric oxalate content. The quantity of sulphur to be added to attain the greatest benefit appeared to depend on discharge current density. It can be

Table 1. Discharges of seawater cells containing cupric oxalate cathodes and Mg alloy AZ61 anodes.

Current density ( $\text{mA cm}^{-2}$ )	Theoretical run (h)	Percentage utilization to			Energy density to 0.8 V ( $\text{Wh kg}^{-1}$ ) <sup>†</sup>
		1.0 V	0.9 V	0.8 V	
1	90	70	78	81	145
5	18	60	75	82	128
10	9	50	66	73	110
20	4.5	—	35	50	66

<sup>†</sup> Based on electrodes, grids and spacers. The weight of the casing, electrolyte and leads was not included.

Table 2. Discharges of seawater cells containing cupric oxalate-sulphur cathodes (mole ratio of 1:1) and Mg alloy AZ61 anodes.

Current density ( $\text{mA cm}^{-2}$ )	Theoretical run (h)	Percentage utilization to			Energy density to 0.8 V ( $\text{Wh kg}^{-1}$ ) <sup>†</sup>
		1.0 V	0.9 V	0.8 V	
1	74	90	92	93	160
5	15	92	94	96	160
10	7.4	85	90	94	140
20	3.7	70	79	90	120

<sup>†</sup> Based on electrodes, grids and spacers, excluding the weight of the casing, electrolyte and leads.

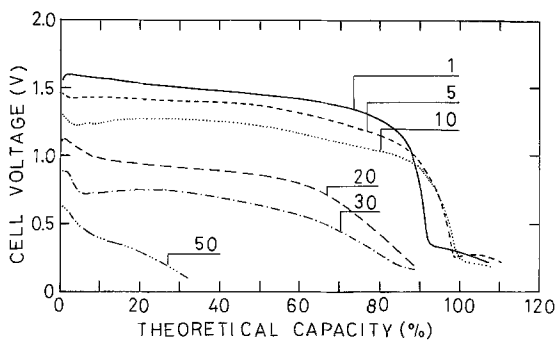


Fig. 4. Discharges of seawater cells with cupric oxalate-sulphur cathodes. The cathode contained a mole ratio of 1:0.5 for cupric oxalate:sulphur.

concluded that at low current densities about 0.5 mole of sulphur per mole cupric oxalate is sufficient but at higher current densities the addition of a stoichiometric quantity of sulphur is necessary, as stated by Wales [4].

### 3.2. Potential sweep voltammetry

Fig. 6 shows the current-voltage curves obtained for cupric oxalate in 3%, 10% and 20% sodium chloride solutions saturated with  $\text{Mg}(\text{OH})_2$ . A current-voltage curve in a buffered oxalate solution is also shown in Fig. 6. The mixture used as active mass was 70 wt% cupric oxalate, 15% graphite and 15% acetylene black. About 35 mg of the mixture was used.

In sodium chloride solutions a double current peak was observed. Peak I, the cathodic current peak, appeared at a less negative potential, moved further less negative and became smaller with

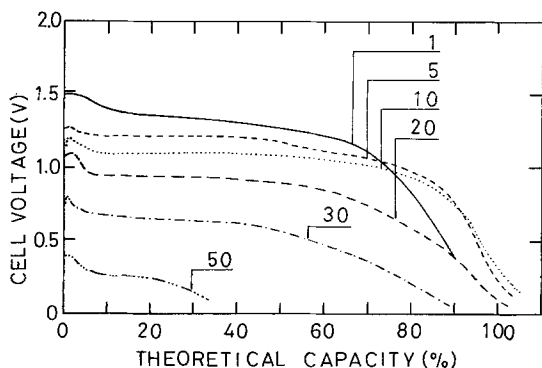


Fig. 5. Discharges of seawater cells with cupric oxalate-sulphur cathodes. The cathode contained a mole ratio of 1:0.1 for cupric oxalate:sulphur.

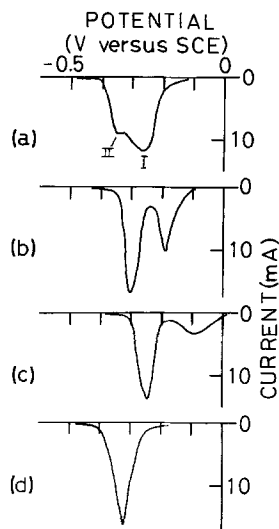
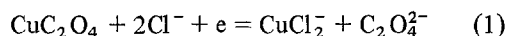


Fig. 6. Voltammetric curves of cupric oxalate in sodium chloride solutions and a buffered oxalate solution (sweep rate:  $0.06 \text{ mV s}^{-1}$ ). (a) 3% NaCl, (b) 10% NaCl, (c) 20% NaCl, (d)  $\text{H}_2\text{C}_2\text{O}_4 + \text{NH}_4\text{OH}$ , pH = 5.

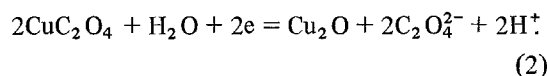
increasing concentration of sodium chloride. Peak II moved slightly in the less negative direction, becoming larger. The total area of the two peaks corresponds to 85–95% current efficiency for all cases shown in Fig. 6. In buffered oxalate solutions a single cathodic peak was observed and it appeared at roughly the same potential in the pH range between 2.1 and 5.9. This current peak can be assigned to the reduction of cupric oxalate to copper metal.

Voltammetric curves for the compounds that were thought to relate to the cupric oxalate electrode were also taken in the same electrolyte (Fig. 7). Cuprous chloride begins to be reduced at a potential less negative by about 40 mV than for cupric oxalate.  $\text{Cu}_2\text{O}$  and  $\text{CuO}$  cannot contribute to the cell efficiency because of their low potential if they were formed during discharge of the cupric oxalate electrode.

The following possible reactions at the cupric oxalate electrode have been proposed by Wales [4] to explain the two-step discharge curves:



or



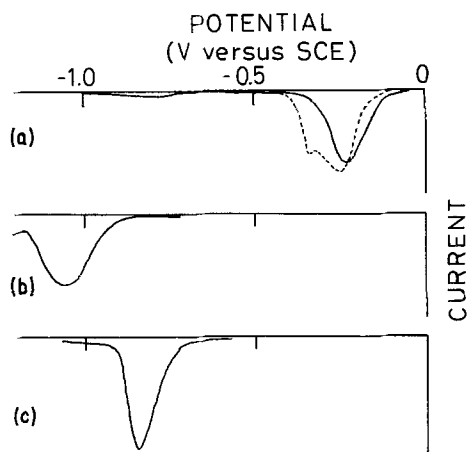
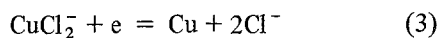
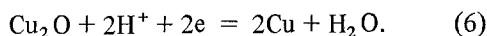
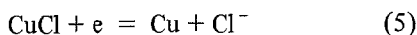
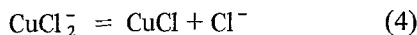


Fig. 7. Voltammetric curves for copper compounds related to cupric oxalate electrode in 3% sodium chloride solution. (a)  $\text{Cu}_2\text{Cl}_2$ , (b)  $\text{Cu}_2\text{O}$ , (c)  $\text{CuO}$ . Broken line is for cupric oxalate.

The monovalent copper compounds produced in Reaction 1 or 2 would be reduced to metallic copper:



or



If Reaction 1 followed by Reaction 3 or 5 were the main reaction, the two peaks in the voltammograms would have almost the same area and a change in height of the first peak would not be expected with increasing concentration of the electrolyte. If Reaction 2 were the predominant reaction, the second peak would appear at much more negative potential than was observed (Fig. 6a and Fig. 7,  $\text{Cu}_2\text{O}$ ).

The results of X-ray diffraction on an almost completely discharged cathode indicated the presence of copper metal and cuprous oxide. For a 34%-discharged cathode (potentiostatically treated at  $-0.19$  V versus SCE in 10% sodium chloride solution) the presence of some  $\text{Cu}_2\text{O}$  and  $\text{Cu}$ , besides cupric oxalate, was confirmed. Many other short lines in the diffraction pattern were recorded, but other impurities which might have been present could not be determined.

A newly proposed reaction sequence for peak I is:

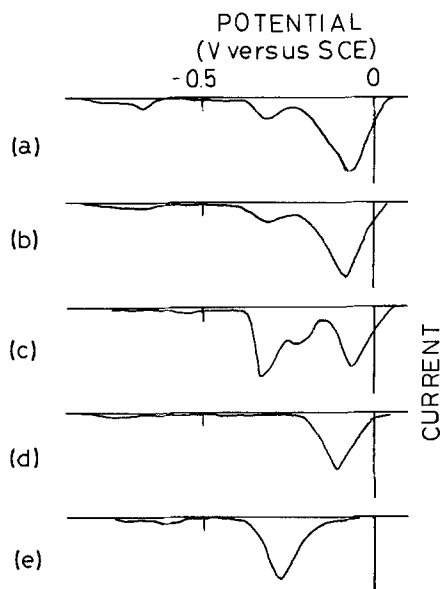
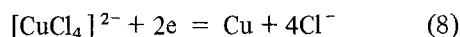
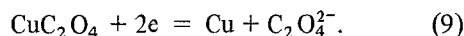


Fig. 8. Voltammetric curves for  $\text{CuS}$  and for cupric oxalate containing S or  $\text{CuS}$ . Cupric oxalate: sulphur = (a) 1:1, (b) 1:0.5, (c) 1:0.2, (d)  $\text{Cu}_2\text{O}_4 + \text{CuS}$ , (e)  $\text{CuS}$  only.



where  $\text{CuC}_2\text{O}_4^*$  means a colloidal state of cupric oxalate or dissolved cupric oxalate. And for peak II:

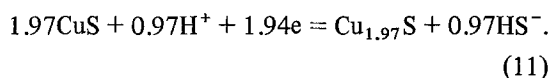
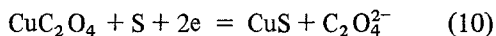


Cupric oxalate tends to enter a colloidal state when it is put in distilled water or in a dilute solution containing no common ions. This behaviour closely parallels that of peak I observed in different concentrations of sodium chloride. In addition, the dependence of  $\text{Cl}^-$  concentration on the potential was about 120 mV/decade. Solid cupric oxalate can be reduced in one step to metallic copper when the concentration of oxalate ions produced by the reduction of colloidal or dissolved cupric oxalate is high enough. It is also assumed that  $\text{Cu}_2\text{O}$ , which was always present in the discharged electrodes containing no sulphur, may have formed by oxidation of copper while drying.

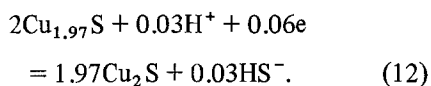
Fig. 8 shows voltammetric curves for cathodes containing cupric oxalate and sulphur or  $\text{CuS}$ , and for a  $\text{CuS}$  electrode in 3% sodium chloride solution. Cupric oxalate containing sulphur begins to

be reduced at a potential about 200 mV more positive than without sulphur and gives three or four current peaks, the last one being extremely small. The mixture containing cupric oxalate and sulphur at a mole ratio of 1:0.5 gave a nearly identical voltammogram as the one containing a mole ratio of 1:1, indicating that the CuS produced first was reduced with cupric oxalate. In the case of a mixture containing cupric oxalate and sulphur with a mole ratio of 1:0.2, the area of the first peak corresponds to about 40% of the theoretical coulombic efficiency based on cupric oxalate content. This also indicates that CuS plays a role in maintaining the high potential. This was confirmed by the results of experiments carried out with a mixture of cupric oxalate and CuS (Fig. 8d). CuS itself transforms into  $\text{Cu}_{1.97}\text{S}$  first, then into  $\text{Cu}_2\text{S}$  [10].

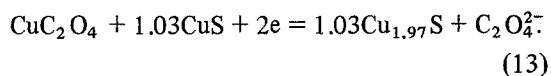
When enough sulphur is present, cupric oxalate is reduced with sulphur, according to Equation 10, producing CuS, which is then converted to  $\text{Cu}_{1.97}\text{S}$  according to Equation 11.



This  $\text{Cu}_{1.97}\text{S}$  can be reduced by the reaction:



When an electrode contains an amount of sulphur less than 0.5 mole per mole cupric oxalate, CuS forms first according to Equation 10, then the CuS transforms into  $\text{Cu}_{1.97}\text{S}$  according to:



If some cupric oxalate still remains at this point, it can be reduced according to Equation 9. Finally,  $\text{Cu}_{1.97}\text{S}$  converts to  $\text{Cu}_2\text{S}$ . This reaction scheme could account for four current peaks in the

voltammograms and the extra capacity observed at low current densities. From the results of X-ray diffraction analysis it can be concluded that the complete reduction of  $\text{Cu}_2\text{S}$  to copper metal does not occur during the cell discharge.

#### 4. Summary

Experiments using different samples of cupric oxalate containing different water contents showed no significant difference in their discharge behaviour in 3% sodium chloride solution. The polystyrene-bonded electrodes are found to discharge up to a current density of  $20 \text{ mA cm}^{-2}$ . These results indicate that these cathodes can be used for low- to moderate-drain applications, such as for life-jacket lights, life-boat lights and emergency radio equipment. The two-step discharge curves of the cell are explained by postulating the reduction of colloidal or dissolved cupric oxalate and solid cupric oxalate.

When sulphur is added to the cupric oxalate cathode, the first product in CuS which is reduced alone or is reduced with cupric oxalate to  $\text{Cu}_{1.97}\text{S}$ . The  $\text{Cu}_{1.97}\text{S}$  is finally reduced to  $\text{Cu}_2\text{S}$ .

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