

# *Voltage increase of copper compound electrodes resulting from the addition of sulphur for seawater batteries*

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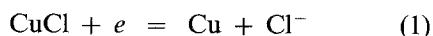
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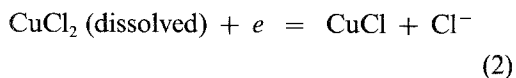
The addition of elemental sulphur to the copper compound cathode active materials increases the voltage by 0.2–0.4 V, depending on the valency of copper and the reactivity between elemental sulphur and the compound used when discharged in neutral or acidic electrolytes. The voltage increase mechanisms were discussed on the basis of the discharge behaviour, voltammetric studies and the analysis of discharge products.

## 1. Introduction

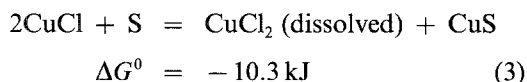
The voltage increase of the copper(I) chloride electrode resulting from the addition of elemental sulphur was discovered by H. N. Honer [1] in 1959 and the mechanism was investigated by Ruetschi and Amlie [2]. This effect represents a very significant development in the technology of the copper(I) chloride–magnesium battery. The reason for the voltage increase observed was explained by the fact that the electrode reaction changes from



to a redox mechanism



at the CuS–solution interface, where copper(II) chloride is generated by the chemical reaction



Although the voltage increase is well explained by this mechanism, the detailed discharge reactions and the discharge products at different depths of discharge were not defined. Subsequently it was observed that the addition of

sulphur to the copper(II) oxalate electrode resulted in an operating potential increase of approximately 0.2 V [3, 4]. Similar voltage increases with copper(II) sulphate were also observed by Matsuno and Kobayashi [5]. The mixes of CuBr–S and CuI–S were evaluated as candidates for cathode material by Margalit [6], but the detailed reactions were not given. These investigations indicate that copper compounds (either soluble, sparingly soluble, copper(I) or copper(II) compounds) increase their potentials when elemental sulphur is added. In order to elucidate the detailed mechanisms, studies were conducted on CuCl, CuBr, CuI, CuSO<sub>4</sub>, Cu(HCOO)<sub>2</sub>, Cu(CH<sub>3</sub>COO)<sub>2</sub> and CuC<sub>2</sub>O<sub>4</sub>.

## 2. Experimental procedure

The cathode mix tested was formed from a blend of a copper compound, sulphur, 10 wt % acetylene black and 5 wt % graphite. The electrolyte used was a 3 wt % NaCl solution. The discharge behaviour was investigated by constant current discharge (1–10 mA cm<sup>-2</sup>) and sweep voltammetry. All electrode potential measurements were made against a saturated calomel electrode (SCE). Discharge products were examined by X-ray diffraction and the microscopy method. The cell assembly and more details of the experimental procedures can be found elsewhere [7].

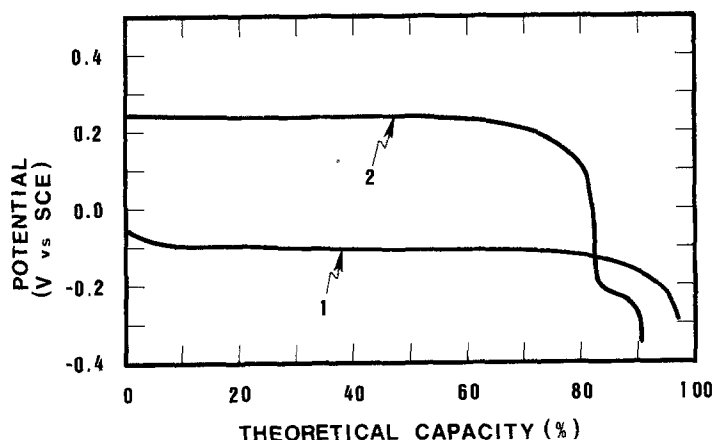


Fig. 1. Half-cell discharge curves of CuCl and CuCl containing sulphur in 3% NaCl electrolyte. Curve 1, CuCl only; curve 2, CuCl-S (mole ratio = 1:0.5).

### 3. Results and discussion

#### 3.1. Copper(I) halides

The discharge reactions for the CuBr electrode containing sulphur are similar to those for the CuI electrode containing sulphur. The CuCl electrode containing sulphur, however, discharges in a different manner. Typical half-cell discharge curves of CuCl and CuCl containing sulphur are shown in Fig. 1. At a discharge current density of  $7 \text{ mA cm}^{-2}$ , a voltage increase of 0.35 V was obtained. Fig. 2 shows voltammograms for the CuCl electrode with and without sulphur taken at a sweep rate of

$0.062 \text{ mV s}^{-1}$ . Arrows in the voltammograms indicate points where samples were taken for the analysis of discharge products.

The CuCl electrode (Fig. 2a) exhibits one cathodic peak (1d) which apparently corresponds to the reduction of CuCl to metallic copper. A CuCl electrode made with 0.25 mol sulphur per mol CuCl gives two main peaks (Fig. 2b). One main cathodic peak together with a small peak was observed for a CuCl electrode containing 0.5 mol sulphur per mol CuCl (Fig. 2c). When a mixture of CuCl and sulphur is wetted, a spontaneous reaction occurs according to Reaction 3 [8]. Its free energy change can be calculated to be  $-10.3 \text{ kJ mol}^{-1}$ , indicating

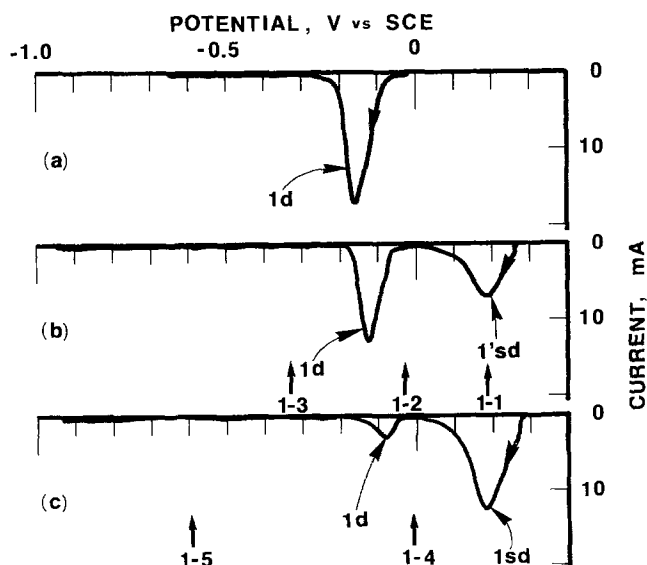
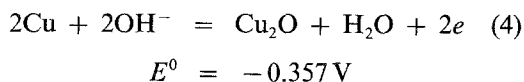


Fig. 2. Voltammograms for CuCl and CuCl containing sulphur (3% NaCl,  $0.062 \text{ mV s}^{-1}$ ). (a) CuCl only; (b) CuCl-S (mole ratio = 1:0.25); (c) CuCl-S (mole ratio = 1:0.5).

Table 1. Phases identified in samples taken at different depths of discharge for a CuCl electrode

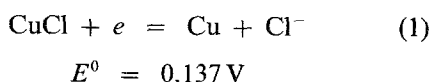
Sample	Phases identified
1-1 (discharged to 0.18 V versus SCE, 25% depth of discharge)	CuCl, CuS, Cu <sub>2</sub> S and a small amount of Cu <sub>1.8</sub> S
1-2 (discharged to -0.04 V, 44% depth of discharge)	CuCl, Cu <sub>2</sub> S and a small amount of CuS
1-3 (discharged to -0.34 V, 85% depth of discharge)	Cu <sub>2</sub> S, CuS, Cu <sub>2</sub> O, Cu and Cu <sub>1.97</sub> S
1-4 (discharged to 0.00 V, 78% depth of discharge)	Cu <sub>1.97</sub> S, Cu <sub>1.8</sub> S and CuS
1-5 (discharged to -0.6 V, 94% depth of discharge)	Cu <sub>1.97</sub> S, Cu <sub>1.8</sub> S and a small amount of CuS

that the great part of CuCl used converts to CuCl<sub>2</sub> and CuS [9]. The phases identified by X-ray diffraction analysis in samples taken at different depths of discharge are given in Table 1. Sample 1-3 contained Cu<sub>2</sub>O which was detected whenever metallic copper was present. Copper(I) oxide can be formed by the oxidation of metallic copper while drying, and also electrochemically according to Reaction 4 after interrupting the discharge current when a cathode active material is still present in the mix. Consequently, copper(I) oxide was not considered as an intermediate in the discharge reactions.

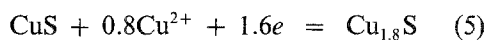


As an intermediate form, low-digenite was noticed in the samples 1-4 and 1-5; its approximate composition is Cu<sub>9</sub>S<sub>5</sub> [10, 11], therefore we represent it as Cu<sub>1.8</sub>S here. The electrochemical reactions assigned to the current peaks in Fig. 2 are as follows.

Peak 1d:

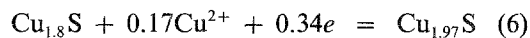


Peak 1sd:



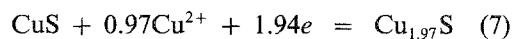
$$E^0 = 0.529 \text{ V}$$

and



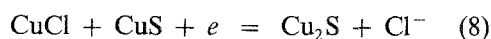
$$E^0 = 0.541 \text{ V}$$

and/or



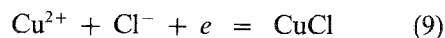
$$E^0 = 0.531 \text{ V}$$

Peak 1'sd:



$$E^0 = 0.532 \text{ V}$$

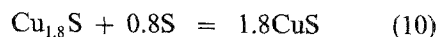
and



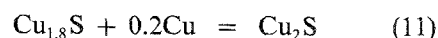
$$E^0 = 0.537 \text{ V}$$

The standard potentials,  $E^0$ , described above were calculated using Gibbs free energies [9, 12]. Estimated values of -78.7 and -85.4 kJ mol<sup>-1</sup> were used for Cu<sub>1.8</sub>S and Cu<sub>1.97</sub>S, respectively.

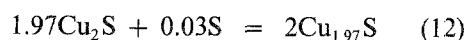
Since Cu<sup>2+</sup> is considered to be discharged on the surface of solid CuS in the case of the CuCl-S mix, Cu<sub>1.8</sub>S or other intermediate phases will form and accumulate there. If sulphur is still present or if metallic copper is formed as in sample 1-3, those intermediates will react with sulphur or metallic copper [10].



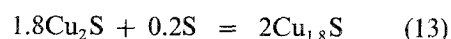
$$\Delta G^0 = -9.5 \text{ kJ}$$



$$\Delta G^0 = -7.5 \text{ kJ}$$



$$\Delta G^0 = -1.0 \text{ kJ}$$



$$\Delta G^0 = -2.2 \text{ kJ}$$

In fact, a sample which had contained Cu<sub>1.8</sub>S exhibited the reflections attributable to CuS with decreased intensity of reflections attributable to Cu<sub>1.8</sub>S after being dried. Reaction 8 was con-

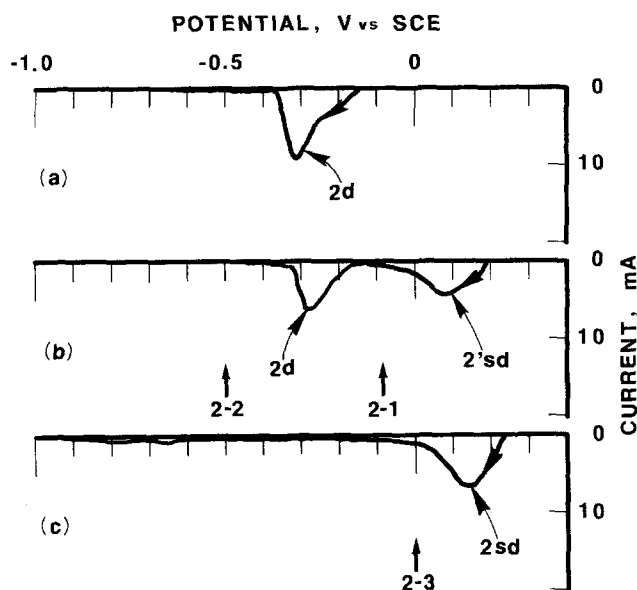
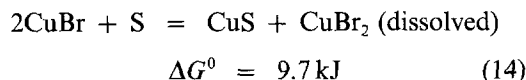


Fig. 3. Voltammograms for CuBr and CuBr containing sulphur (3% NaCl,  $0.062 \text{ mV s}^{-1}$ ). (a) CuBr only; (b) CuBr-S (mole ratio = 1:0.25); (c) CuBr-S (mole ratio = 1:0.5).

firmed by using a mix of CuCl and CuS which discharged at a voltage range 0.2–0.13 V versus SCE and the discharged electrode contained a considerable amount of  $\text{Cu}_2\text{S}$ , as stated by Amlie and co-workers [1, 2]. Reaction 6 indicates that simultaneous reduction of  $\text{Cu}_{1.8}\text{S}$  and  $\text{Cu}^{2+}$  can deliver as high a potential as CuS, according to Reactions 5 or 7.

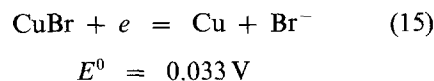
The voltammograms for CuBr with and without S are shown in Fig. 3. The voltammetry peaks for CuBr appear at less positive potential by about 0.1 V than those for CuCl. The reaction



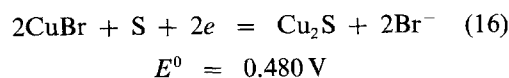
has a positive free energy change. When a CuBr-S mix was wetted by a chloride electrolyte the solution changed colour to blue after several hours and the presence of a small amount of CuS was confirmed by X-ray diffraction. Therefore, very small amounts of  $\text{Cu}^{2+}$  and CuS must be present in the CuBr-S electrode at the beginning of discharge, but their contribution to the discharge would be negligible. The phases identified in the samples taken at different depths of discharge are given in Table 2.

The electrochemical reactions assigned to each peak shown in Fig. 3 are as follows.

Peak 2d:



Peak 2sd:



The reduction peak for CuI containing sulphur is low and broad (Fig. 4), indicating that its polarization is high. Even a CuI electrode containing an excess amount of sulphur (Fig. 4c) gives a peak corresponding to the reduction of CuI to metallic copper, suggesting that complete

Table 2. Phases identified in samples taken at different depths of discharge for a CuBr electrode

Sample	Phases identified
2-1 (discharged to $-0.09 \text{ V}$ versus SCE, 48% depth of discharge)	CuBr and $\text{Cu}_2\text{S}$
2-2 (discharged to $-0.51 \text{ V}$ , 90% depth of discharge)	$\text{Cu}_2\text{S}$ , Cu, $\text{Cu}_2\text{O}$ and a small amount of CuBr
2-3 (discharged to $-0.0 \text{ V}$ , 90% depth of discharge)	$\text{Cu}_2\text{S}$ and a small amount of CuBr

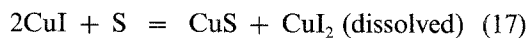
Table 3. Phases identified in samples taken at different depths of discharge for a CuI electrode

Sample	Phases identified
3-1 (discharged to $-0.205$ V, 90% depth of discharge)	CuI, $\text{Cu}_2\text{S}$ and a small amount of $\text{Cu}_{1.97}\text{S}$
3-2 (discharged to $-0.7$ V, 99% depth of discharge)	CuI, $\text{Cu}_2\text{S}$ , $\text{Cu}_2\text{O}$ and small amounts of Cu and $\text{Cu}_{1.97}\text{S}$
3-3 (discharged to $-0.17$ V, 83% depth of discharge)	CuI, $\text{Cu}_{1.8}\text{S}$ , and small amounts of $\text{Cu}_{1.97}\text{S}$ and $\text{Cu}_2\text{S}$
3-4 (discharged to $-0.55$ V, 95% depth of discharge)	$\text{Cu}_{1.8}\text{S}$ , and small amounts of $\text{Cu}_2\text{S}$ and $\text{Cu}_{1.97}\text{S}$
3-5 (discharged to $-0.90$ V, 150% depth of discharge)*	CuS, $\text{Cu}_2\text{S}$ and $\text{Cu}_{1.8}\text{S}$

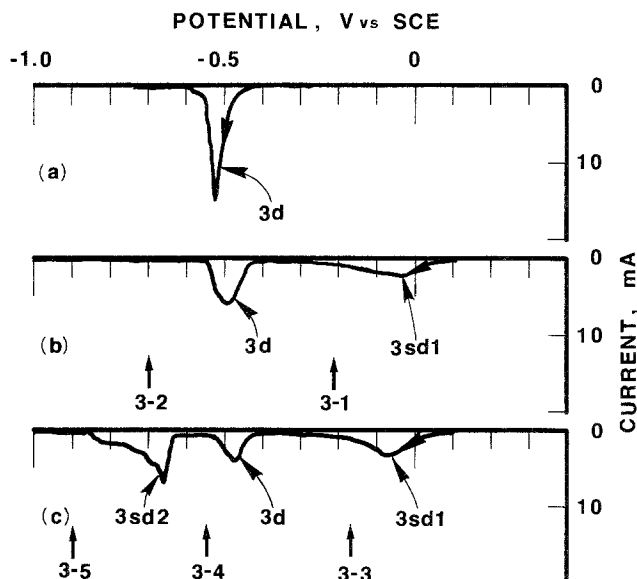
\* The theoretical capacity was based on the weight of CuI. The capacity exceeded 100% can be due to unreacted sulphur and copper sulphides.

utilization at high potential cannot be attained with a CuI-S mix.

Copper(I) iodide does not react with sulphur at room temperature under wet conditions.



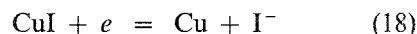
$$\Delta G^0 = 51.7 \text{ kJ}$$



The phases identified in partially discharged CuI electrodes containing sulphur are shown in Table 3.

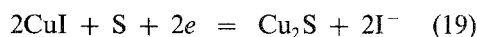
For the voltammetry peaks in Fig. 4 the reaction assignments may be given as follows.

Peak 3d:

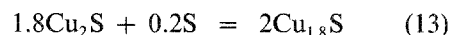
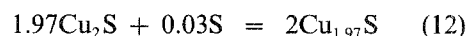


$$E^0 = -0.185 \text{ V}$$

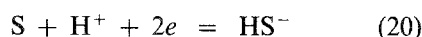
Peak 3sd1:



$$E^0 = 0.261 \text{ V}$$



Peak 3sd2:



$$E^0 = -0.062 \text{ V}$$

For the CuI-S mix, chemical Reactions 12 and 13 would be postulated to explain the existence of  $\text{Cu}_{1.8}\text{S}$  and  $\text{Cu}_{1.97}\text{S}$ . At peak 3sd2, sulphide and polysulphide ions besides  $\text{HS}^-$  may also be formed, and they react with copper sulphides to produce the other forms of copper sulphide.

### 3.2. Soluble copper(II) compounds

We examined the discharge behaviour of

Fig. 4. Voltammograms for CuI and CuI containing sulphur (3% NaCl,  $0.062 \text{ mV s}^{-1}$ ). (a) CuI only; (b) CuI-S (mole ratio = 1:0.5); (c) CuI-S (mole ratio = 1:1).

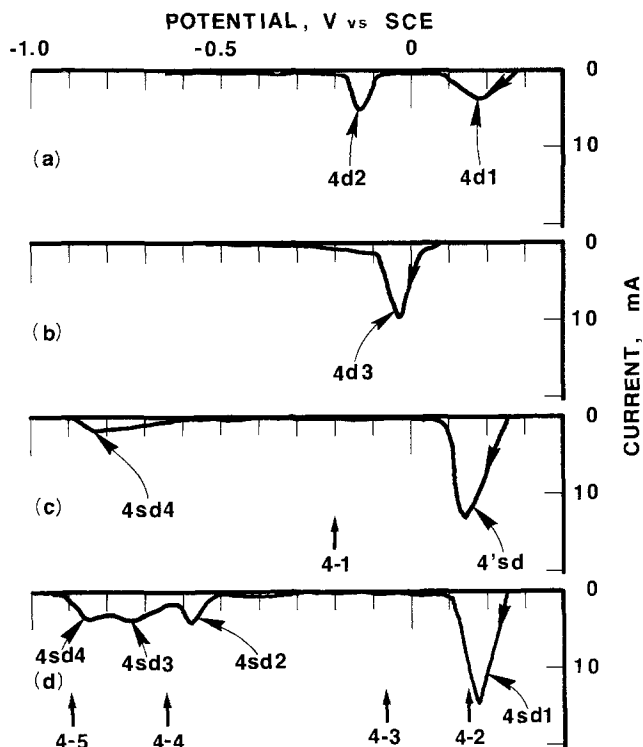


Fig. 5. Voltammograms for  $\text{CuSO}_4$  and  $\text{CuSO}_4$  containing sulphur (3% NaCl,  $0.062 \text{ mVs}^{-1}$ ). (a)  $\text{CuSO}_4$  only; (b)  $\text{CuSO}_4$  only in  $0.25 \text{ M Na}_2\text{SO}_4$ ; (c)  $\text{CuSO}_4\text{-S}$  (mole ratio = 1:0.5); (d)  $\text{CuSO}_4\text{-S}$  (mole ratio = 1:1).

$\text{CuSO}_4$ ,  $\text{Cu}(\text{HCOO})_2$  and  $\text{Cu}(\text{CH}_3\text{COO})_2$  as the soluble copper(II) compound. The results obtained with  $\text{CuSO}_4$  will be described here because the soluble compounds showed similar behaviour. Detailed results for seawater batteries containing  $\text{Cu}(\text{HCOO})_2$  cathodes can be found elsewhere [13].

The voltammograms and half-cell discharges for  $\text{CuSO}_4$  not containing sulphur and containing sulphur are shown in Figs 5 and 6, respectively. Although voltammograms of  $\text{CuSO}_4$  without sulphur indicate the formation of  $\text{CuCl}$

(peak 4d1), a half-cell discharge curve of  $\text{CuSO}_4$  (Fig. 6, curve 1) indicates very little formation of  $\text{CuCl}$ . This is because  $\text{Cu}^+$  is unstable unless halide or cyanide ions are present [9]. For voltammetry studies the amount of  $\text{Cl}^-$  is large enough to stabilize the  $\text{Cu}^+$  formed, as only 40 mg of the cathode mix was used and the mix was loosely pressed in the holder. However, on the half-cell discharges, since the amount of  $\text{Cl}^-$  in the electrode pores is very small compared to the amount of  $\text{Cu}^{2+}$ , almost all the  $\text{Cu}^+$  ions electrochemically generated disproportionate to

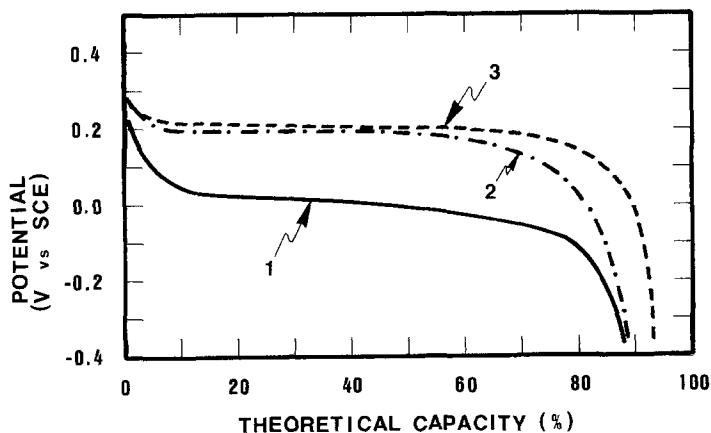


Fig. 6. Half-cell discharge curves for  $\text{CuSO}_4$  and  $\text{CuSO}_4$  containing sulphur in 3% NaCl. Curve 1,  $\text{CuSO}_4$  only; curve 2,  $\text{CuSO}_4\text{-S}$  (mole ratio = 1:0.5); curve 3,  $\text{CuSO}_4\text{-S}$  (mole ratio = 1:1).

Table 4. Phases identified in samples taken at different depths of discharge for a  $\text{CuSO}_4$  electrode

Sample	Phases identified
4-1 (discharged to $-0.2$ V, 88% depth of discharge)	$\text{Cu}_{1.97}\text{S}$ and small amounts of $\text{CuS}$ and $\text{Cu}_{1.8}\text{S}$
4-2 (discharged to $0.126$ V, 63% depth of discharge)	$\text{Cu}_{1.8}\text{S}$ and $\text{CuS}$
4-3 (discharged to $-0.08$ V, 74% depth of discharge)	$\text{Cu}_{1.8}\text{S}$ , $\text{CuS}$ and a small amount of $\text{Cu}_{1.97}\text{S}$
4-4 (discharged to $-0.62$ V, 90% depth of discharge)	$\text{CuS}$ , $\text{Cu}_{1.8}\text{S}$ and a small amount of $\text{Cu}_{1.97}\text{S}$
4-5 (discharged to $-0.90$ V, 130% depth of discharge)*	$\text{Cu}_{1.8}\text{S}$ , $\text{CuS}$ , $\text{Cu}_{1.97}\text{S}$ and a small amount of $\text{Cu}_{1.75}\text{S}^\dagger$

\* The theoretical capacity was based on the weight of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ .

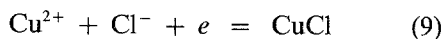
† The approximate composition of this intermediate is  $\text{Cu}_7\text{S}_4$  according to Cavallotti and Salvago [10]. We represent it as  $\text{Cu}_{1.75}\text{S}$  here.

$\text{Cu}$  and  $\text{Cu}^{2+}$ . Therefore, in the case of half-cell discharges, the main discharge reaction is the reduction of  $\text{Cu}^{2+}$  to metallic copper. The reduction peak (4d3), corresponding to the reduction of  $\text{Cu}^{2+}$  to  $\text{Cu}$  in the voltammogram taken in  $0.25$  M  $\text{Na}_2\text{SO}_4$ , appears at less negative potential by about  $0.1$  V than a peak corresponding to the reduction of  $\text{CuCl}$  (4d2), being consistent with the half-cell discharge results (Fig. 6, curve 1).

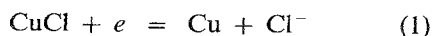
The results of analysis of reaction products are given in Table 4.

The reflections attributable to  $\text{Cu}_2\text{S}$  in the X-ray diffraction patterns appeared for samples discharged to about  $-1.2$  V versus SCE. The main electrochemical reactions assigned to each peak are as follows.

Peak 4d1:



Peak 4d2:

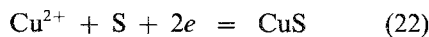


Peak 4d3:

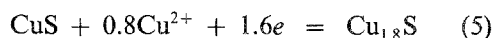


$$E^0 = 0.337 \text{ V}$$

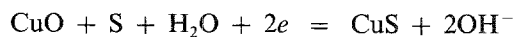
Peak 4sd1:



$$E^0 = 0.590 \text{ V}$$



Peak 4sd2:

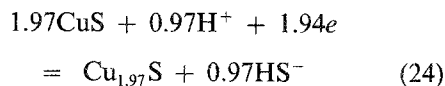


$$E^0 = -0.004 \text{ V} \quad (23)$$

Peak 4sd3:

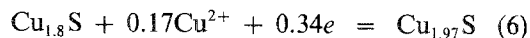
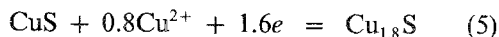
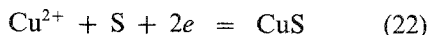


Peak 4sd4:

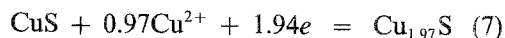


$$E^0 = -0.121 \text{ V}$$

Peak 4'sd:



and/or



The electrochemical reactions assigned to peak 4sd2, 4sd3 and 4sd4 are not well defined because it was difficult to detect a small change in the electrode composition. The assignments described above were based on the voltammograms of a mixture of  $\text{CuS}$ ,  $\text{CuO}$  and  $\text{S}$ , and the discharge products of the  $\text{CuS}$  electrode and the electrode containing  $\text{CuO}$  and  $\text{S}$ .

From these assignments it can be concluded that the voltage increase that occurs with the addition of sulphur to soluble copper compounds is a result of Reaction 22 taking place rather than Reaction 21.

### 3.3. Sparingly soluble copper(II) compounds

Copper(II) oxalate was examined as an example

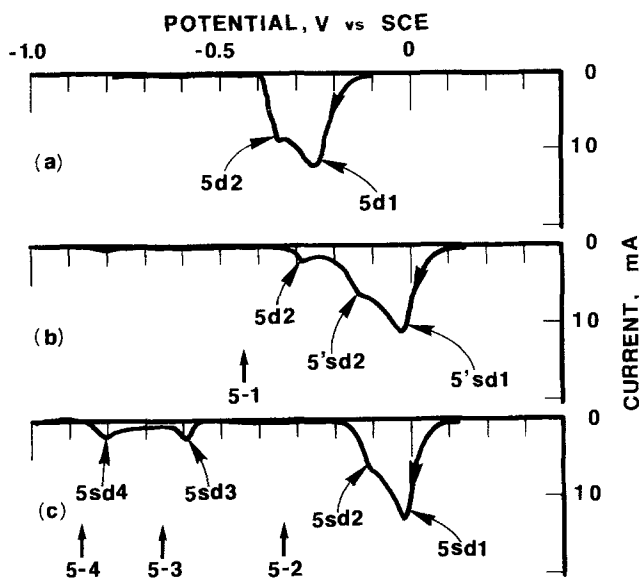


Fig. 7. Voltammograms for  $\text{Cu}_2\text{O}_4$  and  $\text{Cu}_2\text{O}_4$  containing sulphur (3% NaCl,  $0.062 \text{ mV s}^{-1}$ ). (a)  $\text{Cu}_2\text{O}_4$  only; (b)  $\text{Cu}_2\text{O}_4\text{-S}$  (mole ratio = 1:0.5); (c)  $\text{Cu}_2\text{O}_4\text{-S}$  (mole ratio = 1:1).

of a sparingly soluble compound. Its characteristics as a cathode active material in seawater batteries were reported previously [3, 4]. The electrochemical reactions will be summarized below, adding recent experimental results.

When a mixture of  $\text{Cu}_2\text{O}_4$  and S is placed in the electrolyte no spontaneous reaction occurs. A voltage increase of about 0.2 V by the addition of sulphur can be observed from the voltammograms shown in Fig. 7. The phases identified in the discharged electrodes are shown in Table 5.

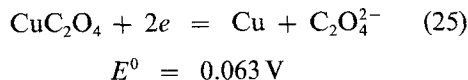
Table 5. Phases identified in samples taken at different depths of discharge for a  $\text{Cu}_2\text{O}_4$  electrode

Sample	Phases identified
5-1 (discharged to $-0.42 \text{ V}$ , 92% depth of discharge)	$\text{Cu}_{1.97}\text{S}$ and small amounts of $\text{CuS}$ and $\text{Cu}_2\text{S}$
5-2 (discharged to $-0.33 \text{ V}$ , 98% depth of discharge)	$\text{CuS}$ , $\text{Cu}_{1.8}\text{S}$ and a small amount of $\text{Na}_2[\text{Cu}(\text{C}_2\text{O}_4)_2]$
5-3 (discharged to $-0.65 \text{ V}$ , 110% depth of discharge)*	$\text{CuS}$ and $\text{Cu}_{1.8}\text{S}$
5-4 (discharged to $-0.88 \text{ V}$ , 130% depth of discharge)*	$\text{Cu}_{1.8}\text{S}$ , $\text{Cu}_{1.97}\text{S}$ , $\text{Cu}_{1.75}\text{S}$ and a small amount of $\text{CuS}$

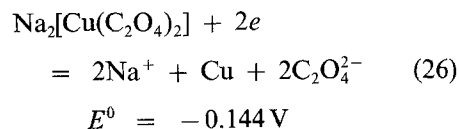
\* The theoretical capacity was based on the weight of  $\text{Cu}_2\text{O}_4$  in the electrode.

An electrochemical reaction(s) was assigned to each voltammetric peak, taking account of the results obtained in a 10% NaCl solution in which high resolution of the voltammograms was attained [4].

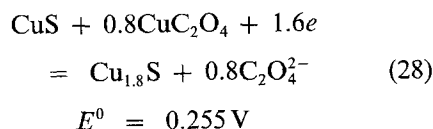
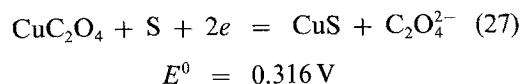
Peak 5d1:



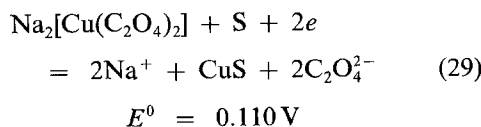
Peak 5d2:



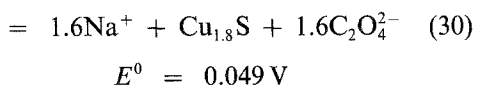
Peak 5sd1:



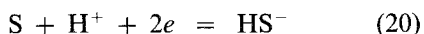
Peak 5sd2:



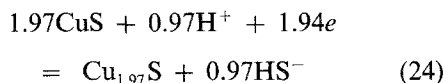




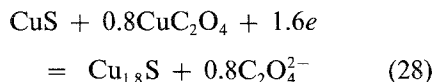
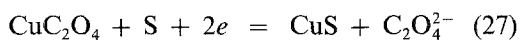
Peak 5sd3:



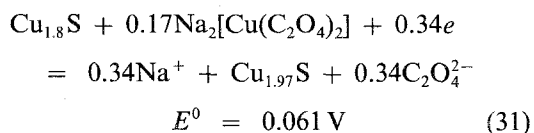
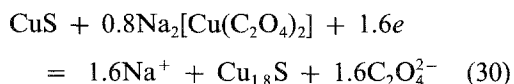
Peak 5sd4:



Peak 5'sd1:



Peak 5'sd2:



It can be seen from these results that sparingly soluble copper compounds containing sulphur give an identical voltage increase of about 0.2 V and identical discharge products to the soluble copper compounds containing sulphur. Therefore, sparingly soluble copper compounds can be classified into the same group as the soluble copper compounds with respect to the effect of added sulphur.

#### 4. Summary

The electrochemical reactions responsible for the voltage increase resulting from the addition of sulphur to the copper compound electrodes were identified. In the discharge reaction sequences,  $\text{Cu}_{1.8}\text{S}$  as well as  $\text{Cu}_{1.97}\text{S}$  was taken into consideration as an intermediate which probably maintains high potentials under simultaneous reduction with the  $\text{Cu}^{2+}$  ions or copper compound active materials, as does  $\text{CuS}$ . The effect of added sulphur can be classified into three categories.

(i) *CuCl-S*. Copper(I) chloride reacts spontaneously with sulphur in neutral and acidic

chloride electrolytes before discharge producing  $\text{CuCl}_2$  and  $\text{CuS}$ . Therefore  $\text{Cu}^{2+}$  is reduced on the surface of  $\text{CuS}$  particles. The main discharge products were  $\text{Cu}_{1.97}\text{S}$  and  $\text{Cu}_{1.8}\text{S}$ . A voltage increase of about 0.35 V was observed

(ii) *CuBr-S and CuI-S*. These copper(I) compounds hardly react with sulphur in the electrolyte. They are reduced simultaneously with sulphur with the formation of  $\text{Cu}_2\text{S}$ . A voltage increase of 0.35–0.4 V was observed.

(iii) *Copper(II) compound-S*. No spontaneous reaction occurs in the electrolytes. Either soluble or sparingly soluble copper compounds are reduced simultaneously with sulphur at more positive potential by 0.2–0.25 V than the electrodes not containing sulphur, producing  $\text{CuS}$ ,  $\text{Cu}_{1.8}\text{S}$  or  $\text{Cu}_{1.97}\text{S}$ , depending on the ratio of sulphur added and discharge depth.

It can be concluded that a mix of a soluble copper(II) compound and sulphur is the most effective cathode mix for seawater-activated batteries among these three groups [5, 13] because the  $\text{CuCl-S}$  mix corresponds to a mix of  $\text{CuCl}_2$  and  $\text{CuS}$  which gives inferior performance to the soluble copper(II) compound-S mix, and the capacity of the mix of  $\text{CuBr}$  and  $\text{S}$  or  $\text{CuI}$  and  $\text{S}$  is low.

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