Copper(II) formate cathodes for seawater batteries

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The preparation of copper(II) formate cathodes, their discharge in magnesium seawater cells, and the discharge reactions are described. This soluble active material could be discharged at high voltages (1.4–1.0 V) with high efficiencies (80–95%) in magnesium cells, when polystyrene solutions were used as the binder to make the cathode plates. For single cells energy densities in the range 70–120 W h kg^{-1} (based on the dry state) were obtained. The $Cu(HCOO)_2$/Mg cell would meet many applications at low or moderate discharge rates as a substitute for the AgCl/Mg cell.

1. Introduction

As cathode active materials for primary and secondary batteries, sparingly soluble compounds have generally been used because of low self-discharge. In the case of reserve batteries including seawater-activated batteries, which are usually stored under dry conditions, soluble compounds could be also successfully employed as the cathode active material because long wet stability is not always required. For example, the use of alkali peroxydisulphates [1, 2], copper(II) sulphate [3], oxyhalogen salts [4] and permanganates [4] has been proposed. Ruetschi and Amlie [5] together with Honer [6] reported that the addition of sulphur to the copper(I) chloride electrode mixture resulted in a potential increase of 0.35–0.45 V. When copper(I) chloride is mixed with elemental sulphur and wetted with a chloride electrolyte, it may be observed that it reacts to form copper(II) sulphide and soluble copper(II) chloride. Therefore, the cathode is considered to be equivalent to a $CuCl_2$ cathode containing CuS. We investigated the possibility of the use of soluble copper compounds as the cathode active material in seawater-activated batteries and recognized the most promising characteristics of copper(II) formate.

2. Experimental details

The copper(II) formate used was labelled as being $Cu(HCOO)_2 \cdot 4H_2O$, and was obtained from Wako Pure Chemical Industries. The water content was measured by thermogravimetric analysis. The sample contained 3.5–3.8 mole H_2O per mole copper(II) formate, which was nearly identical to the nominal formula. The cathode mix tested was 80 wt % $Cu(HCOO)_2 \cdot 4H_2O$, 5 wt % graphite, 5 wt % acetylene black and 10 wt % polystyrene. When sulphur was added the weight per cent of $Cu(HCOO)_2 \cdot 4H_2O$ + S was kept at 80%. Polystyrene (Scientific Polymer Products Inc., average mol. wt.: 22 000) as binder was added in a toluene solution. After toluene was evaporated, 3 g of the cathode mix was pressed onto a copper gauze (48 mesh, 20 mm × 30 mm in size) at a pressure of 200 kg cm^{-2} with approximately half on each side of the current collector. Therefore the cathode had a theoretical capacity of 0.095 A h per square centimetre. The average thickness of the plates after pressing and drying was 3.9 mm. The cathodes were allowed to air dry for at least one week before use in a cell and were wrapped with tea-bag paper. These cathodes were sufficiently hard for normal handling.

The test single cathodes were discharged coupled with two facing AZ 61 magnesium alloy anodes (0.6 mm thick) [7, 8] of equal size to that of the cathode, in excess stagnant electrolyte (about 80 ml) of 3% NaCl. The electrodes were separated by four ribs of 1.1 mm diameter. The discharge was limited by the cathode capacity. Cells were discharged with constant currents at 25 and 2° C.

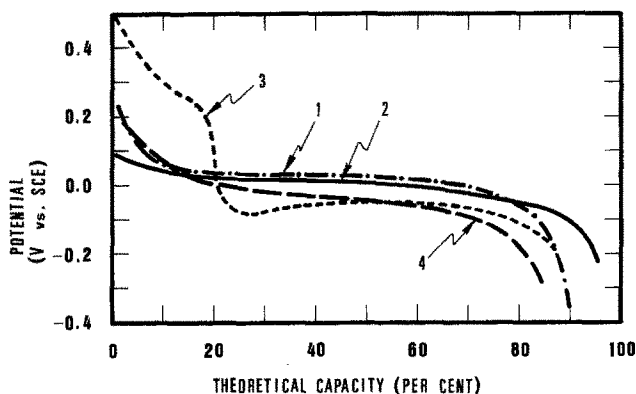The discharge reactions were studied by taking

Fig. 1. Half-cell discharge curves of some soluble copper(II) compounds at about $7\,mA\,cm^{-2}$ in 3% NaCl solution. 1. $CuSO_4$; 2. $Cu(HCOO)_2$; 3. $CuCl_2$; 4. $Cu(CH_3COO)_2$.

voltammograms and the analysis of discharge products. For voltammetry studies the cathode mix used was 70% active mass ($Cu(HCOO)_2 \cdot 4H_2O$ or $Cu(HCOO)_2 \cdot 4H_2O$ + S), 15% graphite and 15% acetylene black by weight, adding no binder, and 40 mg of this mix was used. Cell assembly and detailed experimental procedures were described previously [9].

3. Results and discussion

3.1. *Half-cell discharge curves of soluble copper compounds*

Discharge curves of some soluble copper(II) compounds at about $7\,mA\,cm^{-2}$ are shown in Fig. 1. The active mix contained 70% test active material, 15% graphite and 15% acetylene black by weight, and no binder was used in this experiment. The electrode housing was set upwards. Copper(II) sulphate and copper(II) formate show a good dischargeability. A copper(II) sulphate cathode showed somewhat higher discharge potential than a copper(II) formate cathode in the half-

cell tests. However, in magnesium cells, the copper(II) formate cathode showed better discharge performance on both potential and current efficiency, probably due to the lower solubility of copper(II) formate as shown in Table 1, which lists properties of the two copper(II) compounds. Copper(II) chloride showed a high potential at the beginning of discharge, but its discharge potential dropped to a lower level due to the formation of copper(I) chloride. In addition to this, on account of its deliquescent nature copper(II) chloride has no great advantage as a cathode active material. The discharge curves of formate and sulphate of copper are flat throughout the discharge. This is because the Cu(I) ion is not stable unless enough halide or cyanide ions are present in the pore electrolyte [12]. A worse dischargeability was observed for copper(II) acetate.

3.2. *Single-cell discharges of copper(II) formate/ Mg cells*

Figs. 2 and 3 illustrate typical discharge curves at 25 and $2°$ C, respectively. The results show that

Table 1. *Properties of copper(II) formate and copper(II) sulphate [10, 11]*

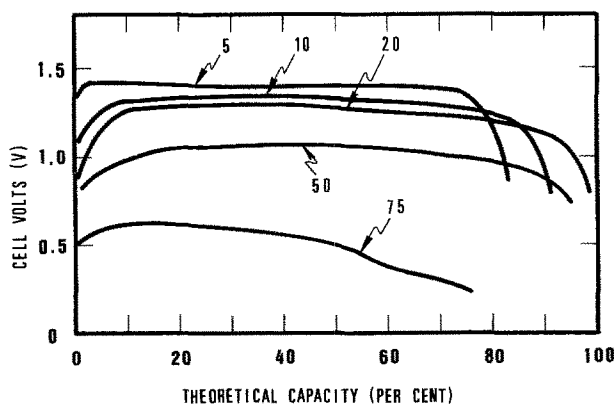| Active material	Copper(II) formate $Cu(HCOO)_2 \cdot 4H_2O$	Copper(II) sulphate $CuSO_4 \cdot 5H_2O$
Formula weight	225.64	249.68
Theoretical capacity ($A\,h\,g^{-1}$)	0.2376	0.2147
Specific gravity	1.81	2.28
Solubility at $25°$ C (g in anhydrous salt per 100 g of water)	12.5	22.7

Fig. 2. Discharge curves of $Cu(HCOO)_2$/Mg cell at 25° C. Numbers in the figure give current densities in $mA\,cm^{-2}$.

these cells have favourably high flat voltage–time discharge curves with high current efficiencies. This system exhibits a lower efficiency at a low current density of $5\,mA\,cm^{-2}$ than at higher current densities, probably due to high self-discharge as a result of the dissolution of $Cu(HCOO)_2$ active material during long discharge. The energy density to 80% of the peak voltage at $20\,mA\,cm^{-2}$ was calculated to be about $120\,W\,h\,kg^{-1}$, based on the dry state excluding the weight of the casing and leads.

The effect of sulphur added to the copper(II) formate cathode was investigated. The discharge curves of cells with $Cu(HCOO)_2$ cathodes containing sulphur at 25° C are shown in Fig. 4. The mole ratio of the cathode mix was 1 : 1 for copper(II) formate : sulphur. The relationships between closed circuit volts and discharge current density are shown in Fig. 5, comparing cells containing the cathodes without added sulphur. The volts plotted were closed circuit voltages when 40% of theoretical capacity of the cathode was removed.

The addition of elemental sulphur to the

$Cu(HCOO)_2$ resulted in an operating potential increase of 0.2–0.3 V at $5–20\,mA\,cm^{-2}$, as observed for copper(II) oxalate cathodes [13, 14]. At high discharge rates, the effect of added sulphur became smaller. From Fig. 5 it is also seen that the discharge potential drops considerably at a high current density, indicating that these cells have a limiting current density and that the copper(II) formate cells can be used at current densities up to 50 and $20\,mA\,cm^{-2}$ at 25 and 2° C, respectively. These discharge rates are considered relatively high with plastic-bonded cathodes. The energy density of the cell containing cathodes with sulphur was nearly identical to those without sulphur because the benefit gained on the voltage is cancelled by the reduced material weight replaced by the sulphur. When sulphur is added and a copper current collector is used, a new problem arises, namely, a tendency for the copper current collector to react with sulphur, resulting in loss of mechanical strength and, in some cases, breakage during prolonged storage over periods of several years.
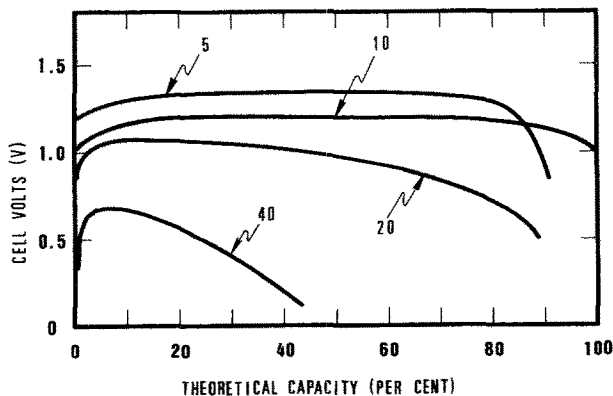

Fig. 3. Discharge curves of $Cu(HCOO)_2$/Mg cell at 2° C. Numbers in the figure give current densities in $mA\,cm^{-2}$.
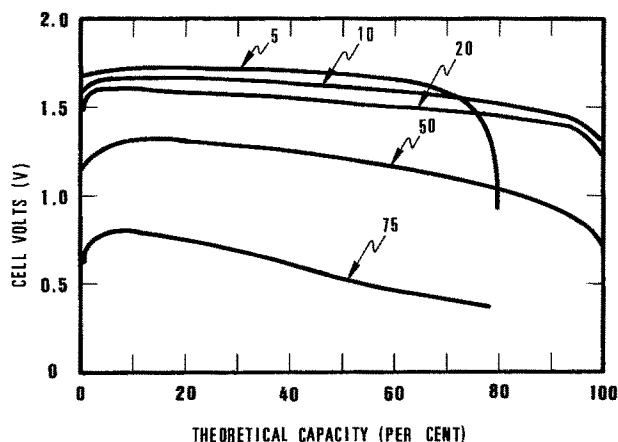
Fig. 4. Discharge curves of $Cu(HCOO)_2$–S/ Mg cell at 25° C. The mole ratio for copper(II) formate : sulphur was 1 : 1. Numbers in the figure give current densities in $mA\,cm^{-2}$.

3.3. Discharges of multi-cell batteries

In the test batteries, cathodes and anodes were the same as those described above. The battery was a five cell device activated with about 2.5 ml of 3% NaCl solution poured into each cell. The discharge curves of the batteries containing cathodes with and without sulphur at $20\,mA\,cm^{-2}$ are shown in Fig. 6. The temperature rose from 20 to 35° C during discharge. The calculated energy density for both cases was about $100\,W\,h\,kg^{-1}$, based on the dry state.

3.4. Comparison of $Cu(HCOO)_2$/Mg cell with AgCl/, CuC_2O_4/, and $PbCl_2$/Mg cells

The performance of the copper(II) formate cell is

compared with those of cells containing different cathode active materials in Fig. 7. All the cells tested were made in our laboratory and they had almost identical capacity. The AgCl cathode was a rolled flat sheet in which a silver gauze collector was incorporated. The surface of the AgCl sheet was slightly reduced with zinc powder to produce metallic silver. For the copper(II) oxalate cell the cathode mix was 66.7% CuC_2O_4, 13.3% S, 5% graphite, 5% acetylene black and 10% polystyrene by weight. For the copper(I) chloride cell the cathode mix was 85% CuCl, 5% graphite, 5% acetylene black and 5% polystyrene. For the lead chloride cell the cathode mix was 86% $PbCl_2$, 5% graphite, 5% acetylene black and 4% polystyrene. The AgCl cell shows superior performance over the other systems. Next come the copper(II) formate, the copper(I) chloride, the copper(II) oxalate-S and the lead chloride cells. The superiority of the AgCl cell becomes more apparent at high

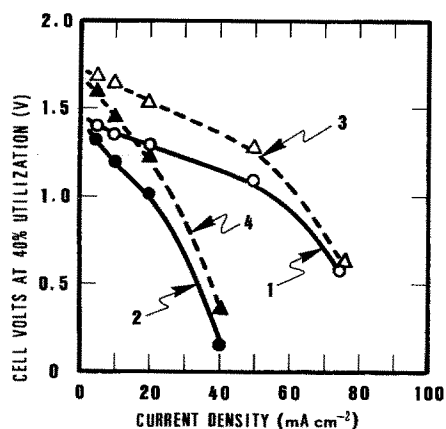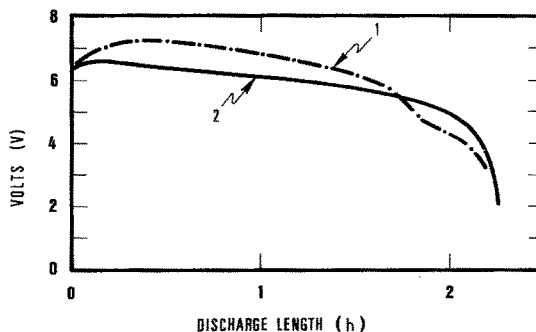Fig. 5. Relationships between closed circuit voltage and discharge current density of $Cu(HCOO)_2$/Mg cells. 1. $Cu(HCOO)_2$/Mg cell at 25° C; 2. $Cu(HCOO)_2$/Mg cell at 2° C; 3. $Cu(HCOO)_2$–S/Mg cell at 25° C; 4. $Cu(HCOO)_2$–S/Mg cell at 2° C.

Fig. 6. Discharge curves of five-cell batteries at room temperature and $20\,mA\,cm^{-2}$. 1. Cathodes containing one mole sulphur per mole $Cu(HCOO)_2$; 2. cathodes containing no sulphur.
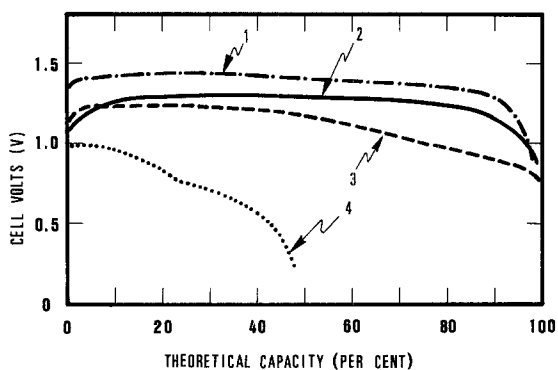
Fig. 7. A comparison of $Cu(HCOO)_2$/Mg cell with AgCl/, CuCl/, CuC_2O_4 + S/, and $PbCl_2$/Mg cells at 20 mA cm^{-2}. 1. AgCl cell; 2. $Cu(HCOO)_2$ cell; 3. CuCl cell and CuC_2O_4 + S cell; 4. $PbCl_2$ cell at 10 mA cm^{-2}.

current densities. For example, the average discharge voltage of the AgCl/Mg cell at 75 mA cm^{-2} was about 1.18 V per cell, while that of the $Cu(HCOO)_2$/Mg cell was about 0.6 V as shown in Fig. 2.

3.5. Electrode reactions of copper(II) formate cathodes

Half-cell discharge curves for $Cu(HCOO)_2$ alone and the mixtures of $Cu(HCOO)_2$ and S at about 7 mA cm^{-2} are shown in Fig. 8. The copper(II) formate cathodes containing 1 mol sulphur per mole copper(II) formate and 0.5 mol sulphur per mole copper(II) formate exhibited nearly identical discharge curves, which show about 0.2 V higher discharge potential than the copper(II) formate cathode without sulphur. Fig. 9 shows voltammograms for the copper(II) formate with and without
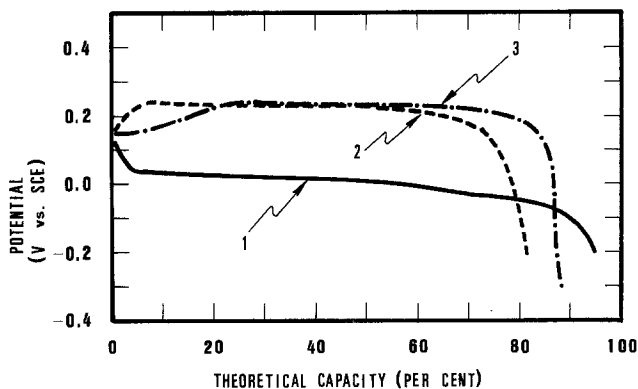
sulphur taken in the 3% NaCl solution at a sweep rate of 0.062 mV s^{-1}. Arrows in the figure indicate points where samples for X-ray diffraction analysis were taken. Two cathodic peaks were obtained for the copper(II) formate, (a) in Fig. 9, indicating the formation of copper(I) chloride. However, Fig. 8 indicates that this formation is very little. This is because Cu$^+$ is unstable unless halide or cyanide ions are present. Since the amount of chloride in the electrode pores is very small in the half-cell discharges, almost all Cu$^+$ ions electrochemically generated disproportionate to Cu and Cu^{2+} [12]. For voltammetry studies, as only 40 mg of the cathode mix was used, the amount of Cl$^-$ is large enough to stabilize the Cu$^+$ formed.

The final reaction product of cathodes containing no sulphur is a red-brown deposit of copper which was identified by X-ray diffraction analysis. The X-ray diffraction patterns of Sample c1, discharged to + 0.166 V vs SCE (about 54% utilization) indicated the presence of unreacted sulphur, CuS and low digenite: its approximate composition is Cu_9S_5, therefore, we will represent it as $Cu_{1.8}S$ here [15]. Samples c2 and c3 gave nearly identical diffraction patterns which indicated that CuS and $Cu_{1.8}S$ were present. The diffraction patterns of Sample c4 indicated the presence of CuS, $Cu_{1.97}S$ and $Cu_{1.8}S$. When a cathode containing 0.5 mol sulphur per mole copper(II) formate was discharged to − 0.21 V (about 89%), it (Sample b1) already contained large amounts of $Cu_{1.97}S$ with small amounts of CuS and $Cu_{1.8}S$. The reflections of Cu_2S were observed after deep discharge (to about − 1.2 V). From these experimental results, possible reaction assignments to current peaks are as follows:

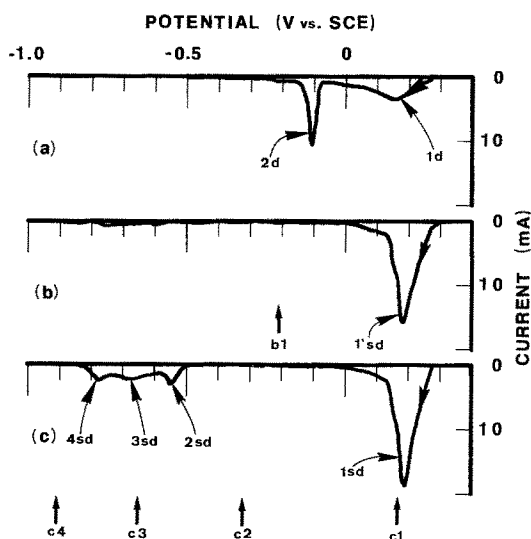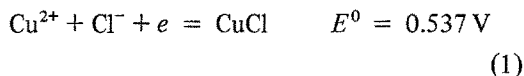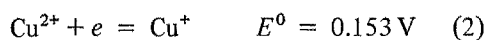Fig. 8. Effect of sulphur added to the $Cu(HCOO)_2$ electrode. 1. $Cu(HCOO)_2$ alone; 2. $Cu(HCOO)_2$ + S (mole ratio = 1 : 0.5); 3. $Cu(HCOO)_2$ + S (mole ratio = 1 : 1).

Fig. 9. Voltammetric curves for $Cu(HCOO)_2$ and for $Cu(HCOO)_2$ containing S taken in 3% NaCl solution at a sweep rate of $0.062\,mV\,s^{-1}$. (a) $Cu(HCOO)_2$ alone, (b) $Cu(HCOO)_2$ + S (mole ratio = 1 : 0.5), (c) $Cu(HCOO)_2$ + S (mole ratio = 1 : 1).

Peak 1d:
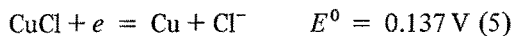
$$Cu^{2+} + Cl^- + e = CuCl \qquad E^0 = 0.537\,V \tag{1}$$

and

$$Cu^{2+} + e = Cu^+ \qquad E^0 = 0.153\,V \tag{2}$$

$$2Cu^+ = Cu + Cu^{2+} \qquad K = 1.5 \times 10^6 \tag{3}$$

that is,

$$Cu^{2+} + 2e = Cu \qquad E^0 = 0.337\,V \tag{4}$$

Peak 2d:

$$CuCl + e = Cu + Cl^- \qquad E^0 = 0.137\,V \tag{5}$$

Peak 1sd:

$$Cu^{2+} + S + 2e = CuS \qquad E^0 = 0.590\,V \tag{6}$$

and

$$CuS + 0.8Cu^{2+} + 1.6e = Cu_{1.8}S$$
$$E^0 = 0.529\,V \tag{7}$$

Peak 2sd:

$$CuO + S + H_2O + 2e = CuS + 2OH^-$$
$$E^0 = -0.004\,V \tag{8}$$

Peak 3sd:

$$S + H^+ + 2e = HS^- \qquad E^0 = -0.062\,V \tag{9}$$

Peak 4sd:

$$1.97CuS + 0.97H^+ + 1.94e = Cu_{1.97}S + 0.97HS^-$$
$$E^0 = -0.121\,V \tag{10}$$

Peak 1'sd:

$$Cu^{2+} + S + 2e = CuS \tag{6}$$

and

$$Cu_{1.8}S + 0.17Cu^{2+} + 0.34e = Cu_{1.97}S$$
$$E^0 = 0.541\,V \tag{11}$$

and/or

$$CuS + 0.97Cu^{2+} + 1.94e = Cu_{1.97}S$$
$$E^0 = 0.531\,V \tag{12}$$
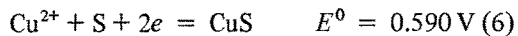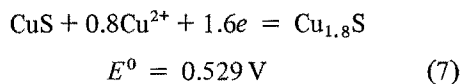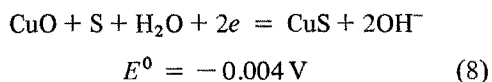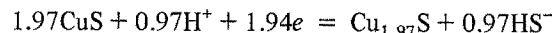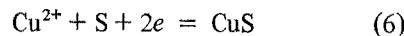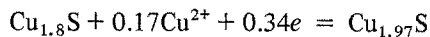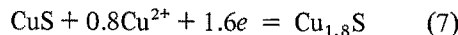
The standard potentials described above were calculated using Gibbs free energies [12, 16, 17]. Estimated values of -78.7 and $-85.4\,kJ\,mol^{-1}$ wer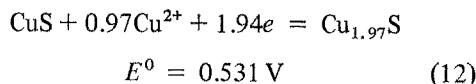e used for the free energies of $Cu_{1.8}S$ and $Cu_{1.97}S$, respectively. The electrochemical Reactions 8–10 are not well defined because it was difficult to identify reaction products of small amounts and to detect small changes in the electrode composition. We tentatively proposed those reactions corresponding to peaks 2sd, 3sd and 4sd as described above on the basis of the voltammetric behaviour of a mixture of CuO, CuS and S. The mixture gave analogous peaks to 2sd, 3sd and 4sd, with regard to locations and shapes [18].

From the reaction assignments it can be concluded that the cell voltage increase by the addition of sulphur to the $Cu(HCOO)_2$ cathode results from the electrode reaction change from Reaction 4 to Reaction 6.

4. Summary

The present study confirmed that soluble copper compounds can successfully work as the cathode active materials in seawater-activated batteries over 10 h when a proper binder is used to make the cathode plates. Among the soluble copper(II) compounds investigated, copper(II) formate was the most promising active material and we believe that in selected applications of low to moderate discharge rates the $Cu(HCOO)_2$/Mg battery can be used as an alternative to the AgCl/Mg battery. Although the cell voltage increases by about 0.2 V when elemental sulphur is added to the copper(II) formate cathode, we recommend the use of

copper(II) formate without sulphur because this voltage increase gives little benefit on the energy density and copper current collectors would be unsuitable when sulphur is added to the cathode.

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