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A water-activated cuprous bromide battery

K. VUORILEHTO* and H. RAJANTIE
Helsinki University of Technology, Laboratory of Corrosion and Material Chemistry, Vuorimiehentie 2, FIN-02150 Espoo, Finland
*(*author for correspondence)*

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Abstract

In this work a water-activated copper(I) bromide battery was developed and investigated. CuBr combined with sulphur as the reactive cathode material was compared with the CuCl-sulphur combination, the anode being in both cases a magnesium alloy. Battery characteristics were tested at room temperature and in an atmosphere simulation chamber because water-activated batteries are mostly used in meteorological radiosondes. Heat evolution was studied calorimetrically, and the potentials of the single electrodes were measured in half-cell experiments. The practical voltages remained significantly lower than the theoretical ones. The low actual voltages of the batteries were found to be caused by the potential loss at the magnesium anode. The heat evolution power of the CuBr battery was approximately 20% lower than the power of the CuCl battery as a result of bromide ions that catalyse the exothermic corrosion reaction of magnesium less than chloride ions. The CuBr battery is environmentally preferable to the CuCl battery because the reaction that produces harmful Cu^{2+} ions does not progress with CuBr. The problem when using CuBr is the slow activation, which can be accelerated by adding soluble salts to increase the conductivity of the electrolyte.

1. Introduction

Water-activated batteries are reserve batteries, to which water is added prior to use. This makes it possible to use very reactive materials without the problem of self-discharge. The water forms the electrolyte with ions that are produced in electrode reactions or liberated from a soluble salt.

Water-activated batteries are used as power sources in radiosondes, air rescue equipment, life jackets and lifeboats, emergency rockets, missiles, torpedoes and underwater research devices. The batteries in question have to withstand long periods of storage without self-discharge. They are exploited under different temperature conditions, especially at very low temperatures. Their current density should be high, but, on the other hand, their lifetime does not need to be long [1].

Radiosondes are the main use of water-activated batteries. A radiosonde is a measuring device that is used for meteorological research in the upper atmosphere. During a sounding the radiosonde is raised by a weather balloon up to height of about $20 \sim 40$ km. Simultaneously it measures and transmits information about temperature, pressure and air humidity.

The conditions during radiosonde soundings in the upper atmosphere are extreme: the temperature decreases to approximately $-60 \sim -90$ °C, and the pressure falls to about 10 mbar. At low pressures the boiling point of water decreases to almost 0 °C whereby the temperature range, in which the battery neither boils nor congeals, is very narrow. The temperature remains low, and the coldness decelerates the cell reactions.

The copper(I) chloride/magnesium battery is the usual and traditional type of water-activated battery [1, 2]. Its problem is the solubility of copper ions, which cause on the one hand corrosion of the magnesium anode and overheating, and on the other hand environmental hazards. The aim of this work was to study copper(I) bromide CuBr as an alternative to CuCl, to find out the differences between the batteries and to develop an optimized CuBr battery. CuBr was chosen for the studies because CuCl and CuBr represent the same kind of compounds, but the reaction that produces soluble copper ions does not occur in the case of CuBr.

2. Experimental details

2.1. *Construction of the batteries*

The battery studied is shown in Figure 1. The anode was a magnesium alloy AZ-31 with 3 mass % aluminium and 1 mass % zinc manufactured by Spectrulite Consortium Inc. (USA). The reactive cathode material was copper(I) bromide CuBr or copper(I) chloride CuCl, both combined with sulphur. The CuBr and CuCl chemicals were manufactured by Riedel-de Haën (Germany). The CuBr:S molar ratios studied were 1:2, 1:1.5, 1:1 and 1:0.5. The cathodes for the reference batteries were prepared using a CuCl:S molar ratio of 1:1.5, as recommended by H.N. Honer [3]. The amount of reactive material was adequate for approximately four hours' use. In addition the cathodes contained 10 mass % graphite as an electronic conductor and 1 mass % magnesium stearate to facilitate moulding of the cathodes. In some experiments, soluble salt (e.g., NaBr or NaCl) was added in the CuBr cathode mix (2 or 5 mass %) to make the electrolyte more conductive. The cathode mixes were prepared in quantities of 200 g and the materials were ground for 30 s in an Ika M20 Universal Mill. The powder was compressed into cathode pellets using a pressure of approximately 8 MPa.

Each cell contained two cathode pellets with a surface area of 2.5 cm × 2.5 cm, that is, a total geometric surface area of 12.5 cm^2. The thickness of the cathode pellets was approximately 0.14 cm. The electrodes were separated by cotton wool (50% cotton, 50% viscose), which was able to absorb the activation water. In some experiments the effect of various salts was studied by dipping the cotton wool into a salt solution and drying the wool before preparing the batteries.

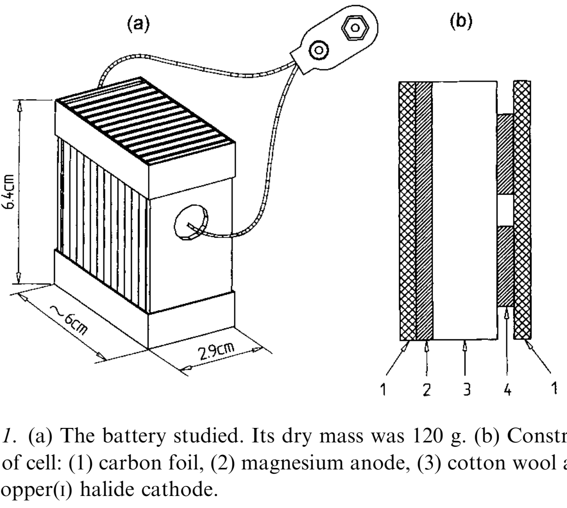

Fig. 1. (a) The battery studied. Its dry mass was 120 g. (b) Construction of cell: (1) carbon foil, (2) magnesium anode, (3) cotton wool and (4) copper(I) halide cathode.

The battery consisted of twelve cells connected in series by an inert carbon foil. The short circuit currents between the cells were eliminated by putting adhesive tape on the edge of the cotton wool. The bottom of the battery was waxed.

The battery was packed in hermetic foil to avoid self-discharge. Prior to use the battery had to be activated by immersing it in tap water for three minutes. The cotton wool was able to absorb approximately 40 g of water (3.3 g per cell). The electrolyte was formed from the water and ions that dissolved from the electrodes. In the CuCl battery the electrolyte was a $MgCl_2$ solution and in the CuBr battery a $MgBr_2$ solution.

2.2. *Reactions in the batteries*

In a traditional CuCl battery the cathode reaction is [1]

$$\mathrm{CuCl} + e^- \rightarrow \mathrm{Cu} + \mathrm{Cl}^- \quad E^\circ = +0.137\ \mathrm{V\ vs\ SHE} \qquad (1)$$

In modern CuCl batteries elemental sulphur is added to the cathode mix. This increases the voltage as a result of the reactions

$$2\ \mathrm{CuCl} + \mathrm{S} \rightarrow \mathrm{CuS} + \mathrm{CuCl_2} \qquad (2)$$

and

$$\mathrm{CuS} + 0.97\ \mathrm{Cu}^{2+} + 1.94\ e^- \rightarrow \mathrm{Cu_{1.97}S}$$
$$E^\circ = +0.531\ \mathrm{V\ vs\ SHE} \qquad (3)$$

as studied by Hiroi [4]. Reaction 2 takes place in an aqueous solution [5], and increases the conductivity of the electrolyte as a result of the formation of soluble $CuCl_2$.

In a pure CuBr battery the cathode reaction would be [4]

$$\mathrm{CuBr} + e^- \rightarrow \mathrm{Cu} + \mathrm{Br}^- \quad E^\circ = +0.033\ \mathrm{V\ vs\ SHE} \qquad (4)$$

When elemental sulphur is added to the cathode mix the voltage increases as a result of the reaction [4]

$$2\ \mathrm{CuBr} + \mathrm{S} + 2\ e^- \rightarrow \mathrm{Cu_2S} + 2\ \mathrm{Br}^-$$
$$E^\circ = +0.480\ \mathrm{V\ vs\ SHE} \qquad (5)$$

A reaction analogous to Reaction 2 does not occur in a CuBr battery because of a positive Gibbs free energy change [4]. This means that no ions dissolve in the water before the discharge reaction (5).

The anode reaction in both batteries is [1, 2]

$$Mg \rightarrow Mg^{2+} + 2\ e^{-} \quad E^{\circ} = -2.360\,\mathrm{V\ vs\ SHE} \tag{6}$$

In an aqueous solution a passivating hydroxide layer is formed on the surface of magnesium, and therefore the electrode potential of magnesium is approximately 0.6 ~ 1.1 V more positive than the theoretical one [2, 6]. The structure of the layer and the reactions depend on the pH of the solution.

The passive layer creates delayed action by preventing the electrode reaction and decelerating the reaction rate. Delayed action is defined as the time that elapses from the battery connection until the battery voltage reaches the required minimum voltage. At the beginning of the discharge pits are formed in the passive layer, and the layer does not recover completely any more. As the metal is able to contact the electrolyte through the pits, the passivation gradually weakens [6, 7]. Aggressive ions, such as chloride, strengthen the formation of the pits. The delayed action is expected to be especially strong in a CuBr battery because no aggressive ions are dissolved until as a consequence of discharge Reaction 5.

Magnesium as an electropositive metal oxidizes (i.e., corrodes) very easily. In addition to the desired electrode reaction (6) a hydrogen-producing corrosion reaction takes place at the anode [1, 6]:

$$\begin{aligned} & Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2 \\ & \Delta H = -353\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{7}$$

This corrosion reaction is strongly exothermic. In cold conditions during radiosonde soundings the corrosion of the magnesium anode produces the heat needed to keep the battery temperature above 0 °C. However, when corrosion catalysts, such as copper, iron, chloride or bromide, are present, corrosion may generate too much heat. As a consequence the water evaporates, the electrolyte diminishes and the battery voltage drops. Copper and iron cause galvanic corrosion, whereas the aggressive ions, chloride and bromide, cause pitting corrosion [8].

Using Equations 2, 3, 5 and 6 the theoretical voltages of CuBr/Mg and CuCl/Mg cells can be presented as follows:

$$\begin{aligned} & \mathrm{CuBr:}\ U^{\circ} = +0.480\,\mathrm{V} - -2.360\,\mathrm{V} = 2.84\,\mathrm{V} \\ & \quad (34.1\,\mathrm{V\ for\ 12\ cells}) \\ & \mathrm{CuCl:}\ U^{\circ} = +0.531\,\mathrm{V} - -2.360\,\mathrm{V} = 2.89\,\mathrm{V} \\ & \quad (34.7\,\mathrm{V\ for\ 12\ cells}) \end{aligned}$$

2.3. *Simulations in the atmosphere chamber*

Battery characteristics were studied in an atmosphere simulation chamber (Weiss, Germany), in which temperature and pressure were adjusted to values similar to those in normal radiosonde soundings. The temperature and pressure profiles during a simulation are given in Table 1. The air flow during radiosonde soundings was simulated by ventilation, and a computer controlled the temperature and the pressure in the chamber and recorded their values. The duration of the simulation program was 150 min. During the first 30 min of discharge the temperature was 25 °C and the pressure was 1015 mbar, as 30 min is the assumed period needed for the ground preparation of a sounding. The batteries were discharged using a direct current of 150 mA (12 $\mathrm{mA\,cm^{-2}}$) and they were required to give at least the cut-off voltage of 15 V, which are typical values needed by a modern radiosonde. The battery voltage was measured during the simulation and presented as a function of time. The time, in which the battery voltage stayed above the cut-off voltage, was determined.

2.4. *Calorimetric experiments*

Heat production of the battery was studied in a thermally insulated Dewar flask at +20 ~ +25 °C. The Dewar flask was filled with water, and the test battery, contained in a small plastic bag, was placed in it. The battery was discharged with a current of 150 mA over a period of 150 min, and the temperature rise of the water was measured. Heat energy and heat evolution power were determined using the heat capacity of water. The

Table 1. Pressure and temperature profiles during an atmosphere simulation. A typical sounding lasts approximately 135 min (including the ground preparation)

Time/min	*p*/mbar	*T*/°C
0–30	1015	+25
35	843	+10
45	572	−15
55	377	−34
65	239	−55
75	148	−60
85	92	−60
95	57	−60
105	35	−60
115	22	−60
125	15	−60
135	12	−60
150	9	−60

Duration of simulation program was 150 min battery voltage was measured as a function of time. The Dewar flask measurements provided valuable data not only about the heat evolution of the battery, but also about the battery characteristics at room temperature and normal pressure.

2.5. *Half-cell experiments*

The cathode and anode potentials were studied in half-cell experiments. The measuring setup is illustrated in Figure 2. The cell was made of acrylic plastic. The working electrode was in contact with the 1.0 molar $MgCl_2$ or $MgBr_2$ electrolyte through a hole (diameter 12 mm) in the cell wall. The electrode was pressed against the wall by a screw with an O-ring as the seal. The reference electrode was Ag|AgCl, and the auxiliary electrode was an inert platinum plate. After a stabilization time of 5 min, the working electrode was discharged for 150 min with a current density of 12 $mA\,cm^{-2}$. The potential of the working electrode was measured as a function of time. The half-cell experiments gave data about the voltage losses at the individual electrodes.

3. Results and discussion

3.1. *Optimized CuBr:S mole ratio*

Voltage curves for the CuBr and CuCl batteries in atmosphere simulations are shown as a function of time in Figure 3. Only the mole ratio of 1:1.5 was selected for Figure 3, since the voltage curves with the other CuBr:S mole ratios were very similar. The maximum voltage under load of the CuBr batteries was approximately 2–3 V lower than that of the CuCl battery. Nevertheless, the voltage of the CuBr batteries dropped slowly and did not fall beneath the cut-off voltage (15 V) significantly faster than the voltage of the CuCl battery. The open circuit voltage of the CuBr batteries was approximately 21.0 V and that of the CuCl battery was 21.5 V.

The summary of the results with various mole ratios is presented in Table 2. The values of the heat evolution power were very high compared to the electric power given by the batteries, which was only approximately 3 W. As can be seen on the basis of both the simulator experiments and the calorimetric measurements, the CuBr:S mole ratio of 1:1.5 gave the best results: the heat evolution power was lower and the duration in the atmosphere simulation longer than with the other CuBr:S molar ratios. Therefore this particular mole ratio was selected for further studies.

The voltage curves of the calorimetric experiments with the copper(I) halide: sulphur molar ratio of 1:1.5 are shown in Figure 4. In these experiments, where the effects of temperature, pressure and electrolyte evaporation were eliminated, the battery voltage remained stable at the value corresponding to the maximum voltage in the atmosphere simulations (Figure 3).

3.2. *Voltage difference*

The actual voltages of both the CuCl battery and the CuBr battery remain at significantly lower values than

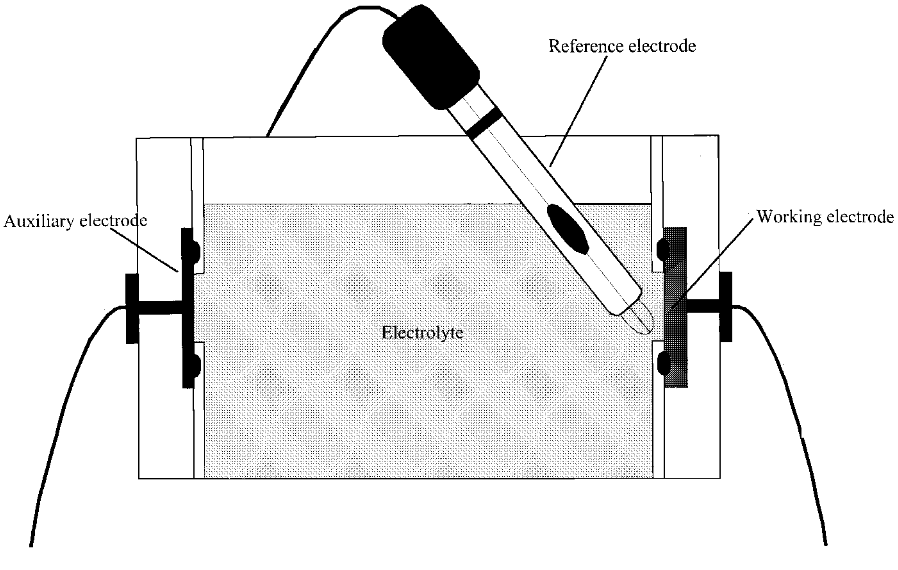

Fig. 2. Measuring setup for half-cell experiments.

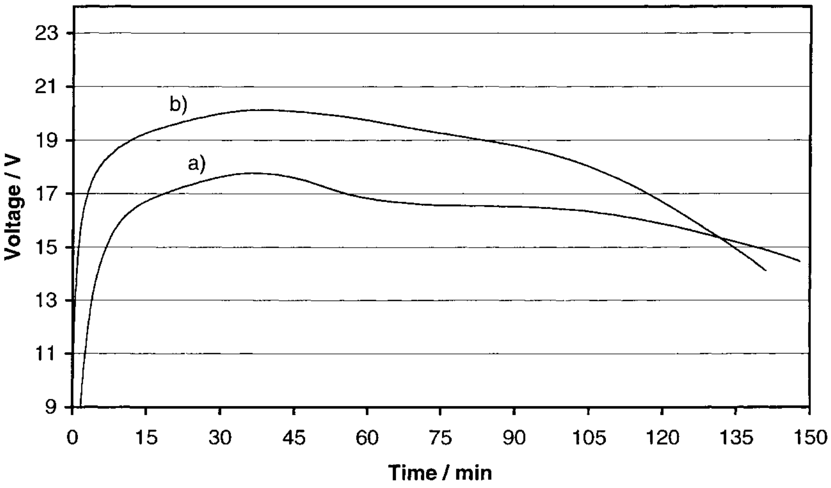

Fig. 3. Voltage curves in the atmosphere simulations for (a) the CuBr battery and (b) the CuCl battery. In both batteries, the copper(I) halide:sulphur molar ratio was 1:1.5. The discharge current was 150 mA (12 mA cm^{-2}).

Table 2. Duration in the atmosphere simulation and heat evolution power of batteries with various copper(I) halide:sulphur molar ratios

Cathode mix	Duration (simul.) /min	Heat evolution power (calorimetric exp.)/W
CuBr:S = 1:2	119	5.1
CuBr:S = 1:1.5	140	4.9
CuBr:S = 1:1	137	5.5
CuBr:S = 1:0.5	128	6.1
CuCl:S = 1:1.5	138	6.0

the theoretical ones. In addition the difference between the maximum voltages of the CuCl and CuBr batteries is approximately 2–3 V, although the theoretical voltage difference is only 0.6 V. Therefore the sources of the difference were investigated.

The actual battery voltage is always lower than the theoretical one, depending on the reaction kinetics and the cell resistance [9]:

$$U = E_t^C - E_t^A - |\eta_C| - |\eta_A| - IR_{\text{cell}} \tag{8}$$

where E_t^C and E_t^A are the thermodynamic potentials for the cathodic and anodic reactions respectively, η_C and η_A are the overpotentials of the electrode reactions, I is the current and R_{cell} is the cell resistance.

A comparison of the voltages of CuCl and CuBr batteries is presented in Table 3. The activation over-

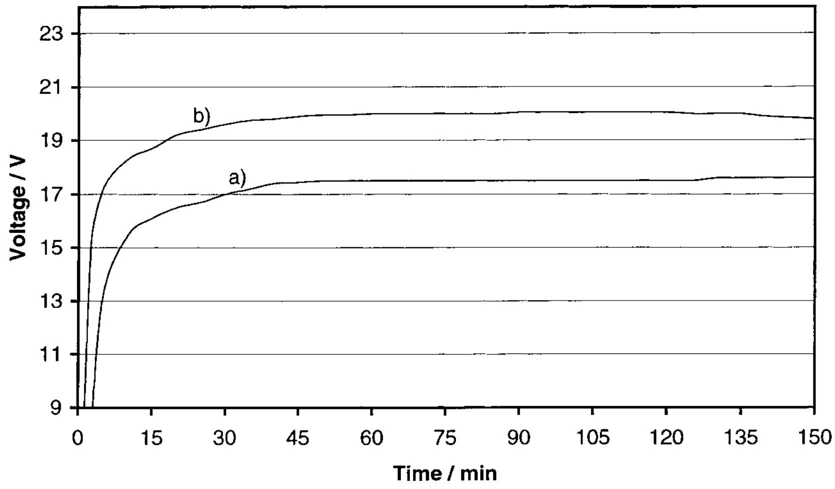

Fig. 4. Voltage curves in room temperature and normal pressure (calorimetric measurements) for (a) CuBr battery and (b) CuCl battery. In both batteries, the copper(I) halide:sulphur molar ratio was 1:1.5. The discharge current was 150 mA (12 mA cm^{-2}).

Table 3. Comparison of voltages of CuCl and CuBr batteries after 35 min of discharge

	CuCl battery	CuBr battery	Difference
Theoretical voltage/V	34.7	34.1	0.6
Activation overpotential η_C/V	−0.8	−1.4	0.6
Loss at the Mg-anode η_A/V	−12.4	−13.4	1.0
IR drop (cathode)/V	−0.1	−0.2	0.1
IR drop (cotton wool)/V	−0.2	−0.2	0.0
IR drop (carbon foil)/V	−0.3	−0.3	0.0
Total	20.9	18.6	2.3

potential η_C at the cathode was estimated in half-cell experiments by subtracting the potential reached at the beginning of the discharge from the theoretical electrode potential. The activation overpotential η_A at the magnesium anode was measured in the same way, though it was not a pure activation overpotential, but merely a voltage loss caused by the hydroxide layer and the hydrogen evolution. This voltage loss depended strongly on the electrolyte solution. The electrode potential of magnesium was -1.33 V vs SHE in a chloride solution and -1.24 V vs SHE in a bromide solution. The *IR* drop of the electrolyte was divided into two components: inside the cathode and in the cotton wool. The *IR* drop inside the cathode was determined in half-cell experiments by subtracting the momentary potential from the potential at the beginning of the experiment. It was assumed that the decrease in the cathode potential with time was caused by the growing *IR* drop when the reaction zone moved from the cathode surface deeper into the cathode. The values in Table 3 were calculated after 35 min of discharge. The *IR* drop of the electrolyte in the cotton wool was determined, using the measured conductivities of 1.0 molar $MgCl_2$ or $MgBr_2$ solutions, 117 and 121 mS cm^{-1}, respectively. In addition to the *IR* drop in the electrolyte there was some *IR* drop in the electric contacts, mainly on the carbon foil. This was measured using an ohmmeter.

It can be estimated that over 40% of the actual voltage difference between CuBr and CuCl batteries is due to the different influence of the halides on the electrode potential of magnesium. The *IR* drop and the activation overpotential at the cathode are negligible compared with the voltage drop at the anode.

3.3. *Heat evolution*

The measured heat evolution power of the CuBr battery was approximately 1 W lower than the value of the CuCl battery. An attempt was made to discover the reasons for this difference.

The average heat evolution power ($\bar{P}$) of the batteries, neglecting entropy effects, can be calculated from Equation 9:

$$\bar{P} = (I \times U\text{-loss}) + (I \text{ of side reaction} \times U \text{ of side reaction}) \quad (9)$$

The U-loss is the voltage difference between the theoretical battery voltage and the voltage achieved in the heat evolution experiments (1.38 V for a CuBr cell and 1.23 V for a CuCl cell). It consists of the *IR* drop and the activation overpotentials. The current of the side reactions can be estimated from the current efficiency (0.67 for CuBr and 0.60 for CuCl), which has been measured previously in connection with corrosion experiments for magnesium [10]. The voltage of the side reaction is calculated to be approximately the difference between the theoretical electrode potentials of hydrogen and magnesium ($-0.50\,\text{V} - -2.36\,\text{V} = 1.86\,\text{V}$ at pH 8.5). The calculation using Equation 9 gives the following result for the average heat evolution powers of the CuBr/Mg and CuCl/Mg batteries with 12 cells:

$$\text{CuBr:}\ 12 \times [0.150\,\text{A} \times 1.38\,\text{V} + (0.150\,\text{A}/0.67 - 0.150\,\text{A}) \times 1.86\,\text{V}] = 4.13\,\text{W}$$

$$\text{CuCl:}\ 12 \times [0.150\,\text{A} \times 1.23\,\text{V} + (0.150\,\text{A}/0.60 - 0.150\,\text{A}) \times 1.86\,\text{V}] = 4.45\,\text{W}$$

The experimental values given in Table 2 were 4.9 W and 6.0 W, respectively.

The experimental values are in good agreement with the theoretically calculated ones. In the real batteries, copper ions had an influence on the corrosion of magnesium, and consequently on the current efficiency. This phenomena was of particular importance in the CuCl battery, in which Cu^{2+} ions dissolved due to Reaction 2. However, the corrosion experiments for magnesium [10] were carried out in the cell without copper. This probably explains the lower theoretical values of heat evolution power. There is a significant difference between the heat evolution powers of the CuBr and CuCl batteries. This is most probably caused by the absence of Reaction 2 in the CuBr battery and by the less aggressive bromide ions that do not affect the corrosion and heat evolution as intensively as chloride ions.

3.4. *Activation time*

The main problem of CuBr batteries is their long activation time, as can be seen in Figures 3 and 4. This means that the battery voltage rises up to the required value very slowly, in approximately 5–10 min. This is probably caused by the low conductivity of the electrolyte. An attempt was made to eliminate the problem by adding different soluble salts, NaCl, NaBr, KBr and Na_2SO_4, to the cathode mix in 2 or 5 mass % and further by adding the salts directly to the cotton wool to accelerate the dissolution.

The results are listed in Table 4. It can be seen that the activation problem is not solved when salt is added to the cathode mix, but the durations of the batteries in the simulation experiments get significantly longer. The salts most probably form pores in the cathode when dissolving and therefore facilitate the contact between the reactive material and the electrolyte. This can be assumed to reduce the *IR* drop inside the cathode. The activation time problem is best solved by adding the salt directly to the cotton wool, which renders the electrolyte conductive immediately after the water-activation. Na_2SO_4 additions seem to have no effect on the battery performance, probably due to the very slow dissolution of this salt.

The soluble salts affect the heat evolution by increasing the corrosion of magnesium. The results are listed in Table 5. As expected, chloride has the strongest effect.

3.5. *An optimised CuBr battery*

The battery voltage of a good CuBr battery should rise relatively fast to the cut-off value (15 V) and stay above it as long as possible. On the basis of the results in Tables 4 and 5, a CuBr battery was constructed with 1% NaCl in the cathode mix and 0.1 M NaCl in the cotton wool. This battery was assumed to have both the advantages of the salt additions: a rapid activation, and pores in the cathodes, but not too high a heat evolution power. NaCl was preferred, as it is not a problem for the environment or for industrial safety. The voltage curve of the battery in the atmosphere simulator is shown in Figure 5. The battery came up to expectations: the activation time was less than 1 minute and it stayed above the cut-off voltage for 150 min. The heat evolution power of the battery was 5.5 W in the calorimetric measurement.

Table 4. Duration in the atmosphere simulation (min)/Activation time (min) with various salt additions
For Na_2SO_4 a concentration of 0.1 M was used to make the normalities equal

	NaCl	NaBr	KBr	Na_2SO_4
2%	148/5	149/6	150/10	136/11
5%	149/4	148/5	149/7	127/7
0.2 M (cotton wool)	138/0	131/1	144/0	137/8

Table 5. Heat evolution power (W) with various salt additions
For Na_2SO_4 a concentration of 0.1 M was used to make the normalities equal

	NaCl	NaBr	KBr	Na_2SO_4
2%	5.4	4.7	4.7	4.7
5%	5.6	5.1	5.3	5.2
0.2 M (cotton wool)	5.2	5.6	5.7	4.9

3.6. *Environmental aspects*

The amount of soluble copper that was able to escape from the battery during the immersion in water was determined. This was performed by analysing the copper content of the remaining activation water colorimetrically.

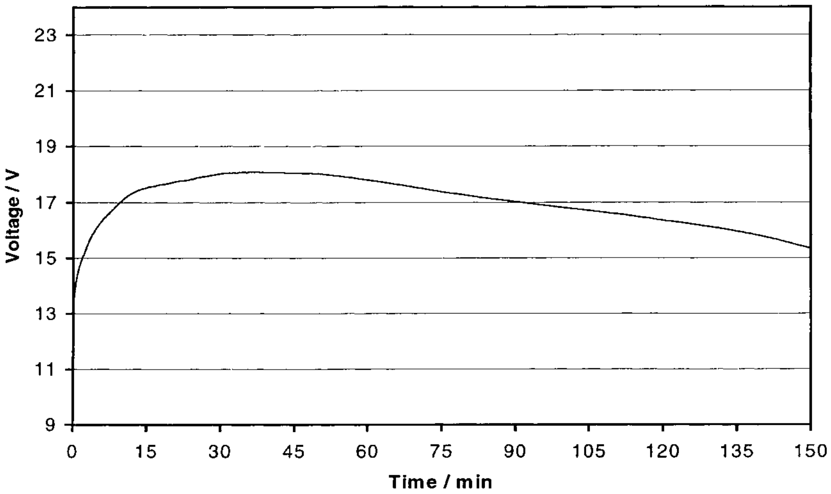

Fig. 5. Voltage curve in the atmosphere simulation for the optimized CuBr battery with 1% NaCl in the cathode mix and 0.1 M NaCl in the cotton wool. The copper(I) bromide: sulphur molar ratio was 1:1.5. The discharge current was 150 mA (12 mA cm^{-2}).

In the case of CuCl batteries, the amount of copper in the activation water was 300–400 μmol. When CuBr batteries with NaCl additions were used, the amount was 40–60 μmol. Furthermore, in the case of CuBr batteries without NaCl additions, the amount of copper was smaller than the detection limit of 25 μmol.

The considerably lower Cu content in the activation water of the CuBr batteries results from the absence of Reaction 2. The low level of soluble copper compounds during activation and discharge of these batteries is ecologically beneficial because Cu is very harmful to aqueous life in water systems. In addition, the low copper content directly affects the heat evolution by not catalysing the corrosion of magnesium too much.

The Cu content was higher in the activation water of the CuBr batteries in which chloride is present. This results most probably from the tendency of chloride to form soluble complexes with copper in the oxidation state I [11].

4. Conclusions

CuBr-sulphur is very suitable for use as a cathode material in water-activated batteries. Although it gives a maximum voltage lower than the traditional CuCl-sulphur battery, the voltage is more stable. The main reason for the actual voltage difference between the CuBr and CuCl batteries is the potential loss at the magnesium anode.

In the CuBr battery, the corrosion of the magnesium anode is less intense than in the CuCl battery, because bromide is a less aggressive ion than chloride. As a consequence, the heat evolution is approximately 20% slower than in the CuCl battery, and the electrolyte does not evaporate, so the battery voltage stays more stable. When electronic devices are used, a stable voltage is preferred.

Since bromide ions do not dissolve before discharge, the delayed action is effective and the activation time is long in the CuBr battery. The problem can be eliminated by adding soluble salts to the cotton wool.

CuBr is ecologically beneficial as it is almost insoluble and does not react spontaneously with sulphur. The disadvantage of the CuBr battery is the high price of the raw material.

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