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Influence of allotropic modifications of sulphur on the cell voltage in Mg–CuI(S) seawater activated battery

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Abstract

The increase in cell voltage of Mg–CuI seawater activated batteries effected by sulphur addition is strongly influenced by the kind of sulphur allotrope used for the purpose. Cyclohexasulphur (S_6), cyclooctasulphur (S_8), and cyclododecasulphur (S_{12}) were evaluated for the benevolence vis-a-vis that of commercial grade sulphur. Sulphur participates in the electrochemical reaction, the elevation in cell voltage being in the order of reactivity of the allotropes: $S_6 > S_{12} > S_8 >$ commercial grade sulphur. Battery performance results are discussed in the light of UV, IR and EPR spectra and magnetic susceptibility measurements. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Sulphur allotropes; Sea-water activated batteries; Cyclosulphur compounds

1. Introduction

It is a common practice to add sulphur to the cathode active material in magnesium–copper compound water activated batteries in order to enhance the cell voltage [1–7]. Besides increasing the cell voltage, sulphur is also reported to promote the utilisation efficiency of the cathode active material [3].

Sulphur is a compound made up of S–S bonds and is known for its allotropic modifications. It has been proven that the different molecular forms of sulphur exhibit different chemical reactivities [8]. Henceforth, it is of interest to examine the effect of allotropic modifications of S on its voltage increasing capacity in a Mg/copper compound seawater activated battery.

As will be discussed in this paper, the influence of allotropic modifications on the voltage elevating effect of sulphur in Mg–CuI cell is examined by battery performance tests which are substantiated by UV, IR and EPR spectral analyses and magnetic susceptibility measurements.

2. Experimental

The cathode active material, viz., cuprous iodide prepared by following the reported procedure [9], was dried in an air oven at 80°C and then ground into a fine powder and sieved on a 100 mesh. 2.56 g of CuI (0.36 Ah), mixed thoroughly with 15% colloidal graphite, constituted the prime cathode depolariser for each plate. Sulphur was added in a desired proportion to CuI + colloidal graphite and the blend was mixed throughly by grinding in a mortar and pestle made of glass. The active material was mounted on a thin copper mesh of dimensions 0.04 m × 0.025 m × 0.002 m, wrapped with filter paper and then pressed using a die on a hydraulic press. Ten tons of compaction pressure applied over the area of the electrode was found to give a good performance; no binder was used.

The anode was made from magnesium alloy (AZ31) sheets of dimensions 0.04 m × 0.0025 m × 0.015 m. The lead connection was provided to the anode by means of metallic rivets fixed on to the magnesium plate. The plates were cleaned with acetone and then with concentrated HCl.

A cathode plate was positioned between two magnesium anodes; a pair of thin PVC wires pasted on to the inner side of the magnesium plates prevented direct contact of the cathode with the anodes [10].

The cell was connected in series to a variable resistor and in parallel to a voltmeter and then immersed in a 100 ml beaker containing 3.3 wt.% NaCl, the latter functioning as the electrolyte. Care was taken to ensure that the metallic rivets and leads did not contact the electrolyte. All the discharges were constant current drains (100 mA) and were carried out at room temperature (25 ± 1°C).

Direct reaction of sulphur and magnesium was prevented by taking CuI in excess to the quantity of magnesium. Therefore, at any stage during discharge, a condition was

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not reached when the prime depolariser was depleted and only Mg and S were left behind.

The commercial grade LR sulphur, a Sarabhai Merck product, was of 92% purity. Among the common impurities that were listed were moisture, acid, arsenic, ash and various carbonaceous compounds.

The GR grade sulphur (99.5% purity) supplied by E. Merck was orthorhombic sulphur, as confirmed by its IR spectra and X-ray pattern [11–13]. It consisted of S_8 molecules in the form of staggered eight-membered rings.

Cyclohexasulphur, S_6, was prepared as follows [14]: Concentrated hydrochloric acid was mixed with a cooled concentrated thiosulphate solution. The resulting mixture of S_6 and S_8 was then extracted with benzene. On cooling the extract, cyclohexasulphur crystallised out in typical orange-coloured rhombohedral crystals.

Cyclododecasulphur (S_{12}), prepared by following the reported procedure [15,16], was a gift sample from Prof. G.V. Subba Rao, Director, CECRI. Its purity was verified by its melting point (140°C) and its mass spectrum [17,18].

Benzene and chloroform were spectral grade E. Merck products. Acetonitrile GR dried (maximum 0.005% H_2O) and potassium cyanide GR were also E. Merck products.

Ultraviolet spectra were obtained with a Hitachi 320 spectrophotometer using a 1 cm fused silica cell. IR spectra were recorded with a Shimadzu IR 408 spectrophotometer with polythene cells in the range 600–200 cm^{-1}. A Polytech FIR-30 spectrophotometer was used for FT-FIR measurements. The EPR spectrum of the sample in the powdered form was recorded on an E4 Varian X-band spectrometer.

The magnetic moment of the product was measured by the Guoy method [19]. For the conductivity measurements, the end-of-discharge product was first washed thoroughly with water, dried at 80°C, ground into a powder and then washed under a stream of water so that the lighter colloidal graphite was washed away. The material thus obtained was dried at 80°C in an air oven for 8 h and then dried in vacuum. After grinding into a fine powder, the product was made into a pellet of 0.006 m diameter and 0.0002 m thickness. Electrical contact points were made with gold deposit/silver paint and the conductivity was measured using an assembled Hall and Van der Pauw system.

3. Results and discussion

Sulphur is a chalcogen element with the outer electronic shell complete but for two electrons. It manifests a very large number of molecular forms. Broadly, two kinds of allotropy can be distinguished in sulphur. First, intramolecular allotropy which accounts for the different molecular species formed by chemical bonding of sulphur atoms and second, intermolecular allotropy which accounts for the different structural arrangements of its molecules in crystals. Thus, a multitude of modifications of elemental sulphur is possible. However, it was restricted in the present study, to employ relatively few experimentally secured sulphur allotropes, viz., cyclooctasulphur, S_8(I), cyclohexasulphur, S_6(II), and cyclododecasulphur S_{12}(II), besides the ordinary commercial grade Indian sulphur(IV). The commercial grade sulphur (roll sulphur as well as flowers of sulphur) contains by far the greatest proportion the orthorhombic sulphur, S_8, which is nothing but the S_α variety. Therefore, the usage of commercial grade sulphur in the present study only signifies the effect of impurities contained in it.

One hypothesis in the voltage increasing effect of sulphur in copper compound batteries is that during discharge, sulphur probably reacts with the highly active copper formed when the prime depolariser is reduced, producing a copper sulphide, thus accounting for the fact that no copper is observed at the end of discharge. This reaction may also prevent copper from plating out on the magnesium, thus deterring premature voltage drop [5,6].

Flerov [4], based on his studies of the Mg–CuI system proposed that, in sulphur benevolence, cuprous sulphide rather than metallic copper is the final discharge product and showed that the reaction responsible for potential increase is

$$e + CuCl + CuS \rightarrow Cu_2S + Cl^-$$

where CuS is formed as follows:

$$2CuCl + S \rightarrow CuS + Cu^{2+} + 2Cl^-$$

Hiroi [3] put forth a different view for the Mg–CuI system, that the electrode reaction, viz,

$$CuI + e = Cu + I; \quad E = -0.185\ V$$

changes in the presence of sulphur to

$$2CuI + S + 2e = Cu_2S + 2I^-; \quad E = -0.261\ V$$

and hence causes the elevation in cell voltage. In a separate study, Hiroi [7] also found a copper valency dependent voltage elevation of magnesium/copper compound cells upon addition of sulphur.

The foregoing hypotheses differ from each other in their prognosis and support respectively, a pure chemical reaction, a combined chemical–electrochemical reaction and a pure electrochemical reaction as being responsible for sulphur benevolence of Mg–CuX batteries. It seems, therefore, important to first ascertain the mechanism of sulphur benevolence in Mg–CuX systems.

3.1. Dependence of cell voltage and cell capacity on sulphur content

Fig. 1 shows the effect of adding commercial grade LR sulphur to CuI on the Mg–CuI battery performance. The discharge curves with 0.5 and 1 wt.% sulphur match with that of CuI without sulphur, indicating the absence of any effect of sulphur at these low contents. As the sulphur content was increased to 2.5 wt.% and above, one observes important changes. At 2.5 wt.% sulphur, the discharge curve

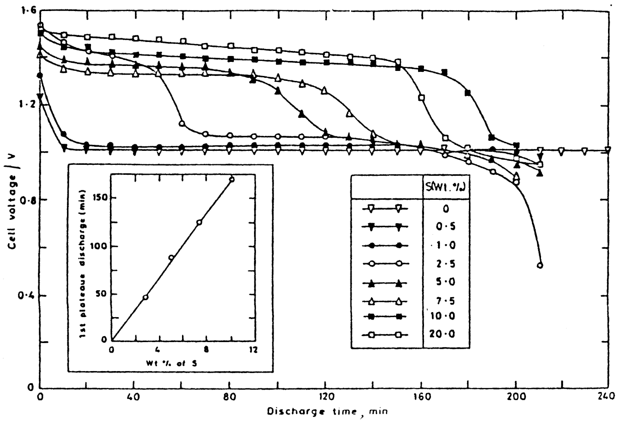

Fig. 1. Dependence of discharge charactristic of Mg–CuI seawater activated battery on S (commercial LR grade) concentration. Inset shows linear variation of 1st plateau discharge with S content.

showed two clear-cut plateaus. When the S addition was increased further, plateau I became longer with concomitant contraction of plateau II. Also, the discharge capacity of plateau I increased linearly with the sulphur concentration. The cell voltage increased steadily with increasing sulphur addition up to 10 wt.% above which the change is small. Thus, an optimum concentration of 10 wt.% sulphur was realised to bring about a 370–400 mV increase in the cell voltage. It should also be noticed that the occurrence of two plateaus was observed only below 10 wt.% sulphur, at and above which only a single plateau was observable.

The above observations suggest that sulphur participated in the electrode reaction, contributing to the cell voltage. As far as the CuI : S ratio was concerned, 10 wt.% S means 10 wt.% CuI which weighed 0.26 g. The corresponding capacity for a 2F reaction for cuprous sulphide formation (also taking into consideration 92% purity of the commercial grade sulphur) was 0.40 Ah, which worked out to be close to a 1 : 1 ratio of CuI : S. In other words, the greatest benefit of elemental sulphur was attained by using it in an approximately stoichiometric quantity. A similar observation has been made by Flerov [4] for the Mg–CuCl battery.

The stoichiometric requirement of sulphur was also verified by the following analysis which was based on the fact that S is soluble in $CHCl_3$ [20] and the solution exhibits a distinct UV spectrum [21]. The end-of-discharge product (confining only to plateau I) at <10 wt.% sulphur was extracted with $CHCl_3$ and the spectrum of the extract was recorded (Fig. 2). Below 10 wt.% S addition, the UV spectrum revealed no absorption at 290 nm, indicating the absence of S. At 10 wt.% S, the UV spectrum had some absorbance corresponding to a small amount of excess sulphur, and at >10 wt.% S, the values at 290 nm were proportional to the content in excess of 10 wt.%.

Another analysis was also done in order to estimate the copper sulphide in the end-of-discharge product at >10 wt.% S. In this analysis, the product was dried, heated to 400°C in a furnace, cooled, powdered and washed under a stream of water. It was then treated with 100 ml ammonium hydroxide (11 g l^{-1}) and 100 ml acetic acid (2.5 g l^{-1}) heated to 65°C. Being maintained at this temperature, oxygen was bubbled through the solution under constant stirring for 3 h. Later the solution was allowed to settle and the copper residue was filtered, washed, dried and weighed [22].

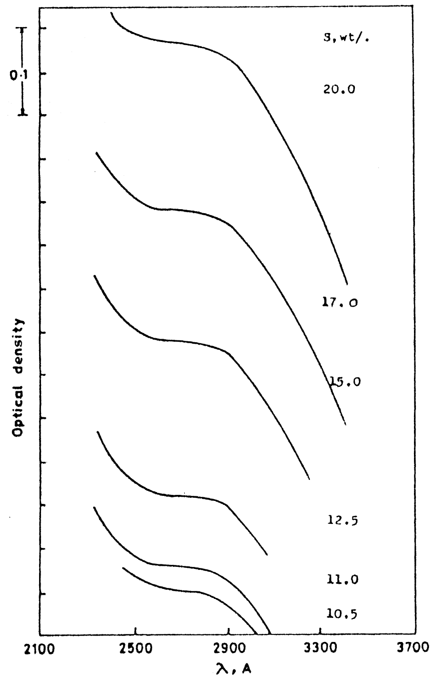

Fig. 2. UV spectrum of the $CHCl_3$ extract of the cathode mix at the end point of plateau I. The mother extract (40 ml) has been 100 times diluted.

In a third set of analyses, the end-of-discharge product corresponding to plateau I was shaken with acetonitrile when CuI was dissolved [23–25]. The weight loss was measured for the little unutilised CuI if any. The residue was then digested with 30% KCN solution when copper sulphide was dissolved. The weight loss measured at that stage corresponded to the sulphide. The remaining residue was washed several times with water, dried and weighed. The weight corresponded to the colloidal graphite. This observation indicates that the end-of-discharge product was only copper sulphide. Thus, the possibility of formation of metallic copper as the reduction product of CuI is ruled out.

3.2. *Effect of allotropic modifications of sulphur*

Fig. 3 reveals the effect of allotropic modifications of sulphur (10 wt.%) on the sulphur benevolence to the Mg–CuI battery. At the midpoint of the flat discharge curve, the elevation in cell voltage caused by the allotropes was as follows:

Ordinary commercial grade sulphur	400 mV
Cycloctasulphur	500 mV
Cyclododeasulphur	560 mV
Cyclohexasulphur	740 mV

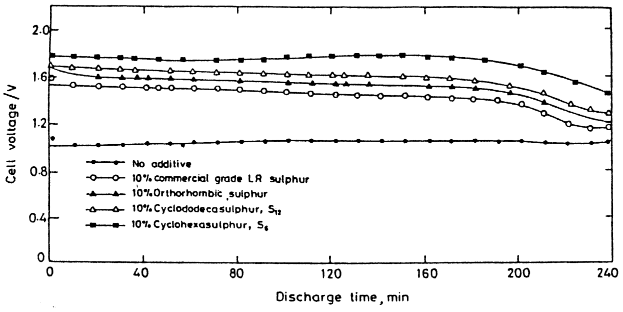

Fig. 3. Effect of allotropic modifications of sulphur on the discharge pattern of Mg–CuI(S) battery.

While the GR grade (99.5% purity) orthorhombic sulphur brought about an increase in cell voltage of 500 mV, the commercial grade sulphur (92% purity orthorhombic sulphur) led to only a 400 mV increase. The striking difference in the degree of benevolence does not appear to be due to the difference in the content of sulphur in the GR grade and the LR grade sulphur samples.

It appears reasonable to attribute the cause to the poisoning effect of impurities contained in the LR grade sulphur. The impurities listed in the contents were acid, moisture, arsenic, ash and carbonaceous compounds. Although the acid or the moisture content is not expected to be deleterious [4] to the performance, the nature of arsenic, ash or carbonaceous compounds needs to be taken into consideration.

Reactions of elemental sulphur are most often degradation reactions of the sulphur–sulphur bond, since elemental sulphur is a compound composed of S atoms naturally linked by S–S bonds. The S atoms in such compounds in elemental sulphur and in many chain-like sulphur compounds mostly react as electrophilic centres (thiophilic), i.e., they are susceptible to nucleophilic attack. In the present case the attack was done by electrons released by the Mg anode.

The first step of this reaction is ring opening, which is the rate-determining step [26–30]. Because of the different energy content of the different sulphur rings, the reaction rate must depend on the size of the rings. In fact, a large difference is exhibited in stability towards light, heat and nucleophiles with the hitherto isolated and characterised ring molecules S_6, S_7, S_8, S_{10} and S_{12} in the solid state, as well as in solution at room temperature [31].

The S_6 and S_{12} rings are thermodynamically unstable and are packed with drastic ring strain [32]. Of these two allotropes, S_6 far exceeds S_{12} in reactivity. Cyclohexasulphur which can be stored for extended period of time as pure crystals or in pure solution, however, decomposes rapidly in the presence of small amounts of impurities. It is sensitive towards light. Also, it is chemically much more reactive than S_8, for instance, with nucleophiles it reacts about 10^4 times faster [33].

The reactivity of S_{12} lies between that of S_8 and S_6 but more towards that of S_8 [34]. Now, it is worth focussing on the different behaviour of sulphur allotropes towards some nucleophiles in certain well-established reactions. A classic example of this type is the reaction of triphenylphosphine with sulphur [30,34]. S_6 in benzene solution reacts at a rate which is 25 000 times faster than S_8 at 7°C, whereas photolytically produced polycatenasulphur reacts immeasurably fast with phosphine. Kinetic measurements at different temperatures in toluene revealed the following activation energies for ring opening: $S_6 = 17.99$ kJ mol^{-1}; $S_8 = 60.67$ kJ mol^{-1} and $S_{12} = 39.75$ kJ mol^{-1}. These values also agree with the heat of combustion of different sulphur rings.

The increase in Mg–CuI cell voltage effected by different sulphur allotropes in the present study, viz., $S_6 = 740$ mV; $S_{12} = 560$ mV and $S_8 = 500$ mV, reveals an order that matches the order of reactivity of these allotropes. This together with the fact that the discharge capacity of the Mg–CuI cell is proportional to the S content of the cathode material contributing to the electrochemical reaction suggests that S is the portal of electron reception. Further, S has the greatest affinity for copper among the metals, except only silver and manganese. Also, between Cu(I) and Cu(II), the Cu(I)–S interaction is more facile.

3.3. The mechano-chemical effect

The suggestion made above of the formation of a [CuI–S] adduct stems from the following observation. When a 1 : 1 mixture of CuI-S was continuously ground together for several hours (9–10 h), a striking variation in colour occurred that ranged from dirty yellow to pistachio green to lead grey to blackish purple to black; this reflects the great affinity of sulphur for copper which is powerful enough to effect compound formation under the influence of mechanical forces alone. In the cathode plate fabrication, the ingredients should be blended well during which operation formation of an adduct of CuI with S could happen easily.

3.4. Analysis of end-of-discharge product

10% orthorhombic sulphur addition was chosen for this purpose. The end-of-discharge product was first washed several times with $CHCl_3$ to remove S if any, and then with CH_3CN to remove CuI, if any. In order to confirm the presence of Cu^+ ions in the sulphide, we found that magnetic susceptibility measurements were a suitable method to detect its diamagnetic nature. However, the copper sulphide isolated in the present study showed some paramagnetism with value of μ_{eff} of 0.56 Bohr magneton. Its EPR spectrum is shown in Fig. 4. IR data (Fig. 5) obtained for the end-of-discharge product at 384 cm^{-1} and 240 cm^{-1} are confirmative of the existence of metal sulphur bonding [37]. In addition, the spectrum also presents absorption at

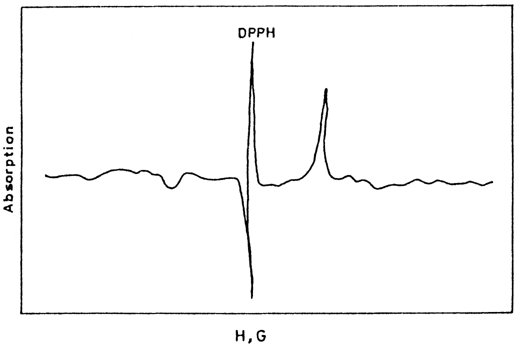

Fig. 4. EPR spectrum of copper sulphide viz., the end-of-discharge product.

174 cm^{-1} which can be associated with metal–halide bonding, particularly a bridging halogen bonding [37]. This orientation indicates the presence of I$^-$ in the end-of-discharge product. The same was confirmed by a positive result in the test for iodide. The weak far-IR absorption confirms metal–metal bonding [37].

It is evident from the absence of diamagnetism that the copper sulphide formed is not cuprous sulphide. At the same time, its paramagnetism is not very high as indicated by its low g value in the EPR spectrum and the low μ_{eff} value. Therefore, it is indicated that it is also not a pure Cu(II) compound [34]. Cuprous–cupric mixed valent compounds, particularly derivatives of cuprous halides [35] and sulphides [36], are quite possible with copper and it is highly probable that one such compound may be formed as a result of the Mg–[CuI–S] battery electrode reaction. To cite an example, CuS which occurs naturally as covellite is not a simple cupric salt but has a rather extraordinary structure, viz., $Cu^{I}_{4}Cu^{II}_{2}(S_2)_2S_2$ [36].

As far as the performance of a battery is concerned, the extent of the electrochemical reaction depends on the electrical conductivity of the intermediate layer formed at the electrode/electrolyte interface. The introduction of S, an electron acceptor into the CuI active material as has been proposed for Cu_2O, should have resulted in a manifold increase in the conductivity of the intermediate [4,36,37] which is depleted during discharge. It is well established that the electrical conductivity of cupric sulphide is greater than that of the cuprous form [38] and naturally the mixed valence Cu^{I}–Cu^{II} sulphide should possess better electrical conductivity than the cuprous form. Also, under certain conditions, for instance under the influence of electric fields [39], the electrical conductivity of cuprous sulphide is much like a metal, resulting in its use as electrodes in certain electric cells.

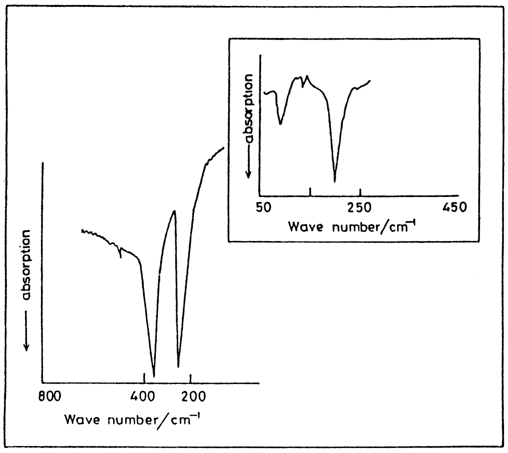

Fig. 5. IR and far IR (inset) spectra of end-of-dishcarge product.

Another point of interest that can be drawn from the sulphur chemistry is that certain reactions of elemental sulphur are remarkably catalysed by trace amounts of basic substances like amines and particularly S^{2-} [40,41]. For instance, the presence of a trace of sulphide ion in a mixture of disulphide and sulphur brings about a rapid sulphuration of the disulphide to polysulphides. The existence of complex sulphides and polysulphides is not uncommon in the chemistry of copper [42,43], and formation of some kind of a polysulphide cannot be ruled out in the Mg–[CuI–S] battery discharge. Some of the complex polysulphides of copper are proven to be good conductors of electricity [44]. Thus, it seems reasonable to speculate that some higher conducting sulphide intermediate was formed, eventually transforming into a Cu(I)–Cu(II) mixed valent sulphide.

However, more experimentation is necessary so that the exact nature of the copper sulphide formed is understood. Our preliminary investigation has shown that the conductivity of CuI which is $3.14 \times 10^{-7}\ \Omega^{-1}\ cm^{-1}$, increased to about $4.82 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ under conditions of 10 wt.% sulphur addition (Table 1). The order of values obtained for the conductivity of the end-of-discharge product tends to indicate that the sulphide formed may be a copper iodide sulphide like the $Cu_{1+x}I_{1+x}S_x$ [45], and some phase transitions during discharge could also be envisaged. The significance of such products is that they have semiconductive properties and that their tunnel-like structures facilitate diffusion of conducting species.

Table 1
Conductivity of end-of-discharge products of sulphur added CuI cathode

S/Wt.%	Conductivity (Ω^{-1} cm^{-1})
0	3.14×10^{-7}
2	3.80×10^{-7}
3	4.44×10^{-6}
4	9.00×10^{-6}
5	1.93×10^{-5}
6	4.87×10^{-5}
7	4.93×10^{-5}
8	1.12×10^{-4}
10	4.82×10^{-4}
12	5.30×10^{-4}
15	6.30×10^{-4}
20	1.93×10^{-7}

4. Conclusions

The observations made in the present study do not support the reactions proposed either by Flerov [4] or Hiroi [7]. On the contrary, it seems reasonable to suggest the following scheme for the electrode reaction.

$$[\mathrm{CuI{-}S}]+\mathrm{e} \rightarrow [\mathrm{CuI{-}S}]^{-} \rightarrow \mathrm{Cu}_{1+x}\mathrm{I}_{1+x}\mathrm{S}_x \quad \text{(major product)} \tag{1}$$

This equation is not a legitimate electrode reaction since it does not specifically identify the species undergoing reduction, i.e., the cathode process responsible for the discharge of the cell. $Cu_{1+x}I_{1+x}S_x$ (although the exact stoichiometry has not been arrived at) may not be the only product; formation of other compounds could also be possible. In the present context of chalcogenide physics, it is worth mentioning about the discovery of superconductivity in compressed sulphur. Struzhkin et al. [46] who have made the discovery report that given the comparative simplicity of elemental sulphur for electronic structure, calculation and knowledge of its high pressure crystal structure, this element should provide important tests of possible new mechanisms for superconductivity. Xu et al. [47] recently reported a large magnetoresistance in silver selenides and silver tellurides. This revolutionary discovery introduces a hitherto unexplored class of magnetoresistive compounds, viz., the silver chalcogenides which by nature are non-magnetic superionic conductors; below 400 K, ion migration is effectively frozen and the compounds are non-magnetic semiconductors [48] that exhibit no appreciable magnetoresistance. Xu et al. showed that slightly altering the stoichiometry can lead to a marked increase in the magnetic response. This finding of a large magnetoresistance is silver chalcogenides enthuses a similar study of the end-of-discharge product of S added CuI because silver and copper belong to the same group of the periodic table.

The findings of Xu et al. and Struzhkin et al. have been reported almost at the same time (November 1997). The two independent works put together present a promising growth for study in copper sulphides. Further, there would be a tremendous impact of such findings on the development of novel seawater activated batteries. Such a proposition is further strengthened by the present observation of influence of sulphur allotropic modifications on the cell voltage of Mg–CuI cells.

Reported evidence shows that several major magneto-structural correlations have arisen out of the studies on Cu(II) halide layer perovskites [49–52] and such materials are of importance in low dimensional magnetism [53]. The observations made in the present study, and arising out of battery performance evaluation, indicates a great scope for further studies that aim at battery as a tool to tap energy, at the same time synthesising novel compounds of practical importance. It is hoped that there would be intense activity in such transdisciplinary areas of investigation. One of the approaches could be to isolate the end-of-discharge products under various conditions of battery performance and characterise their physicochemical properties and electrochemical activity [54,55]. Such studies are presently being attempted in our laboratory, and the results will be embodied in a later publication.

Acknowledgements

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