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SHORT COMMUNICATION

Aromatic disulfides as additives to CuI in Mg–CuI seawater activated batteries

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1. Introduction

Aromatic disulfides may be used as additives to copper compound based cathodes and are superior to elemental sulfur in their efficacy. We have been interested in developing additives more effective than elemental sulfur [1–7] with a view to constructing Mg–copper compound batteries of practical importance. As organic disulfides [8–10] possess electron accepting S—S bonds, we have examined a series of aromatic disulfides (Fig. 1, I–VI) for their benevolence to CuI. Compounds structures are shown in Fig. 1.

2. Experimental details

The cathode active material, namely, cuprous iodide, prepared by following the reported procedure [11], was dried in air at 80 °C and then ground into a fine powder and sieved on a 100 mesh. 2.56 g of CuI (0.36 A h) mixed thoroughly with 15% colloidal graphite constituted the prime depolarizer for each plate. The active material was mounted on a thin copper mesh of dimensions 4.0 cm × 2.5 cm × 0.20 cm, wrapped in a filter paper and then pressed using a hydraulic press. A compaction pressure of 10 t was found to give good performance and no binder was used [12]. The anode was made from magnesium alloy (AZ31) sheets of dimensions 4.0 cm × 2.5 cm × 0.15 cm. 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.

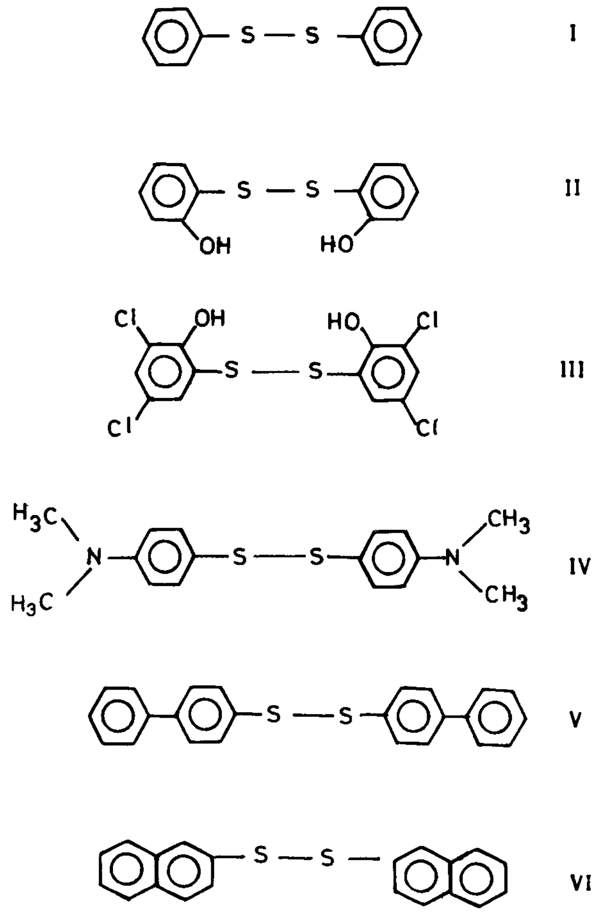

Fig. 1. Aromatic disulfides used as additives to CuI.

A cathode plate was positioned between two magnesium anodes: a pair of thin PVC wires pasted to the inner side of the magnesium plates prevented direct contact of the cathode with the anode [13].

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. All the discharges were constant current drains (90 mA) and were carried out at room temperature.

Magnesium was the limiting electrode in the present study; CuI was taken in excess to the quantity of magnesium. Therefore, at any stage during discharge, a condition was not reached when CuI was depleted and only Mg together with the disulfide additive were left behind.

3. Results

Previously [14] it was found that the greatest benefit of the elemental sulfur additive was obtained by using it in a stoichiometric quantity. Therefore, in the present study the disulfide addition was restricted to a 1:1 molar ratio (Faraday equivalent). Figure 2 shows that all the disulfides used in the present study are superior to elemental sulfur. The trend shows a structure–activity relationship in the efficacy of the disulfide. In the diphenyldisulfide case (Fig. 1, I) copper sulfide and biphenyl were identified among the major products. Liberation of hydrogen sulfide did not accompany the discharge. This observation is indicative of a phenomenon similar to the desulfurization of the disulfides [15, 16].

The benevolence property of elemental sulfur in the Mg—CuX battery is believed [1] to be due to

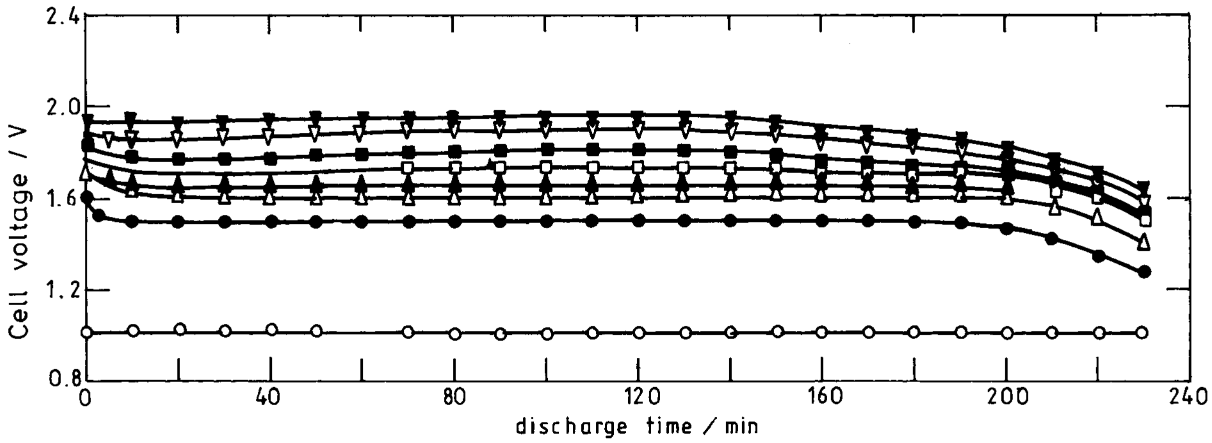

Fig. 2. Effect of addition of organic sulfur compounds on the discharge pattern of Mg–CuI sea water activated battery. CuI: additive is 1:1 molar ratio. Key: (○) no additive; (●) orthorhombic sulfur, (Δ) I; (■) II; (□) III; (■) IV; (∇)V;(▼) VI.

the electrophilic nature of the S—S chain, further strengthened by the powerful copper thiophilicity. The exact chemical/electrochemical reactions involved in the case of aromatic disulfides and the effect of substituents on the performance are under study.

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