

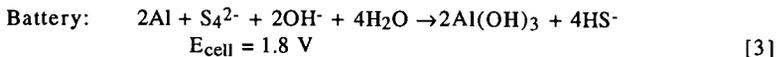
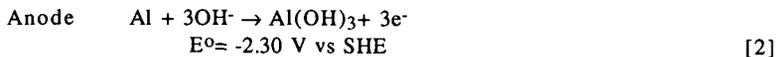
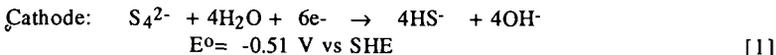
THE HIGH STORAGE CAPACITY OF SULFUR AT LOW TEMPERATURE
NOVEL SOLID SULFUR CATHODES FOR AQUEOUS BATTERIES

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The light weight of sulfur makes metal/molten sulfur batteries attractive for electrochemical energy storage. However, material constraints associated with the requisite high temperatures, have slowed the development of a variety of metal/molten sulfur batteries (1). In a previous study we introduced an alternative high faradaic capacity aqueous sulfur redox cell (2). That study described conductive solutions which by mass could accommodate more sulfur than water, and demonstrated faradaic storage capacities comparable to those in molten sulfur batteries. In a recently letter we presented the utilization of this ambient temperature polysulfide redox reaction with an aluminum anode to introduce a class of aluminum/polysulfide batteries (3).

The battery was expressed by aluminum oxidation and polysulfide reduction for an overall battery discharge consisting of:



In accordance with Eq. [3], this aluminum/polysulfide battery has a theoretical charge capacity of 505, 595, or 724 Ahr/kg calculated respectively using either potassium, sodium or lithium electrolytes.

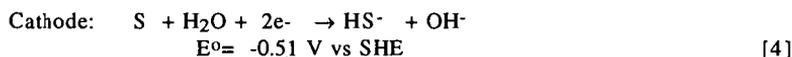
Eq. [1] represents a simplified description of sulfur reduction. Sulfur dissolved in aqueous sulfide solutions gives rise to a variety of polysulfide species, dominated at moderate alkaline pH by the tetrasulfide species, S_4^{2-} (4). CoS is an effective material to electrocatalyze oxidation

and reduction of polysulfide (5). Cathodic polarization losses at thin film CoS electrodes decrease from $-4 \text{ mV cm}^2 \text{ mA}^{-1}$ to $2 \text{ mV cm}^2 \text{ mA}^{-1}$ as temperature increases from 20° to 65°C . Zero valent sulfur added to sulfide solutions may be reduced to the divalent state at faradaic efficiencies approaching 100 percent (2). The electrochemistry of polysulfide solutions reflects the complex speciation in these solutions, and is affected by solution pH, activity and the ratio of dissolved sulfur per sulfide. In concentrated solutions, with the ratio of dissolved sulfur per sulfide increasing from 1 to 3, the polysulfide potentials shifts 150 mV cathodically, a favorable situation for coupling with an Al anode.

Effective aluminum anode utilization requires that the rate of electrochemical oxidation must be high compared to the competing chemical loss reaction. Polarization losses for aluminum oxidation have generally not been investigated in highly concentrated (greater than 10 molal) alkaline solutions useful to maximize energy density of the aluminum/sulfur battery. Polarization losses for aluminum oxidation in a 18 m KOH solution decrease from 6 to $0.4 \text{ mV cm}^2 \text{ mA}^{-1}$ as temperature is increased from 20° to 85°C . Measured polarization is similar in either concentrated sodium or potassium hydroxide electrolytes, and also for aluminum anodes comprised of either 99.999% Al or an alloy containing over 99% Al and added Mg, Sn and Ga.

Initial tests on the aluminum/polysulfide cells consist of non-flow batteries. Anolyte limited cells were discharged to determine the anodic efficiency in highly concentrated alkaline electrolytes. Additives such as metal oxide salts effect cell performance. 10mm Ga_2O_3 added to 18 m KOH anolyte enhances cell voltage, whereas added $\text{In}(\text{OH})_3$ substantially increases anodic capacity. Anodic utilization efficiency is further increased to over 80% by optimization of anolyte volume (3). Al/polysulfide batteries were demonstrated with an energy density of 170 Whr/kg based on materials excluding water (modeling a "water activated" cell) and 110 Whr/kg based on total materials (3). "D" volume (0.05 liter) cells provided a 10.1 Whr energy capacity with an 86% conversion efficiency based on KOH, a 78% conversion efficiency based on K_2S_4 , and an 68% conversion efficiency based on consumed Al. In Table I, the aluminum/polysulfide battery is compared to conventional Zn/carbon and alkaline batteries under standard moderately high current densities. Under these test conditions, the time of discharge advantage of the new cell is evident. Studies of solution and aluminum modification continue to further increase the energy density of the aluminum/polysulfide battery.

In accordance with Eq. 1, at 25°C, the solubility of K₂S₄ is consistent with a maximum charge capacity of 500 Ah/kg solution. Here we investigate an alternative, higher capacity cathode. This new cathode could be capable of direct reduction of elemental sulfur at room temperature. The new maximum storage capacity is substantially increased, and is given by the limit as all solid sulfur is reduced:



$$\text{storage} = \frac{1 \text{ mole (S+H}_2\text{O)}}{(0.032+0.018)\text{kg}} \cdot \frac{2 \text{ faraday}}{\text{mole}} \cdot \frac{96500\text{C}}{\text{faraday}} \cdot \frac{\text{Amp hour}}{3600\text{C}} = 1070 \text{ Ah/kg}$$

This theoretical storage capacity of the solid sulfur cathode is several fold higher than the theoretical storage capacity of conventional aqueous cathodes including PbO₂, NiOOH, MnO₂, HgO, and AgO (1).

The new cathode features solid sulfur in contact with aqueous polysulfide solution. This solid sulfur will not dissolve in a polysulfide solution saturated in sulfur. Initiation of reductive discharge of the cell will generate shorter length polysulfide species:

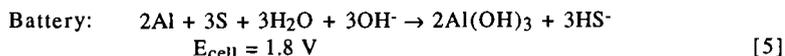


which as represented in Figure 1B then permits dissolution and continued reduction of available solution and solid phase sulfur:



Discharge proceeds until all available zerovalent sulfur (both solid and dissolved) is reduced in accordance with Eq. 1. The solid sulfur maintains longer chain polysulfide species in solution. Longer chain polysulfide species positively shifts and maximizes cell voltage (2). This elemental (solid/solution phase) sulfur cathode has the theoretical advantage of higher storage capacity and higher cell voltage.

The solid sulfur cathode was incorporated into an aluminum cell analogous to the aluminum/polysulfide battery recently described (3). In accordance with Eq. 2 and Eq. 4, discharge of the aluminum/solid sulfur battery is expressed by:



Faradaic capacity of the Al/solid sulfur battery (based on potassium salts and all reactants) is 505 Ah/kg, and the theoretical specific energy is:

$$1.8 \text{ Volt} \times 505 \text{ Ah/kg} = 910 \text{ Wh/kg} \quad [6]$$

This 910 Wh/kg aluminum/sulfur battery theoretical specific energy is approximately 40% higher than the aluminum/polysulfide battery (8), and is 2 to 5 times that of conventional aqueous batteries. Utilization of lighter weight cations than K^+ may further improve the Al/S energy capacity.

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Table I. Comparison of Al/S and conventional aqueous electrochemical storage at 20°C. The aluminum/sulfur cells contain 0.018 L of 7.7 m K_2S_4 catholyte and 0.032 L of 18 m KOH, 10 mm $\text{In}(\text{OH})_3$ in a rectangular cell geometry described in the text.

load	<u>D. size cells, continuous discharge time to 0.65 volts</u>		
	<u>Zinc Carbon (1)</u>	<u>Alkaline (1)</u>	<u>New Aluminum/Sulfur</u>
0.5W	0.5 hours	3.0 hours	7.4 hours
1.0W	1.0 hour	6.5 hours	13 hours
2.3 W	3.5 hours	19 hours	28 hours