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Energetics of a Zinc−Sulfur Fuel Cell

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Energetics of a novel zinc−sulfur charge storage (generalized as Zn + S → ZnS) is explored to access the high (>1000 Ah/kg) charge capacity of sulfur. At 25 °C, the theoretical energy density of the complete Zn/S system is a high 572 Wh/kg, at $E° = 1.04$ V. From 273 to 373 K, the thermodynamic cell potential for 29 possible solution-phase reactions of the system were calculated including a variety of known coexisting aqueous polysulfide species. In this domain zinc sulfide products are thermodynamically preferred over zincate products, which can be advantageous compared to Al/S storage where aluminate is the favored discharge product. Initial experimental feasibility of a zinc−sulfur electrochemical system is explored in a zinc anode/aqueous polysulfide/CoS electrocatalytic cathode cell. Measured sustained cathode capacity approaches the theoretical 2 Faraday/sulfur limit. However, the anode tends to passivate due to the zinc sulfide discharge product, preventing sustained discharge. Passivation is overcome in potassium polysulfide solutions containing concentrated (>10 molal) KOH; this results in efficient, sustained 2 Faraday/Zn oxidation and high zinc−sulfur charge capacities.

Introduction

Contemporary technological and societal demands for higher capacity energy storage provide impetus for the exploration of alternate electrochemical redox couples capable of higher energy storage. Conventional cathodic charge capacities such as 292 and 308 Ah/kg, respectively, for NiOOH and MnO_2 are insufficient for future battery and fuel cell applications. The low weight, low cost, and high two-electron theoretical faradaic capacity of sulfur (1170 Ah/kg), make it an attractive cathode candidate for electrochemical energy storage, but sulfur is one of the most electrically insulating materials. Hence, studies have generally focused on the use of sulfur in the molten (polysulfide) state as a cathode material, as limited to high-temperature batteries and fuel cells.[1−3] However, ambient temperature aqueous potassium polysulfide solutions are particularly soluble and effective as cathodes. Indeed, we have shown that aqueous potassium sulfide solutions can contain, by mass, more sulfur than water, and also that solid-phase sulfur in contact with a thin aqueous alkaline polysulfide interface has a cathodic storage capacity in excess of 1000 Ah/kg.[4−10] Fundamental properties of soluble sulfur electrolytes have also been studied to improve efficiencies in photoelectrochemical solar cells.[11−13]

In 1993 sulfur was proposed as a cathode for aqueous aluminum−sulfur electrochemical storage.[4,7−10] The aqueous alkaline cell discharge reaction depends on the polysulfide species, S_x^{2-}, summarized here for the highly soluble (potassium) tetrasulfide species, with a $\Delta G°$ of −527 kJ mol^{-1}:

$$2Al_{(s)} + S_4^{2-} + 2OH^- + 4H_2O \rightarrow 2Al(OH)_3 + 4HS^- \quad E° = 1.82\ \text{V} \quad (1)$$

In accord with eq 1, the theoretical charge and energy density of the potassium Al/S electrochemical storage are 362 Ah/kg and 659 Wh/kg, respectively. This Al/S redox couple consumes hydroxide (as KOH within the electrolyte) in the formation of the aluminum hydroxide discharge product, increasing its weight, and decreasing its practical energy density. Although an alternate (aluminum) sulfide discharge product would prevent this, the aluminum hydroxide is formed as the thermodynamically favored eq 1 product, and preferred to the sulfide product reaction which, depending on $y = 1.5/(x - 1)$, yields only a $\Delta G°$ varying from −228 to −236 kJ mol^{-1}:[10]

$$Al_{(s)} + yS_x^{2-} + yH_2O \rightarrow {}^1/_2Al_2S_3 + yOH^- + yHS^- \quad (2)$$

where $y = 1.5/(x - 1)$. Further, the observed potential of the aqueous Al/S cell is less than 1.4 V, and this diminishes the maximum energy density of the aluminum−sulfur system to less than 507 Wh/kg (rather than 659 Wh/kg). This lower Al/S oxidation potential in aqueous alkaline media, diminished from the thermodynamic value of 1.8 V, is due to the parasitic competition from the reaction of aluminum with water:[4,7,10]

$$Al_{(s)} + 3H_2O \rightarrow Al(OH)_{3(amorph)} + {}^3/_2H_{2(g)} \quad \Delta G° = -426\ \text{kJ/mol} \quad (3)$$

The intrinsic 820 Ah/kg two-electron theoretical faradaic capacity of zinc (FW = 65.39 g mol^{-1}), is lower than that of the three-electron intrinsic 2980 Ah/kg capacity of aluminum (FW = 26.98 g mol^{-1}). However, zinc has been widely used as a battery anode material for over a century, although without sulfur.[14−18] In this study, despite the higher isolated anodic capacity of aluminum compared to zinc, it will be demonstrated that the zinc−sulfur system can have a considerably higher intrinsic storage capacity compared to the aluminum−sulfur system, and an alternate electrochemical storage system with a generalized discharge reaction is probed:

$$Zn + S \rightarrow ZnS \quad (4)$$

The thermodynamic and initial experimental considerations for a Zn/S electrochemical storage are explored.

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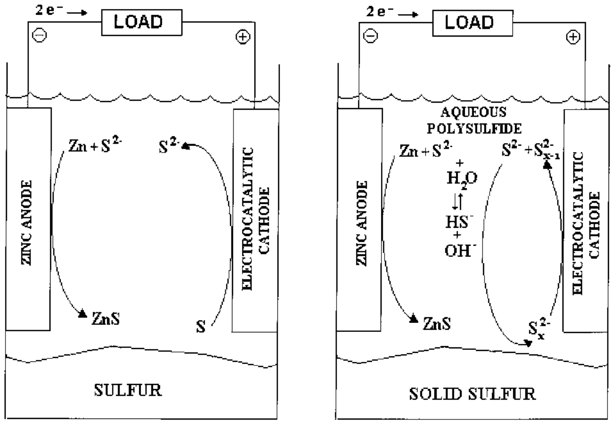

Figure 1. Schematic representation of (left side) generalized Zn/S electrochemical discharge, and (right side) a Zn/S electrochemical storage cell utilizing an aqueous polysulfide interface.

Experimental Section

Analytical grade reagents and distilled, doubly deionized water were used throughout. Similar results were obtained with anode material propared from 99.9% to 99.999% zinc foil from Aldrich or Alfa AESAR. KHS solutions were prepared by saturation of KOH solutions with H_2S (gas) as previously described.[20] Polysulfide solutions are then formed by addition of KOH and sulfur to KHS solutions. CoS electrodes were formed by electrodeposition of Co at 50 mA/cm^2 from 50 °C 2 *m* $CoSO_4$, 0.6 m boric acid, 0.2 *m* NaCl solution onto a brass substrate, followed by oxidation in polysulfide solution as previously described.[21] Note that molality units, m = mol/kg solution, are used in the experiments.

Both thin (7 cm^2) and larger (20 cm^2) Zn/S cells were constructed from sandwiched rectangular Perspex blocks separated by flat Teflon spacers. For the separation of anodic and cathodic compartments Permion HD2291 cation permeable membrane and conventional alkaline cell separators were used. Galvanostatic overpotential measurements and linear voltammetry experiments were performed with a conventional three-electrode potentiostatic configuration and Pine AFCBP1 bipotentiostat/galvanostat. In polarization measurements a Ag/AgCl reference electrode and a Pt foil (2 cm^2) counter electrode were used. The constant load discharges of the Zn/S cells were performed under ±1% precision resistors. Experiments were maintained under thermostatic control to ±0.2 °C.

Thermodynamic Evaluation of Zinc−Sulfur Redox Storage. The electrochemical processes occurring in a zinc−sulfur system can be generalized by the cell illustrated on the left side of Figure 1, and by the traditional half reactions:[19]

$$\text{Cathode: } S_{(s)} + 2e^- \rightarrow S^{2-} \quad E° = -0.58 \text{ V (vs SHE)} \quad (5)$$

$$\text{Anode: } ZnS_{(s)} + 2e \rightarrow Zn_{(s)} + S^{2-} \quad (6)$$

$$\text{Total: } Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)} \quad E° = 1.04 \text{ V} \quad (7)$$

Zn/S electrochemistry is analyzed here first at ambient temperatures, in a system consisting of a zinc anode and a highly concentrated polysulfide cathode in an aqueous electrolyte, and at higher temperatures in the next section. In aqueous solutions, the second acid dissociation constant for H_2S, is smaller than generally recognized, and on the order of 10^{-17}.[20−25]

$$HS^- + OH^- \rightarrow S^{2-} + H_2O \quad pK_2 = 17.3 \quad (8)$$

From this value, S^{2-} activity is negligible over a wide range of pH and sulfide concentrations. The dominant aqueous sulfide species are HS^- and OH^-, and the aqueous electrolyte ZnS reaction is better described by:[19]

$$\text{Cathode: } S_{(s)} + H_2O + 2e^- \rightarrow HS^- + OH^- \qquad E° = -0.48 \text{ V (vs SHE)} \quad (9)$$

$$\text{Anode: } ZnS_{(s)} + H_2O + 2e^- \rightarrow Zn_{(s)} + HS^- + OH^- \qquad E° = -1.52 \text{ V (vs SHE)} \quad (10)$$

$$\text{Total: } Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)} \quad E° = 1.04 \text{ V} \quad (11)$$

Hence, although eqs 9 and 10 involve water, it is not consumed in the process, and the net eq 11 is identical to eq 7. From the discharge reactions, eqs 7 and 11, the faradaic capacity and the theoretical energy density for Zn/S electrochemical storage are 550 Ah/kg and 572 Wh/kg, respectively. The Zn/S energy density value is high compared with the theoretical energy density of conventional aqueous cells, including Pb−acid (170 Wh/kg), Ni−Cd (217 Wh/kg), alkaline Zn−MnO_2 (336 Wh/kg), and zinc−silver (447 Wh/kg).[14]

Compared to Al/S, in the case of Zn/S electrochemical storage at 298.15 K, the formation of ZnS product ($\Delta G° = -201.3$ kJ mol^{-1}) is thermodynamically preferred to the formation of $Zn(OH)_4{}^{2-}$ or $Zn(OH)_2$ ($\Delta G° = -156.3$ kJ mol^{-1}). Hence unlike aluminum, the zinc−sulfur reaction is not expected to consume hydroxide during discharge; leading to more effective utilization of the electroactive materials. After compensation for the aqueous voltage loss in aluminum−sulfur, the 507 Wh/kg energy density of the aluminum−sulfur cell is already less than that of the alternate zinc−sulfur electrochemical storage. The described properties make the Zn/S system potentially more attractive than the Al/S system as an electrochemical power source.

Even in the absence of zinc, thermodynamic data is available for the various polysulfide species, or of the related polysulfide equilibrium or half reactions only in limited temperature ranges and conditions.[2,5,12,26−33] In this study, the thermodynamic potentials for the possible electrochemical reactions for the zinc−sulfur system are calculated over the temperature range (273.15−1273.15 K).

The investigated energetics of the zinc sulfide system focused on the temperature range from 273.15 to 1273 and in which reactions are investigated in aqueous media.

ZnS Thermodynamic Evaluation. The standard reaction potential $E°$, in volts, for a temperature, T, in Kelvin, was calculated from the standard reaction free energy change, in J mol^{-1}, using the Faraday constant, $F = 9.649 \times 10^4$ C mol^{-1}, and the number of the electrons, n:

$$E°(T) = -\Delta G°(T)_{\text{reaction}}/nF \quad (12)$$

where the value of $\Delta G°(T)_{\text{reaction}}$ is the difference of $\Sigma\Delta G°(T)_{\text{products}}$ and $\Sigma\Delta G°(T)_{\text{reactants}}$, as determined for each species participating in the reaction from the difference of the standard enthalpy of formation change, $\Delta H°$ (in units of J mol^{-1}) and $T\Delta S°(T)$, using the standard entropy change, in units of J mol^{-1} K^{-1}. The standard enthalpy change and the standard entropy, $S°$, J mol^{-1} K^{-1}, were calculated from a constant heat capacity, C_p, J mol^{-1} K^{-1}, respectively, by integrating either as C_p dT or C_p dT/t over the from 298.15 K.

At room-temperature sulfur is an insulator, which despite its high intrinsic two Faraday mol^{-1} (FW(S) = 32.07 g mol$^{-1)}$ storage capacity, presents a challenge to its use as a cathode.

TABLE 1: Thermodynamic Data for Different Species at 298.15 K[26]

species	$\Delta H°$ [kJ mol^{-1}][26]	$S°$ [J mol^{-1} K^{-1}][26]	[b]C_p [J mol^{-1} K^{-1}][34]
$H^+_{(aq)}$	0	0	0
$Zn_{(s)}$	0	41.6	25.4
$S_{(s)rombic}$	0	31.8	22.64
$O_{2(g)}$	0	205.028	29.35
$H_{2(g)}$	0	130.684	28.82
$H_2O_{(l)}$	−285.830	69.91	75.291
[a]$Zn(OH)_4{}^{2-}{}_{(aq)}$	−965.567		
ϵ-$Zn(OH)_{2(s)}$	−643.25	81.6	72.383
$ZnS_{(s)sphalerite}$	−206.0	57.5	46.02
$OH^-{}_{(aq)}$	−229.994	−10.75	−148.53
$HS^-{}_{(aq)}$	−17.6	62.9	
$S^{2-}{}_{(aq)}$	33.05	−16.3	
$S_2{}^{2-}{}_{(aq)}$	30.1	28.4	
$S_3{}^{2-}{}_{(aq)}$	25.9	65.5	
$S_4{}^{2-}{}_{(aq)}$	23.0	103.4	
$S_5{}^{2-}{}_{(aq)}$	21.3	140.6	

[a] For $Zn(OH)_4{}^{2-}$, only the $\Delta G°$ value at 298.15 K ($\Delta G°_{298.15K} = -877.4$ kJ mol^{-1}) was available.[26] Hence, $\Delta H°$ was estimated from the $\Delta S°$ value for the similar $Zn(OH)_2$ species ($\Delta S°_{298.15K} = 295.712$ J mol^{-1} K^{-1}). [b] When C_p values were not available, $\Delta G°(T)$ was determined using the temperatures and constant values of $\Delta H°_{298.15\ K}$ and $S°_{298.15K}$.

However, dissolution of zero-valent sulfur in the form of one of the various soluble aqueous polysulfide species, can provide an effective interfacial bridge to the use of sulfur at or near room temperature. This is schematically illustrated on the right side of Figure 1, in which solid sulfur in contact with aqueous alkaline solutions dissolves in the form of polysulfide species, which in the discharge process are reduced while zinc is oxidized. The controlling cell potential for this process will depend on the specific polysulfide species, which is reduced, and on the preferred discharge products. This study predicts the thermodynamically favored discharge reactions. The kinetically favored discharge mechanism may be more complex, involving one or more intermediate steps, as exemplified for the analogous case of polysulfide redox chemistry probed on a cadmium chalcogenide surface.[11]

Aqueous alkaline solutions containing sulfur and sulfide salts, M_xS_y, are associated with an extensive speciation and a complex equilibrium of $M^{2y/x}$, H_2S, HS^-, S^{2-}, $S_2{}^{2-}$, $S_3{}^{2-}$, $S_4{}^{2-}$, $S_5{}^{2-}$, H_2O, H^+, and OH^-.[5,12,30−33] These species can participate in electrochemical processes with zinc to form different products, and electrochemical reactions can be predicted that can potentially occur. The thermodynamic data that was used for the calculations of the theoretical potentials of the various discharge reactions at different temperatures is summarized in Table 1.

Table 2 presents the thermodynamic potentials calculated for 29 different aqueous electrochemical reactions at 273.15, 289.15, and 373.15 K. These reactions may be distributed into four main categories of zinc discharge. Categories i−iii produce a ZnS discharge product, while the fourth category, iv, produces a zincate or zinc hydroxide product. In Table 2, category "i" reactions oxidize a polysulfide reactant to form a shorter chain length polysulfide product:

$$Zn_{(s)} + S_x{}^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + S_{(x-1)}{}^{2-}{}_{(aq)} \qquad (13)$$

Category "ii" reactions oxidize a polysulfide reactant to form a hydrosulfide product:

$$(x-1)Zn_{(s)} + S_x{}^{2-}{}_{(aq)} + H_2O \rightarrow (x-1)ZnS_{(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)} \qquad (14)$$

Category "iii" reactions oxidize a polysulfide reactant to form a sulfide product:

$$(x-1)Zn_{(s)} + S_x{}^{2-}{}_{(aq)} \rightarrow (x-1)ZnS_{(s)} + S^{2-}{}_{(aq)} \qquad (15)$$

As indicated by the consistently larger cell potentials in Table 2 for reactions of categories i−iii compared to category iv, in all cases the ZnS product is energetically preferred to the $Zn(OH)_4{}^{2-}$ or the $Zn(OH)_2$ products.

In aqueous polysulfide solutions, the activity distribution of the coexisting polysulfide species depends strongly on the alkalinity of the solution.[5,11,31−32] The tetrasulfide species, $S_4{}^{2-}$, is the predominant species at pH = 9−14. $S_5{}^{2-}$ dominates at nearly neutral or slightly alkaline solutions. At high pH values (pH = 14−16), consistent with over 1 molar hydroxide concentrations, the main species is $S_3{}^{2-}$. At extremely high pH (pH > 16 occurs in highly concentrated, high activity coefficient, hydroxide solutions[34]) the predominant species are $S_3{}^{2-}$ and $S_2{}^{2-}$. In accord with eq 8, S^{2-} is only significantly active in this highest pH extreme; at smaller pH values, fully reduced sulfur exists in the hydrolyzed form as HS^-. On the basis of this information, and the calculated thermodynamic potentials in Table 2, a prediction of activity favored cell reactions is made and summarized in Table 3. In addition, albeit to a lesser extent, the distribution of polysulfide species is also affected by the ratio of solution phase zero-valent to reduced sulfurs. Hence, as all sulfur approaches the limit of full discharge, the final products must be the fully reduced sulfur species (HS^- or S^{2-}), these minimum cell potential reactions are also included in Table 3.

Initial Experimental ZnS Electrochemical Storage. In this study, the initial experimental demonstration of zinc−sulfur charge storage is confined to a single temperature range (near room temperature) in a single medium (aqueous alkaline electrolytes). Specifically, the viability of facile charge transfer for a zinc anode/aqueous polysulfide/CoS electrocatalytic cathode system is probed. We have previously demonstrated that polysulfide reduction at a CoS electrocatalytic electrode approaches 100 percent efficiency of the two-electron coulomb reduction of all available zero-valent sulfur,[4] and that the sulfur cathode may be repeatedly charged.[5] In the present study, cathodic current is collected by a CoS electrode which can sustain reduce polysulfide oxidization/reduction with a minimal polarization losses (on the order of 1 mV cm^2/mA polarization). Thermodynamically, aqueous polysulfide solutions are unstable, and sulfur, dissolved as polysulfide species, $S_x{}^{2-}$, $x = 2-4$, can decompose to thiosulfate, $S_2O_3{}^{2-}$.[6] In that previous investigation, we concluded that under conditions of high polysulfide concentration and at temperatures up to 85 °C, polysulfide solutions can be extremely stable, and are particularly stable (on the order of years) at temperatures up to 55 °C.[6] Zerovalent sulfur in potassium polysufides can be effectively reduced using a CoS electrocatalyst, either as separated by a cation selective membrane in an isolated cathode half cell, or in a separator free cell. However, oxidation of the zinc anode can be a challenge in this medium.

It is unexpected that zinc can be effectively oxidized as an active anode material in aqueous sulfide solutions. Zinc sulfide is both electrically nonconductive (semiconducting),[35−38] and is also highly insoluble (the solubility product of ZnS is 10^{-25}).[19] Hence, as expected, ZnS can passivate the zinc anode. It is observed that no current (to within 10^{-6} A/cm^2) occurs in attempts to oxidize a Zn metal anode in a solution containing 3 *m* KOH and 3 *m* K_2S_4. Figure 2 compares the conventional high anodic currents, > > 10 mA cm^{-2}, zinc will sustain in

TABLE 2: Possible Reactions Expected for the Zn/S Aqueous Alkaline System, and Their Thermodynamic Potentials at 273.15, 289.15, and 373.15 K

reaction equation	equation	$E°_{reaction}$ at 273.15 K	$E°_{reaction}$ at 298.15 K	$E°_{reaction}$ at 373.15 K
4, 7, 11	$Zn_{(s)} + S_{(s)} \rightarrow ZnS_{(s)}$	1.048	1.043	1.027
i-1	$Zn_{(s)} + S_3^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + S_2^{2-}{}_{(aq)}$	1.016	1.013	1.005
i-2	$Zn_{(s)} + S_4^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + S_3^{2-}{}_{(aq)}$	1.021	1.018	1.010
i-3	$Zn_{(s)} + S_5^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + S_4^{2-}{}_{(aq)}$	1.029	1.026	1.017
ii-1	$Zn_{(s)} + S_2^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow ZnS_{(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)}$	0.798	0.777	0.714
ii-2	$2Zn_{(s)} + S_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 2ZnS_{(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)}$	0.907	0.895	0.859
ii-3	$3Zn_{(s)} + S_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 3ZnS_{(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)}$	0.945	0.936	0.910
ii-4	$4Zn_{(s)} + S_5^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 4ZnS_{(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)}$	0.966	0.958	0.937
iii-1	$Zn_{(s)} + S_2^{2-}{}_{(aq)} \rightarrow ZnS_{(s)} + S^{2-}{}_{(aq)}$	0.826	0.806	0.744
iii-2	$2Zn_{(s)} + S_3^{2-}{}_{(aq)} \rightarrow 2ZnS_{(s)} + S^{2-}{}_{(aq)}$	0.936	0.924	0.890
iii-3	$3Zn_{(s)} + S_4^{2-}{}_{(aq)} \rightarrow 3ZnS_{(s)} + S^{2-}{}_{(aq)}$	0.954	0.946	0.919
iii-4	$4Zn_{(s)} + S_5^{2-}{}_{(aq)} \rightarrow 4ZnS_{(s)} + S^{2-}{}_{(aq)}$	0.973	0.966	0.944
iv-1	$Zn_{(s)} + S_{(s)} + 3OH^-{}_{(aq)} + H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + HS^-{}_{(aq)}$	0.731	0.810	1.083
iv-2	$Zn_{(s)} + S_2^{2-}{}_{(aq)} + 2OH^-{}_{(aq)} + 2H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + 2HS^-{}_{(aq)}$	0.498	0.544	0.682
iv-3	$Zn_{(s)} + S_3^{2-}{}_{(aq)} + 3OH^-{}_{(aq)} + H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_2^{2-}{}_{(aq)} + HS^-{}_{(aq)}$	0.716	0.780	0.973
iv-4	$Zn_{(s)} + S_4^{2-}{}_{(aq)} + 3OH^-{}_{(aq)} + H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_3^{2-}{}_{(aq)} + HS^-{}_{(aq)}$	0.723	0.786	0.978
iv-5	$Zn_{(s)} + S_5^{2-}{}_{(aq)} + 3OH^-{}_{(aq)} + H_2O_{(l)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_4^{2-}{}_{(aq)} + HS^-{}_{(aq)}$	0.729	0.793	0.985
iv-6	$2Zn_{(s)} + S_3^{2-}{}_{(aq)} + 5OH^-{}_{(aq)} + 3H_2O_{(l)} \rightarrow 2Zn(OH)_4^{2-}{}_{(aq)} + 3HS^-{}_{(aq)}$	0.607	0.662	0.827
iv-7	$3Zn_{(s)} + S_4^{2-}{}_{(aq)} + 8OH^-{}_{(aq)} + 4H_2O_{(l)} \rightarrow 3Zn(OH)_4^{2-}{}_{(aq)} + 4HS^-{}_{(aq)}$	0.645	0.703	0.877
iv-8	$4Zn_{(s)} + S_5^{2-}{}_{(aq)} + 11OH^-{}_{(aq)} + 5H_2O_{(l)} \rightarrow 4Zn(OH)_4^{2-}{}_{(aq)} + 5HS^-{}_{(aq)}$	0.666	0.726	0.904
iv-9	$Zn_{(s)} + S_{(s)} + 4OH^-{}_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S^{2-}{}_{(aq)}$	0.761	0.839	1.122
iv-10	$Zn_{(s)} + S_2^{2-}{}_{(aq)} + 4OH^-{}_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + 2S^{2-}{}_{(aq)}$	0.556	0.602	0.741
iv-11	$Zn_{(s)} + S_3^{2-}{}_{(aq)} + 4OH^-{}_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_2^{2-}{}_{(aq)} + S^{2-}{}_{(aq)}$	0.745	0.810	1.002
iv-12	$Zn_{(s)} + S_4^{2-}{}_{(aq)} + 4OH^-{}_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_3^{2-}{}_{(aq)} + S^{2-}{}_{(aq)}$	0.751	0.815	1.007
iv-13	$Zn_{(s)} + S_5^{2-}{}_{(aq)} + 4OH^-{}_{(aq)} \rightarrow Zn(OH)_4^{2-}{}_{(aq)} + S_4^{2-}{}_{(aq)} + S^{2-}{}_{(aq)}$	0.758	0.822	1.015
iv-14	$2Zn_{(s)} + S_3^{2-}{}_{(aq)} + 8OH^-{}_{(aq)} \rightarrow 2Zn(OH)_4^{2-}{}_{(aq)} + 3S^{2-}{}_{(aq)}$	0.651	0.706	0.872
iv-15	$3Zn_{(s)} + S_4^{2-}{}_{(aq)} + 12OH^-{}_{(aq)} \rightarrow 3Zn(OH)_4^{2-}{}_{(aq)} + 4S^{2-}{}_{(aq)}$	0.684	0.742	0.917
iv-16	$4Zn_{(s)} + S_5^{2-}{}_{(aq)} + 16OH^-{}_{(aq)} \rightarrow 4Zn(OH)_4^{2-}{}_{(aq)} + 5S^{2-}{}_{(aq)}$	0.702	0.762	0.942
iv-17	$Zn_{(s)} + 2H_2O_{(l)} \rightarrow Zn(OH)_{2(aq)} + H_{2(g)}$	0.414	0.419	0.427

TABLE 3: The Dominant Aqueous Zinc−Sulfur Battery Polysulfide Species, Sulfur Products, and Corresponding Electrochemical Reactions at Different pH Ranges

pH range	dominant polysulfide species	main product	final discharge product	activity favored reaction	discharged cell reaction
7−9	S_5^{2-}	S_4^{2-}	HS^-	i-3	ii-1
9−14	S_4^{2-}	S_3^{2-}	HS^-	i-2	ii-1
14−16	S_3^{2-}	S_2^{2-}	HS^-	i-1	ii-1
> 16	S_3^{2-}, S_2^{2-}	S_2^{2-}, S^{2-}	S^{2-}	i-1	iii-1

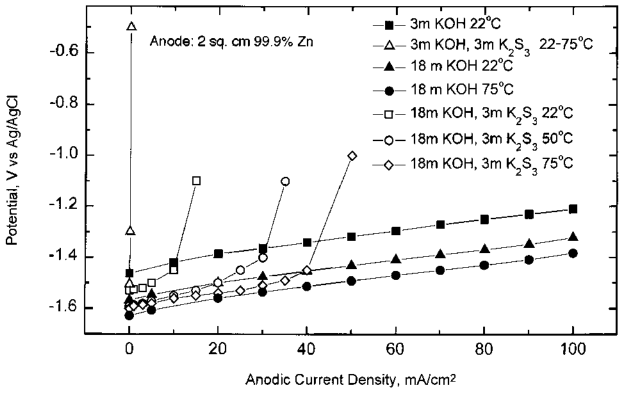

Figure 2. Galvanostatic oxidation polarization of a 99.9% zinc anode in several aqueous alkaline solutions, both with and without added polysulfide.

sulfur-free alkaline KOH solution (in the absence of polysulfide) to those in polysulfide solutions. In either a 3 *m* KOH or an 18 *m* KOH, at room temperature through 75°C, high zinc anodic currents are evident. While as seen in the figure, the same anode is completely passive in the 3 *m* KOH and 3 *m* K_2S_4 electrolyte (to within approximately 3 orders of magnitude).

Unexpectedly, as observed in Figure 2, a high current density of zinc oxidation occurs in a 18 *m* KOH and 3 *m* K_2S_4 electrolyte. Current densities increase on the order of 1000-fold compared to the less alkaline polysulfide electrolyte, and current densities of over 10 mA cm^{-2} on planar zinc electrodes are sustained. Evidently, the high hydroxide concentration permits facile charge transfer, despite competing zinc sulfide passivation. This effective zinc oxidation, despite the presence of sulfide, as well as the high capacity due to the zinc sulfide discharge product, permit demonstration of viable zinc−sulfur electrochemical storage.

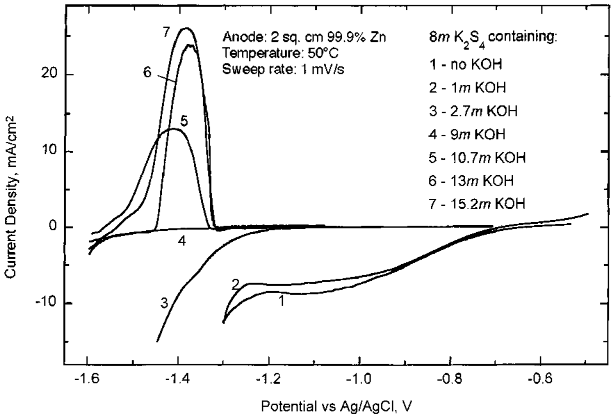

Figure 3. Zinc anode linear voltammetry at 1 mV/s in 50 °C 8 *m* K_2S_4 solution also containing various concentrations of KOH.

The activation of a zinc anode in aqueous polysulfide solution is further probed in Figures 3−6 at 50 °C using low sweep rate (1 mV/s) linear voltammetry. Figure 3 summarizes the results of a planar zinc anode oxidized in a 8 *m* K_2S_4 solution also containing various concentrations of KOH. Significant oxidation currents, in excess of 10 mA cm^{-2}, are sustained in solutions containing greater than 10 *m* KOH concentration. No zinc anodic oxidation current is observed in the 8 *m* K_2S_4 solutions containing less concentrated solutions ([KOH] ≤ 9 m). At lower

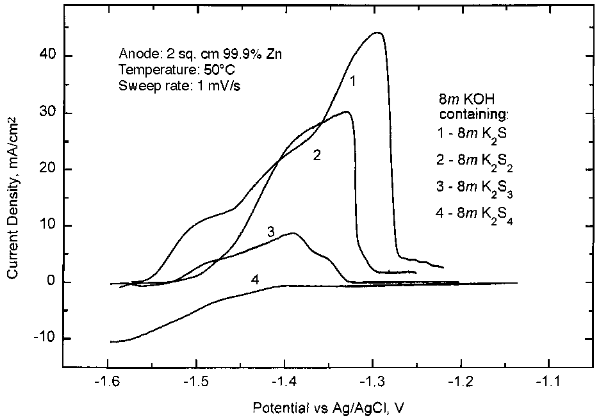

Figure 4. Zinc anode linear voltammetry at 1 mV/s in 50 °C 8 *m* KOH solution also prepared with either 8 *m* K_2S, 8 *m* K_2S_2, 8 *m* K_2S_3, or 8 *m* K_2S_4.

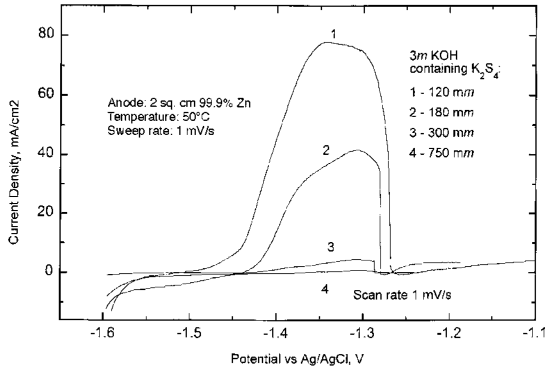

Figure 5. Zinc anode linear voltammetry at 1 mV/s in 50 °C 3 *m* KOH solution also prepared with either 0.12 *m*, 0.18, 0.20, or 0.75 *m* K_2S_4.

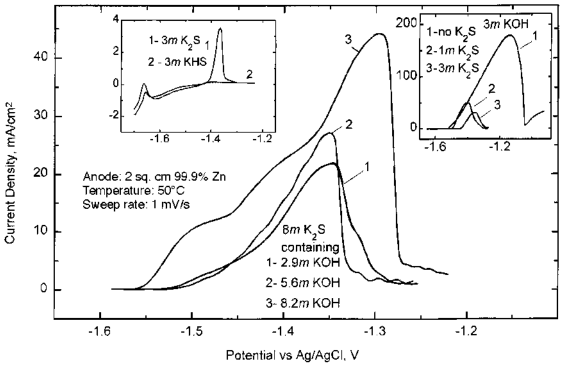

Figure 6. Zinc anode linear voltammetry at 1 mV/s in 50 °C in various aqueous electrolytes. Main figure electrolytes: 8 *m* K_2S solution also prepared with either 2.9, 5.6, or 8.2 *m* KOH. Left inset electrolytes: 3 *m* K_2S or 3 *m* KHS. Right inset electrolytes: 3 *m* KOH with either no K_2S, or either 1 or 3 *m* K_2S.

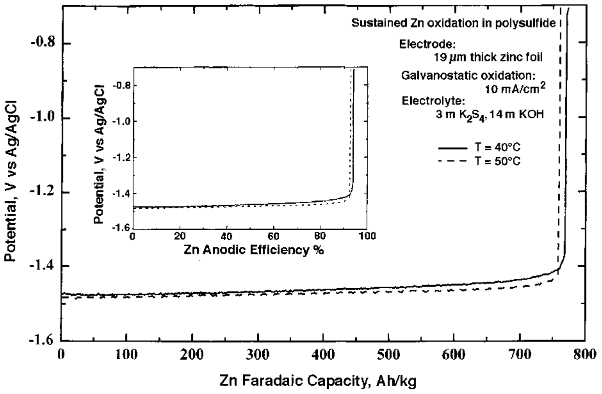

Figure 7. 10mA/cm^2 galvanostatic discharge of a Zn foil (thickness 19.2 μm), working electrode in excess 3 *m* K_2S_4, 14 *m* KOH electrolyte. The horizontal units are calculated from the product of measured time and constant current density, as normalized to the initial electrode mass. Counter electrode: CoS. Reference electrode: CoS, and potentials were then recalculated versus Ag/AgCl using the fixed solution potential for CoS of −0.68 V vs Ag/AgCl.[19] Inset: recalculated to zero-valent zinc two-electron capacity.

concentrations of hydroxide, consisting of 0 to 2.7 *m* KOH in curves 1 to 3, no zinc anodic oxidation occur, and the observed cathodic currents are consistent with polysulfide reduction occurring on the zinc anode. Figure 4 summarizes the results of a planar zinc anode oxidized in a fixed 8 *m* KOH solution also prepared with either 8 *m* K_2S, 8 *m* K_2S_2, 8 *m* K_2S_3, or 8 *m* K_2S_4. The first of these solutions contains no reducible sulfur, while the second, third, and final of these solutions, respectively, contain 8, 16, and 24 *m* zero-valent sulfur. In this figure it is observed that higher concentrations of dissolved zero-valent sulfur progressively passivate the zinc electrode to the extent that no anodic current is observed in the 8 *m* KOH solution containing 8 *m* K_2S_4.

For the zinc electrode, Figure 5 summarizes the K_2S_4 passivation concentration in a fixed 3 *m* KOH solution, also prepared with 0.12 *m*, 0.18, 0.20, or 0.75 *m* K_2S_4. The zinc is fully passivated in the latter solution, and only at [K_2S_4] $<$ 0.2 *m* are significant anodic currents observed. Finally, Figure 6, summarizes the electrochemical activity of the planar zinc electrode in a variety of potassium hydrosulfide or sulfide solutions, containing no zero-valent sulfur. The small second acid dissociation constant of K_2S, with a p$K_a \cong 17$, dictates that in the absence of sulfur, the majority of dissolved sulfide does not form S^{2-}, but rather is hydrolyzed to form solution-phase hydrosulfide, HS^-, and hydroxide, OH^-. In the left figure inset the zinc anode is full passive in the 3 *m* pure (KOH-free) KHS solution, whereas a small zinc oxidation current is observed in the solution nominally prepared as 3 *m* K_2S, but better described in solution as containing equal concentrations (3 *m*) of both KHS and KOH. In the right figure inset each electrolyte contains 3 *m* KOH, and as expected, the zinc anode is most active in the sulfide-free electrolyte and anodic currents are progressively diminished when prepared with 1 or 3 *m* K_2S. Analogously, the main portion of Figure 6 illustrates that for a constant 8 *m* concentration of K_2S, the measured zinc anodic current is progressively higher for higher KOH concentrations.

Coulombic efficiency reflects the degree of completion of an electrode process. The effectiveness of zinc oxidation in alkaline sulfur electrolytes was experimentally determined in a galvanostatic measurement. This was accomplished by driving a planar zinc electrode at constant current to complete anodic consumption, and comparing the measured coulombs liberated to the theoretical available two faradays per mole of zinc in the mass of exposed zinc. As shown in Figure 7, a planar zinc discharges to a high Coulombic efficiency (in excess of 90% of the theoretical storage capacity, or more than 750 Ah per kilogram of zinc). It is also interesting to note in the figure, that even at this relatively high sustained current density of 10 mA cm^{-2}, the anodic discharge potential is smooth and decreases by only 50 mV through 90% of the zinc discharge. This initial result,exemplifies facile anodic charge transfer for the zinc sulfur system and is expected to be further improved with optimization and variation of the zinc surface area, cell

TABLE 4: The Distribution of Species in a Variety of Electrolytes Calculated Using the Previously Described Computer Iterative Model and Equilibria Constants[12a]

nominal composition	concentration (moles per liter)				
K_2S	0	0	3	3	3
Sulfur	0	0	0	9	9
KOH	3	18	3	3	18

species in solution	concentration (moles per liter)				
$[H_2S]$	0	0	<0.1	<0.1	<0.1
$[HS^-]$	0	0	3.0	<0.1	<0.1
$[S^{2-}]$	0	0	<0.1	<0.1	<0.1
$[S_2^{2-}]$	0	0	0	<0.1	<0.1
$[S_3^{2-}]$	0	0	0	0.2	0.2
$[S_4^{2-}]$	0	0	0	2.6	2.6
$[S_5^{2-}]$	0	0	0	0.2	0.2
$[OH^-]$	3.0	18.0	6.0	3.0	18.0

[a] Individual electrolytes are described in each separate column. A solution with nominal a composition of 3 molar K_2S and 9 molar sulfur is equivalent to a solution with a nominal concentration of 3 molar K_2S_4.

configuration, and variations of the zinc and polysulfide electrolyte composition.

Coupled with the known facile charge transfer for the polysulfide cathode, the Figures 1−7 anode results provide the initial basis for viability of zinc/sulfur electrochemical storage using a zinc anode in contact with aqueous polysulfide. Table 4 presents the calculated concentration variation of dominant species in aqueous alkaline polysulfide solutions covering the range of polysulfide solutions in which zinc effectively discharges at high current densities and to high Coulombic efficiency. The distribution of species is calculated in accordance with spectrally determined equilibria constants.[12] In the high alkaline domain investigated, it is seen in the table that the predominant reduced sulfide species in solution is HS^-, and the significant polysulfide species are S_3^{2-} and mainly S_4^{2-}. In particular it should be noted in the table that the dominant solution-phase polysulfide species in a 3 *m* K_2S_4 solution remains tetrasulfide, S_4^{2-}, in both the (Zn nonactive) 3 *m* KOH electrolyte, as well as in the (Zn active) 18 *m* KOH electrolyte. Hence, the range of concentrated polysulfide solutions resulting in unusually high zinc oxidation faradaic efficiency, cannot be correlated to substantial variations of the distribution of species in solution. It is beyond the scope of this initial investigation to elucidate the specific mechanism by which polysulfide solutions sustain Zn oxidation, but only in the presence of high hydroxide activities. However, the thermodynamically favored ZnS product occurs, and in the above absence of correlation to the distribution of polysulfide species in solution, it is likely that the facile zinc oxidation occurs via electrochemical oxidation to zincate followed by chemical reaction to zinc sulfide.

A typical discharge of a Zn/S electrochemical cell is presented in the inset of Figure 8. The open circuit onset potentials and discharge potentials of the complete cell, the Zn anode potential, and the electrocatalytic CoS cathode potential were measured. Anode, cathode, and reference electrodes were maintained in the aqueous alkaline polysulfide solution under thermostatic conditions, and as shown, a discharge is sustained for the bulk of (∼85%) the discharge without significant variation in cell voltage. Zn/S cells were discharged under constant load conditions with ±1% precision resistors. Such a cell can be discharged at high current densities while sustaining low polarization losses as summarized for a variety of current densities in the main portion of Figure 8.

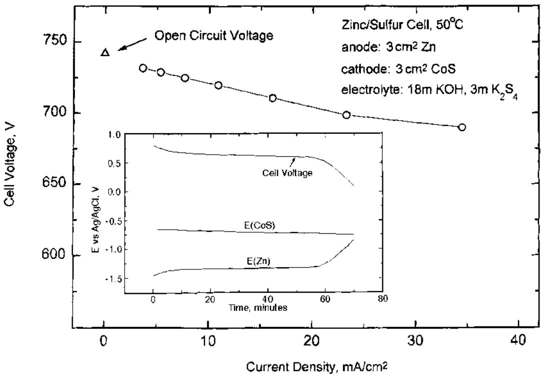

Figure 8. Current density/voltage polarization for a zinc−sulfur cell containing aqueous potassium polysulfide electrolyte. Cells included a silver chloride reference electrode and a 99.9% zinc anode and CoS electrocatalytic cathode in 50(×b1×b1±1) °C 18 *m* KOH, 3 *m* K_2S_4 electrolyte, and was discharged with a constant load (resistor). Figure inset: Potential variation with time during discharge of a zinc/sulfur cell. The top, middle, and lower curves, respectively, represent full cell, cathode, and anode potentials separately monitored during constant resistive load discharge.

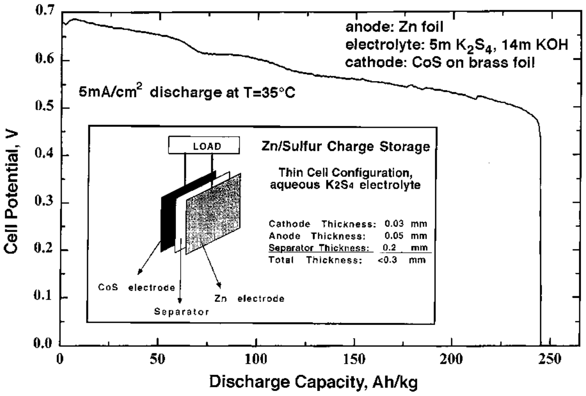

Figure 9. Constant current load (5 mA/cm^2) discharge at 35 °C of a zin−sulfur cell using the thin cell configuration shown in the figure inset. Current/voltage polarization for a zinc−sulfur cell containing aqueous potassium polysulfide electrolyte. Anode: 7 cm^2 Zn foil. Electrocatalytic cathode: 7 cm^2 CoS on thin brass foil. Electrolyte: 5 *m* K_2S_4, 14 *m* KOH.

An initial optimization of a prototype zinc−sulfur electrochemical fuel cell, was studied in a thin cell configuration. The thin cell utilized the sub-millimeter inter-electrode dimensions summarized in the inset of Figure 9. In static (non flow) discharges, the cell was observed to maintain low polarization compared to large gap cells, for electrolytes with higher polysulfide concentrations, and when discharging the cell at a lower temperature of 35 °C. The cell discharges to high Coulombic efficiency of ∼80% for both the available zinc and zero-valent sulfur, and yields a high faradaic capacity of 250 Ah per kilogram of active materials, based on the cell's total mass of zinc, polysulfide, and potassium hydroxide. This high value of faradaic capacity is promising. Future experiments include an excess zinc anode in which an external reservoir of polysulfide is pumped into and through the cell.

Conclusions

Thermodynamic considerations of a novel zinc−sulfur electrochemical storage are presented, and the inital experimental capablities of this system are explored. On the basis of the thermodynamic calculations, it can be expected for the zinc−polysulfide aqueous alkaline system, that over a wide range of temperatures, from 273 to 373 K, the anodic reaction of zinc with sulfide (polysulfide) will be preferred to that of zinc with hydroxide. This minimizes the total system mass and increases the energy density. A high energy density of storage (572 Wh/kg at 298.15 K), coupled with the low cost of zinc and sulfur are competitive with alternate existing electrochemical storage systems.

Initial experimental feasibility of the zinc−sulfur electrochemical system was explored in a zinc anode/aqueous polysulfide/CoS electrocatalytic cathode cell. Measured sustained cathode capacity approaches the theoretical 2 Faraday/sulfur limit. However, the anode tends to passivate due to the zinc sulfide discharge product, preventing sustained discharge. Passivation is overcome in potassium polysulfide solutions containing concentrated (>10 molal) KOH, resulting in efficient, sustained 2 Faraday/Zn oxidation and high zinc−sulfur charge capacities.

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