Aluminum Anodic Behavior in Aqueous Sulfur Electrolytes

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We report on an unexpected domain of high Coulombic efficiency for electrochemical oxidation of aluminum in aqueous polysulfide solutions at high current density for the process: $AI + 3OH^- \rightarrow Al(OH)_3 + 3e^-$. This high-efficiency domain, of importance to battery processes, includes aluminum oxidation in a wide range of solutions containing concentrated dissolved zerovalent sulfur. As expected at lower concentrations of dissolved sulfur, aluminum electrochemical oxidation is inefficient, due to various exothermic parasitic reactions, including: $Al(c) + yS_x^{2-}(aq) + yH_2O(1) \rightleftharpoons \frac{1}{2}Al_2S_3(c) + yOH^-(aq) + yHS^-(aq), y = 1.5/(x - 1),$ and $Al(c) + 1.5S_2^{2-}(aq) + 3H_2O(1) \rightleftharpoons Al(OH)_3(amorph) + 3HS^-(aq)$. However, at high polysulfide and sulfur concentrations, the Coulombic efficiency can approach 100%. This domain of high efficiency is correlated to an observed cathodic shift with increasing sulfur concentration, leading to improved chemical passivation at the aluminum surface.

Introduction

From the perspective of high faradaic storage, the light weight of many sulfur and sulfide compounds is attractive, and various mechanisms of charge transfer have been investigated, including intercalation and bond breaking, in these compounds.1 Concentrated aqueous polysulfide solutions provide a medium for highly reversible two-electron redox chemistry at, or near, room temperature.^{2,3} The spontaneous degradation of these solutions, to thiosulfate, has recently been investigated, and in many cases kinetic stability on the order of years to decades is feasible.⁴ Aqueous polysulfide electrolytes are also used for fundamental investigations of high energy conversion efficiency^{5,6} and moderately stable7 photoelectrochemical solar cells. We previously presented a high faradaic capacity aqueous sulfur redox cell.3 That cell utilized electrolytes which by mass could accommodate more reducible sulfur than water. The resultant electrolyte retains the substantial Coulombic capacity found in molten sulfur battery electrodes yet operates at room temperature and is highly conductive. The polysulfide cathode has a charge capacity of up to 500 Ah/kg and may be further extended to 1070 Ah/kg by use of a solid sulfur cathode with a polysulfide solution interface:²

$$S + H_2O + 2e^- \rightarrow HS^- + OH^-, E^0 = -0.51 V$$
 (1)

In accord with its electrochemical and chemical characteristics, aluminum can provide a complementary anode to a cathode such as sulfur. As with sulfur, aluminum is an abundant material and has an unusually high charge capacity. The alkaline electrochemical oxidation of aluminum may be represented as follows:

$$Al + 3OH^{-} \rightarrow Al(OH)_{3} + 3e^{-}, E^{o} = 2.30 V$$
 (2)

We investigated electrochemical storage which couples the high faradaic capacity of sulfur cathodes with an aluminum anode to exemplify a novel class of aqueous aluminum/sulfur batteries.^{2,8–10} Previously, we studied the intermediate current discharge domain $(0.1-10 \text{ mA/cm}^2)$ of the Al/S battery. These investigations were directed toward a high-energy density,

moderate-power density, self-contained cell and utilized a separated anode and cathode compartment. High-energy density was provided by demonstrating that aluminum could be successfully discharged in highly concentrated alkaline anolytes containing greater than 18 m (sulfur free) KOH while coupled with the separated highly concentrated sulfur cathode.

In principle, the direct electrochemical oxidation of aluminum in aqueous alkaline polysulfide solution, rather than in sulfur free electrolytes, will increase both the energy density and the discharge current density of the aluminum/sulfur battery. This would permit a separator free cell without the polarization losses associated with the separator and facilitate investigation of the high-current density region of the aluminum/sulfur battery. This high-current density domain, with discharge rates of 100 mA/ cm² and higher, is of particular relevance for high-power applications. Yet the chemical reactions of aluminum in polysulfide are highly exothermic and are expected to interfere with the desired electrochemical oxidation:

Al(c) +
$$yS_x^{2^-}(aq) + yH_2O(1) \rightleftharpoons \frac{1}{2}Al_2S_3(c) + yOH^-(aq) + yHS^-(aq), y = 1.5/(x-1), \Delta G^\circ = -228 \text{ to } -236 \text{ kJ mol}^{-1}$$
(3)

with ΔG° , determined by $\Delta G^{\circ}_{f}(Al_{2}S_{3}(c)) = 492.5 \text{ kJ mol}^{-1,11}$ and with the free energies of formation for polysulfides of 79.5, 73.6, 69.0, and 65.7 kJ mol⁻¹, respectively, for the dominant aqueous polysulfide species S_{2}^{2-} , S_{3}^{2-} , S_{4}^{2-} , and S_{5}^{2-} , and the known predominance of HS⁻ in alkaline sulfide solutions.¹² Al₂S₃ can also decompose to Al(OH)₃, as exemplified by the similar chemical reaction of Al with S_{2}^{2-} :

Al(c) +
$$1.5S_2^{2^-}(aq)$$
 + $3H_2O(l)$ ≈ Al(OH)₃(amorph) +
 $3HS^-(aq), \Delta G^\circ = -509 \text{ kJ mol}^{-1}$ (4)

In this paper we present an unexpected stable domain for aluminum electrochemical oxidation in aqueous polysulfide solutions. Despite the presence of sulfur, the faradaic discharge of aluminum is shown to approach 100% Coulombic efficiency in a wide range of concentrated aqueous sulfur electrolytes.

Experimental Section

Materials. Analytical grade reagents and distilled, deionized water were used throughout. K₂S solutions were prepared as

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previously described.³ K₂S₄ is then nominally formed upon addition of sulfur. Anode materials included Alcan International 99.999% Al or Alcan International EB50V alloy or AB50V Al alloy (now available as DH50V) containing >99% Al alloyed with Mg, Sn, and Ga. CoS electrodes were formed by electrodeposition of Co at 50 mA/cm² from a 50 °C 2 *m* CoSO₄, 0.6 *m* boric acid, 0.2 *m* NaCl solution onto a 25 μ m brass substrate followed by oxidation in polysulfide solution as previously described.⁸

Instrumentation and Measurement Techniques. Miniature Al/S cells (containing 0.5 cm² aluminum anodes) were discharged to investigate anodic effects in the high-current region. The cell configuration contained an 0.5 cm² aluminum anode and a substantially larger (3 cm²) CoS cathode. In each cell one side of the aluminum anode was exposed to the electrolyte and the second side encapsulated with epoxy. Utilization of closely spaced parallel anode and cathode electrodes results in a uniformity of field gradient and a greater uniformity of anodic electrode consumption than available with a conventional threeelectrode potentiostatic configuration. Resistive discharge permits access to higher absolute currents than achievable with conventional potentiostats. We have previously demonstrated that these cells provide an excellent representation of substantially larger (68 cm²) flow redox cells containing a solid (aluminum) anode and a liquid phase cathode.¹³ In the present study cathodic current is collected by an effective CoS electrocatalytic electrode. A typical discharge of one of the miniature Al/S configuration cells is exemplified by a cell containing a Fisher 476340 silver chloride reference electrode and a 0.5 cm² anode (one side exposed) with the exposed side spaced 1 mm from a 3 cm² CoS electrocatalytic cathode in 25 mL of stirred alkaline polysulfide electrolyte. The oversized cathode insured that in all cases the significant portion of the investigated potential drop originated at the anode (as determined by separate and simultaneous monitoring of anode and cathode potentials).

Anode, cathode, and reference electrodes were maintained in temperature-controlled stirred aqueous alkaline polysulfide solutions. The open circuit onset potentials and discharge potentials of the complete cell and the anode and cathode potentials were measured using three-channel data acquisition collection on a Cambridge Instruments Superscope. Al/S cells were discharged under constant load conditions with $\pm 1\%$ precision resistors. Discharge times varied from minutes to hours varying with the time necessary to achieve complete consumption of the anode material exposed to the solution.

Coulombic efficiency reflects the degree of completion of an electrode process. This efficiency is experimentally determined during aluminum oxidation by comparing the coulombs generated to the theoretical faradaic equivalents available in the mass of exposed anode. Coulombs generated were verified on a EG&G PAR 379 digital coulometer. Coulombic efficiency measurements are consistent with repeat measurements reproducible to a maximum standard deviation of $\pm 3\%$. In the case of measurements at 75 °C in a highly alkaline (9 *m* KOH) electrolyte, two outlier data points were rejected when epoxy encapsulation separated from the aluminum anode, exposing both sides of the electrode.

Results and Discussion

Aluminum Parasitic Oxidative Reactions. Aluminum is susceptible to parasitic losses which compete with its preferred electrochemical oxidation. These parasitic losses include (i) aluminum/solvent chemical reactions, (ii) reduction of H^+ , and (iii) aluminum/cathode chemical reactions. Reactions of aluminum with the solvent include the following:

$$Al(c) + 3H_2O(l) \rightleftharpoons Al(OH)_3(amorph) + {}^3/_2H_2(g), \Delta G^{\circ} = -426 \text{ kJ mol}^{-1} (5)$$

$$Al(OH)_3(amorph) \rightleftharpoons Al(OH)_3(aq), \Delta G^\circ = 43 \text{ kJ mol}^{-1}$$
 (6)

Al(III) is distributed into a variety of solution phase species related to pH:

$$Al(OH)_3 \rightleftharpoons AlO_2^- + H^+ + H_2O, \log(K) = -13.5$$
 (7)

$$Al(OH)_3 + OH^- \rightleftharpoons Al(OH)_4^-, \log(K) = -0.5 \quad (8)$$

$$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-, \log(K) = -32.3$$
 (9)

$$\operatorname{Al}^{3+} + \operatorname{OH}^{-} \rightleftharpoons \operatorname{Al}(\operatorname{OH})^{2+}, \log(K) = 9.1$$
 (10)

Reduction to H_2 , parasitic loss mechanism ii, is thermodynamically preferred to aluminum oxidation, eq 2, even in alkaline solutions:

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$
, $E(pH \ 14, unit \ OH^- \ activity) = -0.83 \ V$ (11)

but kinetically may be minimized, by solution phase addition or anode alloying of materials such as tin which suppress hydrogen evolution.^{8,13–18} Additionally, when an aluminum anode is in intimate contact with a solution phase cathode, direct (chemical) reaction with the cathodic component will decrease the effectiveness of anodic oxidation by parasitic loss mechanism iii:

$$xAl(c) + ycathode(aq) \rightarrow Al_x cathode_y$$
 (12)

The discharge of the aluminum/solid sulfur battery may be expressed as:^{2,8,9}

$$2AI + 3S + 3OH^{-} + 3H_2O \rightarrow 2AI(OH)_3 + 3HS^{-},$$
$$E_{coll} = 1.8 \text{ V} (13)$$

The faradaic capacity of the Al/S battery (based on potassium salts) is 505 Ah/kg, and the theoretical specific energy is

$$1.8 \text{ V} \times 505 \text{ Ah/kg} = 910 \text{ Wh/kg}$$
 (14)

Previously, we investigated aluminum/sulfur cells configured to minimize the effect of eq 12, by preventing interaction between solution phase sulfur and aluminum. This was accomplished with separate anodic and cathodic compartments, separated by a cation selective membrane, to prevent direct contact of aluminum and sulfur and facilitating the intermediate current density discharge domain of the Al/S battery. This study provides the first investigation of aluminum oxidation in aqueous polysulfide electrolytes and furthers the study of batteries based on aluminum and polysulfide or solid sulfur redox couples. We report on discharge characteristics of the aluminum/sulfur battery in the high-current density domain (up to 1 A/cm²) and investigate electrochemical action of the aluminum anode directly immersed in a variety of polysulfide media.

Oxidation in High-Polysulfide and High-Sulfur Electrolytes. The effectiveness of aluminum oxidation in polysulfide electrolytes may be measured by comparison of the percentage of the available 3 faradays/mol liberated during anodic con-



Figure 1. Effect of the variation of the ratio of (zerovalent) sulfur to sulfide on the anodic charge capacity at 75 °C. The cell electrolyte contained 3 m K₂S_n, 3 m KOH, and 6 mm Na₂SnO₃ (where n in K₂S_n = 1, 2, 3, or 4). Cells were discharged over a 2 Ω precision (1 Ω cm²) load to provide a current density of ~0.5 A/cm². Figure inset: sulfur to sulfide ratio effect on the Al anodic potential either (a) under onset (open circuit) conditions or (b) during 0.5 A/cm² cell discharge conditions.

sumption in accordance with eq 2. In each Coulombic efficiency measurement, the aluminum anode was oxidized to completion.

Figure 1 presents the effectiveness of aluminum oxidation in alkaline solutions at 75 °C containing a fixed concentration of potassium sulfide and containing a variety of concentrations of added zerovalent sulfur. Parasitic chemical reaction impact detrimentally on the electrochemical oxidation of aluminum by providing a nonelectrochemical pathway for aluminum consumption. The solution phase reactions of aluminum and sulfur in eqs 3 and 4 are highly exothermic. Hence as expected, increasing the concentration of zerovalent sulfur, in a 3 m potassium sulfide electrolyte, substantially decreases the aluminum Coulombic efficiency for up to 1 m added sulfur. This is consistent with the parasitic chemical reaction of aluminum and dissolved sulfur. Unexpectedly, at even higher concentrations of added sulfur, the Coulombic efficiency improves, and in solutions containing 4 m and higher added sulfur, electrochemical oxidation of aluminum occurs even more efficiently than in the potassium sulfide electrolyte containing only hydroxide and reduced sulfur (HS⁻ or S²⁻).

When the current density is increased, the aluminum oxidation Coulombic efficiency further improves, approaching 100%. Hence, the 92% efficiency, shown in Figure 1 for aluminum oxidation in 3 m K₂S solutions containing 6 m reducible sulfur, improves to $100 \pm 3\%$, when the current density is increased from 0.5 to approximately 1 A/cm². The increase in current density occurs due to a decrease of the discharge load, from 1 to 0.5 Ω cm². A 3 m K₂S solution containing 6 m reducible sulfur can be equivalently described as a 3 m K₂S₃ solution, and a similar phenomenon is observed when the concentration of K₂S₃ is varied (maintaining a fixed 2:1 ratio of dissolved sulfur to sulfide). This is measured for the same aluminum anode discharged at 0.5 Ω cm², in a 75 °C electrolyte containing, as before, 3 m KOH, 6 mm Na₂SnO₃ but varying K_2S_3 concentrations from 0 to over 8 m. The aluminum oxidation Coulombic efficiency is 82% in the K₂S₃ free electrolyte and



Figure 2. Electrolyte additive effect on the anodic charge capacity and discharge potential of aluminum/sulfur cells at 75 °C. The electrolyte contained 3 *m* KOH, 3 *m* K₂S₃, and the indicated metal oxide salt, where In(III), Ga(III), and Sn(IV) were respectively added as In(OH)₃, Ga₂O₃, and Na₂SnO₃. Anodes consisted of 99.999% aluminum. Cells were discharged over a 2 Ω precision load to provide a current density of ~0.5 A/cm².

as expected, due to the parasitic reaction of aluminum and solution phase sulfur, drops to 65% when 0.3 m K₂S₃ is in solution. The aluminum Coulomb efficiency drops further to 41% when 1.0 m K₂S₃ is in solution. Unexpectedly the aluminum efficiency increases to 71% when 2.0 m K₂S₃ is in solution and further increases to 100% when 3, 6, or 8.3 m K₂S₃ is in solution.

Coulombic conversion efficiency directly impacts on the efficacy of related electrochemical storage. In the ensuing sections, parameters affecting oxidative discharge of aluminum in the unusual 'high Coulombic conversion efficiency' polysulfide electrolytes, such as $m K_2S_3$, will be investigated to probe this effect and to further enhance anodic charge transfer.

Effect of Solution Phase Additives. Small (millimolal) concentrations of solution phase additives are expected to have substantial effects on the anodic characteristics of aluminum discharge in aqueous alkaline media.^{8–10,13–16} As previously evidenced by a decrease in polarization losses and an increase in the rate of parasitic chemical reactivity of aluminum in (polysulfide free) alkaline solutions, added Ga(III) can act as an aluminum activator, such as via the catalytic removal of inhibiting aluminum oxide surface layers. In an opposite manner, added indium acts to passivate the aluminum surface.^{13,16} Figure 2 presents the effect of small concentrations of solution phase additives on the discharge characteristics of a 99.999% pure aluminum anode at high oxidation rates in alkaline polysulfide solutions at 75 °C. The figure compares the measured anode potential to the degree of anodic discharge.

Comparison of the top (with a gallium additive) and bottom (without a solution phase additive) curves of Figure 2 indicates that the presence of sulfur can substantially affect the discharge characteristics of aluminum. Specifically, we observe that both gallium and indium solution phase additives act in a manner opposite to that in sulfur free aqueous alkaline electrolytes. It was previously observed in these sulfur free electrolytes that, compared to In(III), small concentrations of Ga(III) act to remove the protective aluminum oxide overlayer, substantially decreasing the aluminum oxidation Coulombic efficiency and anodically shifting the aluminum potential by 100 mV.⁸ In Figure 2 it is seen that in dissolved alkaline sulfur solutions, rather than acting as a solution activator, the presence of dissolved gallium cathodically shifts the aluminum potential, increases polarization losses, and acts to further stabilize the aluminum as evidenced by the increase in aluminum Coulombic efficiency. In the presence of sulfur it is evident that the Ga(II)/ aluminum oxide overlayer interaction no longer dominates. Alternately, added solution phase indium increases (anodically shifts) the aluminum potential and evidently increases the chemically reactivity of the metal as evidenced by a decrease in Coulombic efficiency. Added stannate results in a more uniform anodic discharge as evidenced by the smooth oxidation potential compared to the discharge in other electrolytes.

Effect of Aluminum Modification. As an alternative to the use of solution additives, aluminum may also be activated by incorporation of magnesium, tin, indium, gallium, or other metals directly (alloying) into the anode.^{17,18} Comparison to one such Al alloy is presented in Table 1, both with and without the presence of solution phase additives. As seen in this table, an aluminum alloy containing small amounts (less than 1%) of added tin and gallium provides higher anode discharge efficiencies. This alloy also results in lower polarization losses compared to the pure aluminum anode. Such alloy characteristics are advantageous, and in accordance with Table 1, it is useful to characterize anodic oxidative behavior at this alloy electrode and in an alkaline polysulfide solution containing 6 mm added sodium stannate, which further stabilizes aluminum oxidation. Unlike the pure aluminum anode, in the case of the gallium-containing alloy, additional solution phase gallium can activate the aluminum surface. This is evidenced, in Table 1, at particularly elevated (95 °C) temperatures by the substantially diminished anode efficiency in the Ga(III)-containing electrolyte.

Effect of Polysulfide Speciation. Aqueous solutions containing sulfur and a sulfide salt, $M_x S_y$, result in extensive speciation and a complex equilibrium of $M^{2y/x+}$, H_2S , HS^- , S^{2-} , S_2^{2-} , S_2^- , S_3^{2-} , S_4^{2-} , S_5^{2-} , H_2O , H^+ , and OH^- . The associated equilibria have been investigated and described as follows: 15,19-25

$$H_2 S \rightleftharpoons H^+ + HS^- \tag{15}$$

$$HS^{-} \rightleftharpoons H^{+} + S^{2-} \tag{16}$$

$$H_2 O \rightleftharpoons H^+ + OH^-$$
(17)

$$(x-1)S_{x+1}^{2^{-}} + HS^{-} + OH^{-} \rightleftharpoons$$

 $xS_{x}^{2^{-}} + H_{2}O, x = 2-4$ (18)

Table 2 presents the calculated concentration variations of dominant species in aqueous alkaline polysulfide solutions used in this study, calculated in accordance with spectrally determined equilibria constants.²⁴ In the high-alkaline domain investigated, it is seen in the table that the predominant reduced sulfide species in solution is HS⁻, and the predominant polysulfide species are S_3^{2-} and S_4^{2-} . In particular it should be noted in the table that the range of concentrated polysulfide solutions resulting in unusually high aluminum oxidative efficiency can not be correlated to substantial variations of the distribution of species in solution.

Sulfur Cathodic Shift of Aluminum Potential. Figure 3 presents the cathodic shift of the anode onset potential observed with polysulfide concentration variation. It is seen that this cathodic shift occurs primarily at low (less than $2 m K_2 S_3$) added

 TABLE 1:
 Effect of Aluminum Anode Composition on the

 Anodic Charge Capacity of Aluminum/Sulfur Cells at 75 °C^a

anode composition	added aqueous salt	[salt] (m <i>m</i>)	<i>Т</i> (°С)	anode Coulombic efficiency (%)
99.999% Al	none	0	75	75
99.999% Al	Na ₂ SnO ₃	6	75	72
99.999% Al	In(OH) ₃	6	75	70
99.999% Al	Ga_2O_3	6	75	91
AB50V Al	none	0	75	81
AB50V Al	Na ₂ SnO ₃	6	75	92
AB50V Al	In(OH) ₃	6	75	84
AB50V Al	Ga_2O_3	6	75	78
AB50V Al	Na_2SnO_3	60	75	76
AB50V Al	Na ₂ SnO ₃	6	95	50
AB50V Al	Ga ₂ O ₃	6	95	2

^{*a*} The electrolyte contained 3 *m* KOH, 3 *m* K₂S₃, and the indicated metal oxide salt. 0.05 cm² anodes consisted of 99.999% aluminum or an alloy (AB50V) containing over 99% aluminum and alloyed with less 1% combined Mg, Sn, and Ga. Cells were discharged over a 2 Ω precision load to provide a current density of ~0.5 A/cm².

 TABLE 2: Distribution of Polysulfide Species in a Variety of Electrolytes Calculated Using the Previously Described Computer Iterative Model²⁴ and Equilibria Constants^{21 a}

nominal composition	concentration (M)						
electrolytes							
K_2S	3	3	1.5	3	3		
sulfur	0	6	3	1	6		
KOH	3	3	3	3	0		
species in solution							
H_2S	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
HS ⁻	3.0	0.4	0.2	2.5	0.6		
S^{2-}	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1		
S_2^{2-}	0	< 0.1	< 0.1	< 0.1	< 0.1		
S_3^{2-}	0	1.7	0.8	0.4	1.2		
S_4^{2-}	0	0.9	0.5	0.03	1.2		
S_5^{2-}	0	< 0.1	< 0.1	< 0.1	< 0.1		
OH^{-}	6.0	3.4	3.2	5.5	0.6		

^{*a*} Individual electrolytes are described in each separate column. A solution with a nominal composition of 3 M K₂S and 6 M sulfur is equivalent to a solution with a nominal concentration of 3 M K₂S₃.



Figure 3. K_2S_3 concentration effect on the Al anodic potential either (a) under onset (open circuit) conditions or (b) during 1 A/cm² cell discharge conditions.

polysulfide concentrations and does not correlate with the domain of enhanced stability.

A partial understanding of the phenomenon of the enhanced aluminum oxidation efficiency, despite the presence of an increasing concentration of reactive polysulfide, is provided by probing anodic potential under load. The domain of enhanced aluminum stability is correlated with an increase in polarization at the aluminum/polysulfide interface. As seen in Figure 3, in the absence of dissolved sulfur, in 3 *m* KOH, 6 m*m* Na₂SnO₄, the aluminum potential under a load of 0.5 Ω cm² (an anodic current density of approximately 1 A/cm²) is observed to be -1.7 V versus AgCl. This potential shifts positive by 0.15 V (to -1.55 V versus AgCl) with the addition of 1 *m* K₂S₃. Compared to the polysulfide free electrolyte, the potential further shifts positive by several hundred millivolts with respective addition of 3 or 8 *m* K₂S₃. The concentration region causing a consistent increase in polarization correlates with the observed enhancement of efficiency in the main portion of the figure.

As evidenced by the observed increased polarization loss at the aluminum/polysulfide interface, the presence of high concentrations of polysulfide results in increased passivation of the aluminum electrode surface. In electrolytes containing low polysulfide, the chemical reactivity of zerovalent sulfur with aluminum tends to dominate this competing passivation phenomenon, resulting in depressed Coulombic efficiencies. In electrolytes containing high concentrations of dissolved polysulfide, the effect of the passivated aluminum tends to dominate, improving stability by diminishing the rate of competing parasitic loss and resulting in high anodic Coulombic efficiencies.

The inset of Figure 1, reporting on anode potential effects with increasing concentrations of dissolved sulfur in fixed sulfide concentrations, substantially supports the correlation previously discussed, regarding the Figure 3 results for electrolytes of increasing polysulfide concentration. It is seen that the domain of enhanced aluminum stability is correlated with an increase in polarization at the aluminum/polysulfide interface. Here, the presence of high concentrations of zerovalent sulfur tends to passivate the aluminum surface. In electrolytes containing less than 2 m dissolved sulfur, the chemical reactivity of the dissolved sulfur with aluminum tends to dominate this passivation phenomenon resulting in depressed Coulombic efficiencies. In electrolytes containing over 2 m dissolved sulfur, the effect of the passivated aluminum tends to dominate, improving stability and resulting in high anodic Coulombic efficiencies.

Effect of Anodic Current Density and Temperature. Planar aluminum is capable of sustaining galvanostatic oxidation in excess of 1 A/cm² in aqueous alkaline media. The deleterious effects of eqs 5 and 12 can be diminished by taking advantage of the very high rates of electrochemical oxidation on aluminum. For a system in which eq 2 is fast, compared to the forward parasitic reactions in eqs 5 and 12, discharge of aluminum will proceed at a high Coulombic efficiency. We recently demonstrated that for an aluminum/ferricyanide battery, with aluminum in direct contact with solution phase cathodic $KFe(CN)_6^{2-}$, aluminum anodic efficiencies of 81% could be achieved at high rates (0.8 A/cm²) of discharge. Although anodic efficiencies were seen to improve at high-current density, in that study there was no indication¹³ that increasing concentrations of the cathodic species could result in enhanced anodic stability, nor that a maximum (100%) aluminum anodic efficiency could be attained. as observed at approximately 1 A/cm² current density in 75 °C polysulfide solutions containing 3 m or higher K_2S_3 solutions.¹³

Figures 4 and 5 present anodic behavior with variation of current density in polysulfide solutions. At higher discharge current densities, the rate of the electrochemical reaction increasingly dominates the competing parasitic chemical reaction, and discharge efficiencies are expected to improve. Consistent with this expectation, and as seen in Figure 4, the



Figure 4. Current density effect on the charge capacity of aluminum anodes oxidized in 3 *m* KOH, 3 *m* K₂S₃, and 6 m*m* Na₂SnO₃. 0.5 cm² AB50V aluminum anodes were discharged over 1, 2, 4, 8, or 15 Ω precision resistors to generate the indicated current densities.



Figure 5. Current density effect on the anodic discharge potential of aluminum in aqueous alkaline polysulfide solution. The electrolyte is comprised of 3 *m* KOH, 6 m*m* Na₂SnO₃, and an indicated concentration of K_2S_3 .

aluminum Coulombic efficiency at 75 °C improves from 25% to 100% as current density increases from 120 to 920 mA/cm² in alkaline polysulfide solutions. This trend of increasing Coulombic efficiency with increasing current density is repeated at both 20° higher and lower temperatures. Additionally, it is seen in Figure 4 that aluminum electrochemical utilization in 3 m K₂S₃ polysulfide respectively improves as the temperature is lowered from 95 to 75 °C and then to 55 °C.

As seen in Figure 5, lower temperatures increase polarization losses at the anode. At the current densities studied, polarization losses are highly linear and may be summarized by a linear slope. In a 3 *m* KOH, 3 *m* K₂S₃ electrolyte this polarization is 1.3 mV cm² m A⁻¹ at 55 °C, compared to 0.4 mV cm² mA⁻¹ at 75 °C. Also presented in Figure 5 are high-anodic current densities, in excess of 2 A/cm², sustainable in 1 *m* K₂S₃. In this figure a comparison of the polarization losses in the 1 and 3 *m* K₂S₃ electrolytes (0.2 compared to 0.4 mV cm² mA⁻¹ at 75 °C) is consistent with the Figure 3 description of lower anodic polarization losses at lower concentrations of dissolved polysulfide.

Oxidation in Concentrated Alkaline Electrolytes. Figure 6 presents the effect of the variation of KOH concentration in



Figure 6. KOH concentration effect on the anodic charge capacity at 75 °C. The electrolyte contained 3 m K₂S₃, 6 mm Na₂SnO₃, and the indicated concentration of KOH. Anodes consisted of 0.5 cm² AB50 aluminum alloy. Cells were discharged over a constant 2 Ω precision load to provide a current density of ~500 mA/cm².

aqueous polysulfide electrolytes on the anodic charge capacity at 75 °C. As shown in the final column of Table 2, calculation of the speciation equilibration of alkaline polysulfide solutions indicates that, even for the 3 m K₂S₃ electrolyte, nominally prepared to contain no added KOH, there will be significant free hydroxide in solution. However, this electrolyte will contain substantially less free hydroxide than solutions containing 3 m or higher added KOH. In accordance with eq 3, diminished KOH can negatively impact on the forward rate of aluminum electrochemical oxidation. This is reflected in the lower anodic efficiencies and higher polarization losses in polysulfide electrolytes containing less than 3 m KOH polysulfide in Figure 6 and the figure inset. At concentrations of KOH greater than 3 m, anodic polarization losses diminish. However, at these high concentrations of added KOH, the anodic efficiency also decreases. This reflects an increase in chemical reactivity of hydroxide and a relative increased competition of the parasitic chemical reaction (eq 5).

Reduction and Stability of Aqueous Sulfur. CoS provides an effective electrocatalytic surface for aqueous sulfur reduction, eq 1, with small polarization losses on the order of 1 mV cm² mA^{-1,2} Similarly, CuS reduces polysulfide with low overpotential.²⁶ However, unlike CoS, CuS is unstable in these electrolytes. The copper sulfide electrode dissolves in solution on the order of days. Compared to both CoS and CuS, Pt and carbon are poor aqueous sulfur electrocatalysts and exhibit 1 order of magnitude greater overpotential.²⁷ Thermodynamically, aqueous sulfur solutions are unstable decomposing to thiosulfate, S₂O₃²⁻:

$$S_{dissolvd}(S_x^{2^-}, x = 2 - 4) + OH^- \rightarrow \frac{1}{4}S_2O_3^{2^-} + \frac{1}{2}HS^- + H_2O$$
 (19)

We have observed at $T \le 85$ °C that aqueous sulfur solutions are extremely stable under conditions of high polysulfide concentration (>5 *m* K₂S₄) and low KOH concentration, and the reaction is consistent with a sulfur decomposition activation energy of 104 (±5) kJ mol⁻¹ and with a rate-limiting step inverse first order in [HS⁻] and first order in [OH⁻] and [S₅²⁻].⁴

Simultaneous Anodic Potential and Efficiency Enhancement. As demonstrated, small changes in solid and solution phase aluminum chemistry are expected to vary electrochemical behavior and can lead to further stabilization of discharge characteristics. Indeed a second alloy (EB50V), also containing 99% aluminum and Mg but smaller concentrations of Sn and Ga compared to the alloy (AB50V)²⁸ used in the majority of the studies in this paper, evidences improved discharge behavior. At moderate current density (120 mA/cm²) and 55 °C, the second alloy displays considerably enhanced aluminum conversion efficiency. Similarly at higher current density and temperature (600 mA/cm² and 75 °C) the second alloy exhibits higher Coulombic efficiency in the presence of either a 6 mm Sn(IV) solution phase additive (EB50V efficiency of 98% compared to 92% for AB50V) or a 6 mm Ga(III) solution phase additive (Coulombic efficiency approaching 100% compared to 78% for AB50V). The high-polysulfide concentration domain need not prevent high anodic potentials, and modifications in the alloy can further anodically shift these potentials. For example at 55 °C, the EB50V alloy in 3 m K₂S₃, 3 m KOH electrolyte exhibits an anodic open circuit potential of -1.95V versus AgCl, improved (anodically shifted), compared to that shown of -1.7 V versus AgCl in Figure 5 for the AB50V alloy.

The domain of concentrated polysulfide solutions resulting in efficient aluminum oxidation does not mean to infer that a final optimization of aluminum/aqueous sulfur chemistry has been presented for electrochemical storage. However, discharge of an aluminum sulfur battery utilizing an aluminum anode in situ in an aqueous polysulfide electrolyte, as theoretically described by eqs 13 and 14, appears to be feasible. The discharge of one such battery (monitoring the anode and cathode full cell potential during discharge) is described in the Experimental Section and leads to high voltage and anodic efficiency. When the cell utilized a EB50V alloy anode, used a 55 $(\pm 1)^{\circ}$ C 3 m KOH, 3 m K₂S₃, 6 mm Na₂SnO₃ electrolyte, and was discharged with a 15 Ω resistor, the cell voltage was nearly constant (slowly decreasing from 0.9 to 0.8 V) for 7 h and then decreased rapidly in the eighth hour as the available aluminum was consumed. During discharge the cell generated a constant potential at the CoS electrode of -0.8 V vs AgCl and an anode potential diminishing from -1.74 to -1.64 V. The cell exhibits an open circuit voltage of 1.2 V, a stable and long duration (greater than 7 h) discharge voltage of approximately 0.9 V at 120 mA/cm², and a Coulombic efficiency of 80%.

Conclusions

This study has probed discharge characteristics of the aluminum/sulfur battery in the high-power density domain and investigated electrochemical action of the aluminum anode in a variety of polysulfide media. We find an unexpected domain of high Coulombic efficiency for aluminum oxidation in a wide range of solutions containing over 2 m polysulfide or added zerovalent sulfur. As expected at lower concentrations, aluminum decomposes during anodic consumption in a variety of parasitic reactions resulting in low Coulombic efficiency. The high-Coulombic efficiency domain is correlated to increased passivation at the aluminum surface and can yield highefficiency and high-power electrochemical storage discharges of relevance to electric vehicle applications. The observed decomposition at lower current density can lead to shortened cell shelf life. This problem may be mitigated, by utilization of a modified fuel cell configuration, in which polysulfide (aqueous sulfur) is externally stored and flows into contact with the aluminum anode only during cell discharge.

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