

BEHAVIOR OF A SODIUM-SULFUR CELL WITH A DYNAMIC SULFUR ELECTRODE

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Summary

A sodium-sulfur cell was constructed with sodium polysulfide circulating in a narrow annulus around a β -alumina tube. The absence of carbon mat in the electrode reduced the current collector surface area appreciably, localized the electrochemical reactions, and ultimately led to film formation on the electrode. The results are consistent with existing models and interpretations of sulfur electrode behavior. Film formation on the electrode is responsible for the rather poor electrical characteristics of the cell.

1. Introduction

The role of the sulfur electrode in sodium-sulfur batteries has been investigated thoroughly. Models have been proposed to explain the operation of this electrode and its influence on cycling performance [1 - 4] while kinetic studies have considered the electrode reactions occurring in polysulfide melts [5 - 8]. All the cells are based on an arrangement where the polysulfide melt is static. In the various designs the carbon felt (saturated with molten sulfur) is held in a reactant chamber surrounding the β -alumina electrolyte. Sufficient sulfur is required to prevent the reaction with discharged sodium from forming polysulfides higher than Na_2S_3 . This condition compels the use of a sulfur reservoir whose size contributes to the total cell resistance.

In the present work a Na-S cell with a "dynamic" sulfur electrode was constructed. Sodium polysulfide circulated in a narrow annulus around the β -alumina tube. No carbon electrode resistance felt was present because it would tend to impede flow. This design offered an opportunity to determine whether a very different sulfur electrode concept could be explained by the existing theories developed for static systems.

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2. Cell design

A schematic of the circulating polysulfide cell is shown in Fig. 1. It closely resembles the 16 A h capacity test cell employed in earlier studies [9]. Appropriate modifications were made for the sulfur electrode and the fluid flow system. The sulfur compartment contained a graphite sleeve which established a 1.5 mm annulus around the β -alumina tube. In the prototype cells this distance is 7 mm. Thus, the sulfur electrode resistance was reduced commensurately.

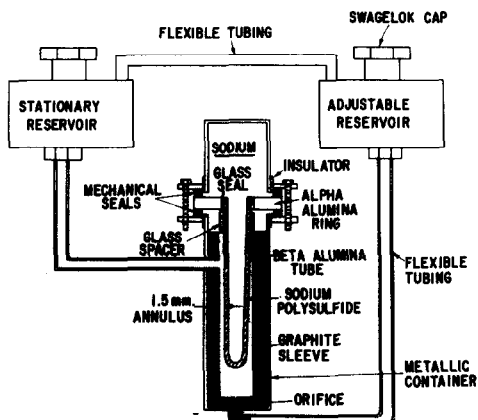


Fig. 1. Schematic diagram of sodium-sulfur cell with dynamic sulfur electrode.

The flow system consisted of two stainless steel reservoirs, the annular space around the β -alumina tube, and an orifice at the bottom of the chamber. One of the reservoirs was connected to the cell by flexible stainless steel tubing. The orifice produced the necessary pressure drop, while other factors such as friction, elbows, diameter changes, etc., were minor contributions. A pulley system (not shown) adjusted the height of the movable reservoir relative to the stationary one. The height difference (Δh) between the two created the required pressure head to force flow through the orifice. A volumetric flow rate of $0.2 \text{ cm}^3/\text{min}$ or an annular velocity of $3.7 \text{ mm}/\text{min}$, corresponded to a 111 mm height difference. The relation between volumetric flow rate and Δh is linear, and this enabled the flow rate to be doubled when desired. Fluid velocity was such that the annular volume of liquid was completely refreshed in 20 min. The position of the movable reservoir was changed every three hours to avoid depletion (*i.e.*, it was either 111 mm above or below the fixed reservoir). The flow rate was constant because the large reservoir diameter made the Δh between reservoirs much larger than the Δh within a reservoir as it emptied or filled.

The absence of carbon mat meant that an initial discharge into pure sulfur would be difficult. Thus, Na_2S_5 was used as the starting catholyte and the cell was designed for 9 A h operation. In this way the final discharge

composition was Na_2S_3 and the cell would operate solely within the one phase region. Sodium polysulfide was prepared by a method similar to that of Rosen and Tegman [10]. The mixture was prepared by heating weighed amounts of vacuum-dried Na_2S (99.9) and S (99.999). The Na_2S_5 mixture was ground, filled into a Pyrex glass tube, evacuated, and sealed. It was heated at 230°C for 16 h and at 400°C for 0.5 h. The Na_2S_5 was loaded into the reservoir *via* a Swagelok fitting, evacuated, and sealed. All handling operations were performed in a dry box (N_2 atmosphere) of less than 30 p.p.m. moisture content.

3. Cell performance

The discharge characteristics of the cell at three different current densities are compared in Fig. 2. The initial state of charge was identical for all cases, and a constant current discharge to 1.5 V was used. It is evident that cell discharge was shallow for the conditions investigated. To achieve a greater depth of discharge, the cell was placed on open circuit and allowed to recover for prolonged periods (*e.g.*, several hours) between discharges. Although this process was reasonably successful at 30 mA/cm^2 (referred to the geometric surface area of the β -alumina tube), rapid polarization continued to occur at the higher current densities. Increasing the flow rate did not alter the behavior.

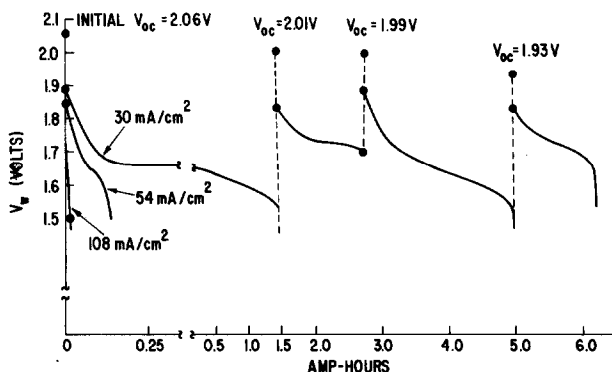


Fig. 2. Discharge characteristics of experimental cell.

When the cell was placed on open circuit, the transient response was able to provide additional information concerning the cell. The initial sharp change in potential was followed by a continuous, but slow, increase to a limiting voltage. The former indicates the IR drop, while the latter represents the slow drift back to the open circuit voltage (V_{oc}) as determined by the melt composition. This response was affected by the value of the cell working voltage (V_w) prior to opening the circuit. Below 1.5 - 1.6 V, a well de-

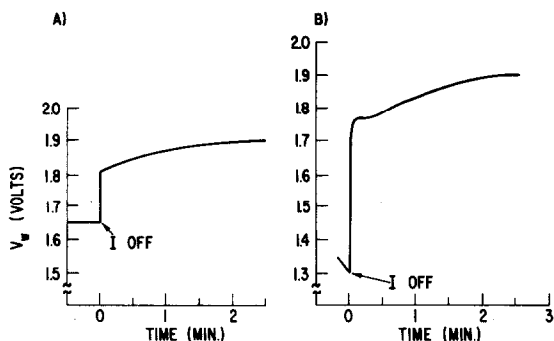


Fig. 3. Transient voltage response of cell when placed on open circuit. (a) Discharged to 1.65 V; (b) Discharged to 1.3 V.

finied plateau was observed (Fig. 3). It will be shown later that this behavior is associated with certain processes occurring at the melt/electrode interface.

The charging behavior was somewhat different from that of discharge. The voltage-time curve was erratic, and rapid fluctuations were common. A typical trace is shown in Fig. 4. Polarization occurred as a function of time

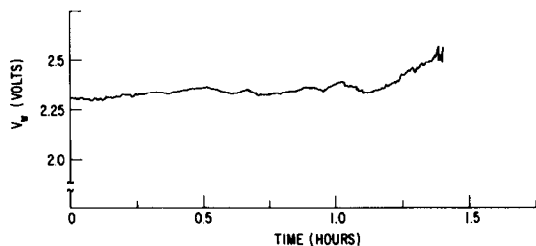


Fig. 4. Voltage-time trace of cell during charge.

and current density in much the same manner as discharge (Fig. 2). The open circuit voltage displayed extremely interesting behavior; its value never reflected the melt composition. Instead, a rather high V_{oc} was attained (2.06 - 2.08 V — larger than even the initial V_{oc}) within a very short charging time (minutes). Recovery periods were necessary to achieve greater charging depths, but V_{oc} remained unaltered. The transient response consisted of only the instantaneous potential drop.

Cell resistance was expected to be appreciably lower than that observed in prototype cells because of the annulus used in the sulfur compartment. The initial cell resistance, 0.11 ohms, agreed well with the value calculated for a cell with Na_2S_5 melt in the present geometry (0.10 Ω). Subsequent values for cell resistance were always larger, even when current interruption and a.c. methods were employed. Cell resistance was decidedly lower on discharge than during charge, and non-ohmic at smaller current densities (1 - 5 mA/cm^2) as well.

4. Discussion

(a) Review of sulfur electrode studies

The sulfur electrode models and voltammetric studies of polysulfide melts arrive at certain important conclusions regarding sodium-sulfur cell operation and interfacial reactions, respectively. The models are concerned with the electrochemical reaction rate distribution under various conditions. Potential distribution calculations indicate that in conventional Na-S cells, as the carbon matrix resistance increases, the reaction rate becomes increasingly concentrated at the container wall [1, 3]. In the most extreme case, when the carbon resistance is infinitely great, all the reaction would be expected to occur at the container wall. It would seem that the absence of carbon mat in the present cell arrangement would correspond to this situation from both physical and mathematical standpoints. Existing models, unfortunately, yield an indeterminate solution for this particular case of infinite carbon resistance.

The electrochemical studies represent an independent means of establishing what processes prevail within the sulfur electrode. Table 1 summarizes

TABLE 1

Proposed explanations for various regions of current-potential curve [5]

Potential range (V)	Mechanism
<i>Cathodic region</i>	
0 to 0.4 - 0.5	Diffusion controlled redox mechanism
0.4 - 0.5 to 1.5 - 1.8	Diffusion limited region — Na ₂ S _x film present
1.5 - 1.8 to 2.0 - 1.8	Modification of film
> 2.0	Sodium deposition
<i>Anodic region</i>	
0 to 0.1 - 0.2	Diffusion controlled redox mechanism
0.1 - 0.2 to 0.8 - 1.0	Sulfur formation

the explanation proposed by Armstrong *et al.* [5] for the current-potential curve of a carbon-sodium polysulfide system. There is general agreement on this model by other investigators as well [6 - 8]. In the cathodic region (corresponding to cell discharge) the current becomes diffusion limited at 0.4 - 0.5 V once a film, probably Na₂S₂, is produced on the electrode. High resistance values are also observed [6, 7]. Anodic curves are associated with the production of elemental sulfur. Direct observations during the cycling of thin-layer cells supports this contention [8, 11]. A recent paper [3] described the difficulties encountered in trying to compare the calculated potential differences with experimental results from voltammetric studies.

In the present work, however, the reaction rate is highly localized, and a situation arises where the potential differences are so large that the concern for corrections to the reversible potential can be ignored. Thus, the existing sulfur electrode theories and interpretations strongly suggest that the dynamic sulfur electrode is extremely susceptible to film formation on charge and discharge.

(b) Evidence for electrode film formation on discharge

The operating characteristics of the experimental cell seem to verify the conclusions cited above regarding film formation at the container wall. The evidence for film formation on discharge includes the following effects: increase in cell resistance above certain potentials, the open circuit transient response, and the time required to polarize the cell.

The increase in cell resistance occurred in a manner analogous to that reported for voltammetry studies [6]. In Fig. 5, literature results are com-

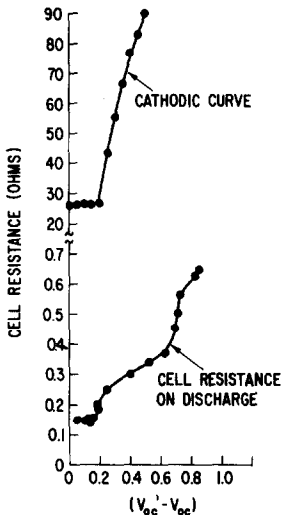


Fig. 5. Cell resistance as a function of the displacement from equilibrium potential; (upper) from voltammetry of polysulfide melts [6], (lower) this investigation.

pared with those from the present investigation. V_{oc}' is part of the instantaneous potential drop (see Fig. 3) used in calculating cell resistance, R_c :

$$R_c = \frac{\Delta V}{I} = \frac{V_w - V_{oc}'}{I} \quad (1)$$

where V_w is the working voltage of the cell and V_{oc}' is an apparent open circuit voltage determined by local melt composition. V_{oc} is the true open circuit voltage based on the ampere-hours of sodium added to the melt. Therefore, $V_{oc}' - V_{oc}$ measures the deviation of the system from its equilibrium value. In the present experiment, the cell was discharged from a

starting composition of Na_2S_3 (filled reservoir). Within 10 mA h various V_{oc}' values were achieved. The resulting plot (R_c vs. $V_{oc}' - V_{oc}$) may be qualitatively compared with the voltammetry work because both studies represent melt resistance as a function of the deviation from the equilibrium potential. The voltage region where cell resistance increases agrees reasonably well with both the Ford results [6] (Fig. 5) and those of Armstrong *et al.* [5]. The formation of an Na_2S_2 electrode film was postulated in both of these investigations.

The open circuit transient response was also consistent with reported work. Above $V_w = 1.6$ V the voltage increased continuously and smoothly towards V_{oc} (Fig. 3(a)) in a manner compatible with a diffusion controlled process [5]. Below this potential, the shape of the voltage-time trace was altered (Fig. 3(b)). In analogous experiments using square pulse measurements on stationary disc electrodes, non-uniformities in the decay characteristics were considered to be evidence of a film on the electrode surface [5, 12]. The voltage region where these irregularities were first observed correlates well with the $V_{oc}' - V_{oc}$ values of increasing resistance (Fig. 5).

Once the polysulfide film is formed, the discharge behavior is believed to become diffusion controlled [5]. This hypothesis was verified by measuring the time required to achieve a certain potential drop. In the experiment the cell was discharged to a potential where film formation was expected to occur (1.3 V). After a short recovery time it was then subjected to a discharge-recovery cycle in which the cell would recover to a desired V_{oc}' and then be discharged to 1.65 V. The time required for various potential drops ($\Delta V = V_{oc}' - V_w$) is illustrated in Fig. 6. The cycling procedure

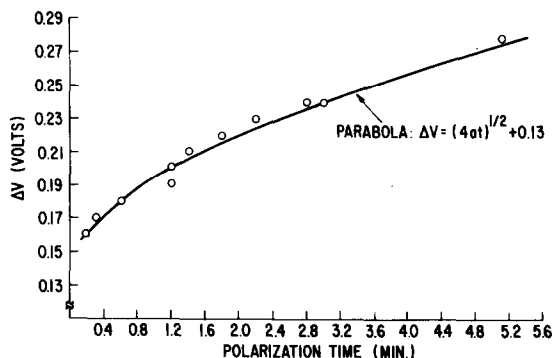


Fig. 6. Time required to achieve various potential drops once polysulfide film is formed.

was designed to maintain a relatively constant film thickness. Short recovery times ensured the presence of the layer, and a working voltage of 1.65 V should not promote excessive film growth. The reasonably good parabolic curve of ΔV vs. t is consistent with a diffusion limiting process and offers further evidence of film formation during discharge.

(c) Evidence for electrode film formation on charge

There are several results which support the contention that sulfur films were formed at the graphite electrode during charge. The erratic voltage traces observed in this study (Fig. 4) parallel the noisy and irreproducible results reported for the anodic voltammetry of polysulfide melts. Production of a passivating sulfur film was considered to be responsible for this behavior [5, 7, 8]. The greater cell resistance on charge for reasonably low values of $V_w - V_{oc}$ (<0.2 V) is also indicative of an insulating film. Finally, the anomalously high V_{oc} registered throughout the charge cycle was extremely close to the equilibrium potential of a sulfur-saturated melt [13]. This represents fairly definitive evidence of a sulfur-rich layer because a sulfur phase forms from a polysulfide melt once the equilibrium potential is attained [8].

5. Conclusions

The behavior of a sodium-sulfur cell with a dynamic sulfur electrode can be explained by the models and interpretations developed for static systems. The absence of carbon mat in the cell reduces the current collector surface area from $\sim 10^4$ cm² to ~ 25 cm². Reaction rate distribution models predict that this causes electrochemical reactions to become highly localized, which ultimately leads to film formation. Many of the results obtained in the present work could be compared with those from voltammetric studies, particularly when the latter were beyond the linear regime. Thus, it appears likely that a polysulfide film (possibly Na₂S₂) formed on the graphite wall during cell discharge and that a sulfur layer was produced there during charge. The dynamic nature of the polysulfide melt had no discernible effect on film formation. The presence of these films was responsible for the rather poor characteristics exhibited by the cell. This situation was exacerbated when current levels representative of normal battery operation were applied.

Acknowledgments

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