APPLICATIONS OF CARBON IN THE SODIUM-SULFUR BATTERY

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A brief description of the sodium-sulfur battery will serve as a basis for a more detailed discussion of the use of graphite as a current collector and inert electrode. The battery operates in the range of 300-400°C, liquid sodium being oxidized at the negative electrode and liquid sulfur being reduced at the positive graphite electrode. The liquids are separated by β or β''-alumina solid electrolyte which is highly selective to the passage of sodium ions. The sodium ions passing through the solid electrolyte combine with reduced sulfur to form a continuous solution of sodium polysulfide compounds, Na_2S_x, the nominal value of x varying from 5.2 to 2.7 as the reduction proceeds. A miscibility gap occurs between sulfur and $Na_2S_{5.2}$, polysulfide being virtually insoluble in the sulfur phase. The end of discharge is signaled by the precipitation of Na_2S_2. Thus discharge may be viewed as the two phase reduction of sulfur to $Na_2S_{5.2}$, followed by the one phase reduction of $Na_2S_{5.2}$ to $Na_2S_{2.7}$. The battery is reversible and may be recharged to about 90% of the original amount of sulfur.

Materials problems in the battery are due to the corrosiveness of the sulfur-polysulfide system. The container as well as the inert electrode needs to be considered. Most metals corrode, at least to the extent that the corrosion products cause a gradual decrease in battery efficiency and capacity. Some metals, such as Mo, are protected to a degree by metal sulfide film formation, while others, such as Al and Cr are protected by their oxides. Oxides generally are stable in molten polysulfides; e.g., Cr_2O_3, ZrO_2, $La_{0.84}Sr_{0.16}CrO_3$, Ta doped TiO_2, Fe doped $CaTiO_3$, and glass such as the borosilicate glasses. Some carbides and nitrides have been found to be stable under certain test conditions; e.g., SiC. Carbon is stable, and, as we shall see, carbon is the only readily available material which meets most of the requirements for the inert sulfur electrode. (The materials problems related to the container for the sulfur-polysulfide system will not be discussed.)

One desirable structure for the sulfur electrode is a graphite felt. The properties of the felt which relate to the performance of the electrode are: pore volume or felt density, surface area, compressibility, two-dimensional resistivity, nature of surface adsorption sites, and structural integrity. In order to understand the relationship of these properties to electrode performance, a more detailed description of the electrode reaction is required.

A typical sodium-sulfur cell consists of a β''-alumina tube filled with sodium. Graphite felt surrounds the outside of the tube and a protected metal container surrounds the graphite felt so that the β''-alumina tube and the metal container are concentric. The sulfur is stored in the porous graphite felt. The graphite surface in close proximity to the β''-alumina is the electrochemical reaction site; the remainder of the graphite felt serves as a storage and supply bed for sulfur and polysulfide, and as a radial current collector from the reaction site to the conductive container wall. The container serves as an axial current collector. The rationale for this structure may be perceived through an examination of the relevant resistivities. Both the β''-alumina and the polysulfide melt have resistivities of about 4 ohm·cm at operating temperatures. The β''-alumina is thin (0.1-0.3cm); therefore, the ohmic loss is kept small. For most applications the amount of sulfur and polysulfide stored in the felt requires a felt thickness of about one cm. The resistivity of a typical graphite felt is 0.3 ohm·cm; this is low enough to provide satisfactory radial conductivity over the one cm distance. Furthermore, it constrains the electrochemical reaction to the close proximity of the β''-alumina since the electronic conduction through the felt is much greater than the ionic conduction through the polysulfide melt.

The details of the chemical reaction have been given previously (1). In summary, the discharge reaction is diffusion controlled in the one phase region and under mixed kinetic and diffusion control in the two phase region. The cathodic reaction may be generalized as:

$$S_4^= + 2e^- = 2S_2^= \qquad (A)$$

$$4S + 2S_2^= = 2S_4^= \qquad (B)$$

$$\overline{4S + 2e^- = S_4^=} \qquad \text{Net Reaction}$$
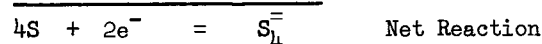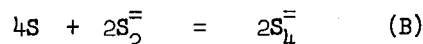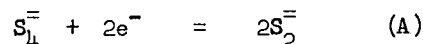
If any $S_3^=$ ions are formed, they disproportionate to $S_2^=$ and $S_4^=$. In the sequence: S, $S_5^=$, $S_4^=$, $S_2^=$, a mixture of two separated species will chemically react to form the intermediate species.

In the two phase region the polysulfide is electrochemically reduced by (A), but regenerated by the chemical reaction (B). In the one phase region the net reaction is reaction (A) by itself. The consequence of these reactions is that a counter diffusion of the polysulfide ions exists at the electrode; e.g., $S_2^=$ and $S_4^=$ in reaction (A). Mass transport polarization occurs. This polarization has been measured in actual cells and can be the largest contribution to the lowering of the cell voltage. It has been found that the cell voltage can be increased (mass transport polarization decreased) by increasing the surface area of graphite felt in the region adjacent to the β''-alumina tube. The increased electrode area

permits a decrease in the diffusional flux and in the concentration gradients of reactants and products. In the two phase region, the sulfur phase must be brought into contact with the polysulfide phase in order to facilitate reaction (B). Since sulfur is very viscous at the temperature of cell operation (sulfur, $\sim$ 20 poise; polysulfide $\sim$ 20 centipoise), it is desirable to have open regions in the storage and supply regions of the felt. It has been experimentally demonstrated that the lighter sulfur will rise in open vertical channels and the heavier polysulfide will fall at rates in excess of the supply requirements of the reaction. Thus natural convection can be an aid to the transport of electrode reactants and products. The open regions in the felt have several other influences. First, graphite is preferentially wettable by sulfur, having an advancing contact angle of about 25°, whereas polysulfide has an angle of about 90° (1). Thus if the cathode space is underfilled with sulfur, the sulfur will wick into the felt. Vapor transport of sulfur can then occur in the open regions. Also the open regions can fill with polysulfide as discharge progresses. Thus preferential wicking can be an effective means of enhancing a counterflow of reactant and product. The importance of wicking is especially relevant during charging of the battery. On charging, at the transition from the one phase to the two phase melt (at 40% of full charge) sulfur is formed at the electrode. The sulfur is an insulator and halts further charging, unless special means are used. One such means is to coat the graphite with an oxide such as Al_2O_3. The graphite becomes wettable by polysulfide, and the sulfur is expelled from the electrode surface. At $350^{\circ}C$ and at currents of $100mA/cm^2$ the utilization (% of capacity for total conversion of Na_2S_3 to sulfur) for a cell with open regions and Al_2O_3 coated felts was 82%, while an identical cell except with untreated felts yielded 34%. On charging during the two phase regime, the polysulfide is oxidized directly to sulfur, and since reactant and product are essentially immiscible, very little diffusion occurs. Means to improve performance must rely on other modes of mass transport, such as differential wicking or convection.

The density or pore volume of the porous electrode will affect mass transport by wicking, convection and diffusion within the porous body. Cells using vitreous carbon foam electrodes of different pore size (but equal bulk void volume) gave nearly identical performance.

The compressibility and elasticity of the electrode material are relevant in terms of the electronic contact of the porous electrode with the axial current collector or container. It has been found that the contact resistance is low, even when the electrode is not tightly compressed or cemented against the container. Apparently ionic bridging through the melt between slightly separated electronic contacts provides low impedance connections.

In summary, porous carbon or graphite structures in tubular cells provide:

1. good radial conductivity

2. adequate structural integrity for incorporating open regions

3. adequate elasticity for good electrical contact to the container

4. adsorption characteristics conducive to mass transport by differential wicking

5. surface area high enough to minimize mass transport polarization

6. density and pore size within a range which permits adequate storage capacity and adequate mass transport.

1. Tischer R. P. and Ludwig F.A., In Advances in Electrochemistry and Electrochemical Engineering (Edited by H. Gerischer and C. W. Tobias), Vol. 10, pp. 391-482. John Wiley & Sons, New York (1977).