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Direct calculation of the sulphur electrode resistance in sodium-sulphur cells

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A simple model is used to compute the resistance of the sulphur electrode as a function of charge. It is shown that the general network used for the simulation of the behaviour of the sulphur electrode can be simplified because of the relatively small value of the polarization resistance. Reasonable assumptions concerning the distribution of reactants and products are discussed. The model is able to assess the contribution of the sulphur electrode to the total cell resistance for a 16 A h capacity cell.

1. Introduction

The results reported by the various groups engaged in sodium-sulphur battery research clearly indicate that the successful performance of these cells is critically dependent upon the design of the sulphur electrode [1–4]. A number of models have been proposed to explain how this electrode operates and how it influences cycling behaviour [5–8]. The approach in these studies generally involves the determination of the electrochemical reaction rate distribution under various conditions. In the present communication a different description of the sulphur electrode is considered. A simple model is developed for directly calculating the resistance of the sulphur electrode as a function of charge. This derivation differs from previous work which treated a single polysulphide composition within the one phase region. From the model one may assess the contribution of the sulphur electrode to the total cell resistance during cell discharge and charge. This, in turn, leads to certain implications concerning cell behaviour.

2. Formulation of the model

2.1. *Electrical network*

The electrical network for simulating the cycling behaviour of the sulphur electrode is shown in Fig. 1. Networks of this or a similar type were previously used in characterizing porous battery electrodes [9, 10]. The sulphur electrode is divided into a total of n small segments. The electronic current flowing through the resistor R_m of the carbon fibre matrix of segment m is designated by I_m and the respective ionic current passing through the resistor P_m of the melt is represented by J_m. The electrochemical reaction occurring in segment m is described by the polarization resistor, Z_m. In general, Z_m may be more complex than simply a linear function of the polarization current $(I_m - I_{m-1})$ flowing through Z_m. The current I_0 leaving the cell at the container wall is electronic. R_0 represents the contact resistance between carbon fibres and the wall but it may also include an electronic resistance arising from a thin corrosion layer on the wall. The current entering the cell through the resistance R_β of the solid electrolyte (beta or beta″ alumina) is ionic.

The network formulation requires that one solves a system of $2n$ linear equations in order to obtain the currents I_m and J_m as a function of

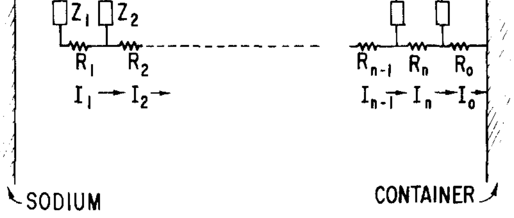

Fig. 1. Electrical network for the simulation of the sulphur electrode.

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the electronic, ionic and polarization resistances for each of the n segments. In the present work, however, this approach was simplified because the polarization resistance, Z_m, was estimated to be at least one order of magnitude less than R_m and P_m. This result was supported by a.c. measurements on laboratory cells. The methods used to arrive at the approximation are detailed below.

2.2. *Parallel resistance approximation*

The applicability of the approximation is indicated by both calculated and experimental results. The former involves computing Z_m and comparing it with corresponding R_m and P_m values. From this approach rather small polarization resistances are obtained. This result is supported by impedance measurements on Na/S cells during cycling. The ohmic behaviour is independent of frequency and state of the cell charge and, therefore, quite consistent with the contention that Z_m is substantially less than R_m or P_m. Thus, the simplification that R_m and P_m are essentially in parallel with each other is a reasonably good approximation.

Z_m is calculated by first obtaining the total polarization resistance of the sulphur electrode and then multiplying it by an appropriate factor for a given segment m. A system of segments is readily developed by letting the sulphur electrode in our laboratory be represented by a number of thin annular shells, 7 cm in length (Fig. 2). If $r_m - r_{m-1} = 0{\cdot}04$ cm then there are two segments of high resistance type VM0031 carbon mat and 14 of the low resistance VM0032 carbon mat [6]. To express a distance within the sulphur electrode one uses the following expressions.

$$\begin{aligned} r_m &= r_0 + x \\ x &= m_1(0{\cdot}04) + m_2(0{\cdot}04) \end{aligned} \tag{1}$$

where r_m is the outer radius of segment m, r_0 is the radius of the solid electrolyte, m_1 is the number of segments in the mat 31 region and m_2 is the corresponding number with mat 32. The volume of any segment, V_m, becomes

$$\begin{aligned} V_m &= 7\pi(r_m^2 - r_{m-1}^2) \\ &= 7\pi(r_m - r_{m-1})(r_m + r_{m-1}) \end{aligned} \tag{2}$$

The total polarization resistance is obtained by considering the weight of carbon fibre used in the laboratory cell (16 A h), its BET surface area and the polarization resistance in the linear region of the current–potential curve [11].

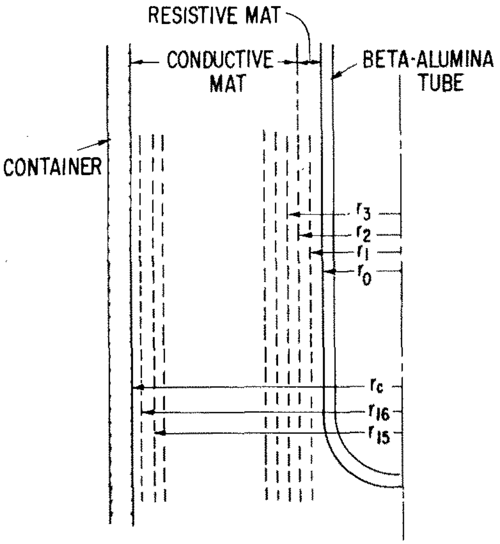

Fig. 2. Schematic diagram of the sulphur electrode compartment.

$$Z = \frac{0{\cdot}2\,\Omega\,\mathrm{cm}^2}{(3{\cdot}7\,\mathrm{g})\,(0{\cdot}4\,\mathrm{m}^2\,\mathrm{g}^{-1})\,(10^4)} = 1{\cdot}35 \times 10^{-5}\,\Omega. \tag{3}$$

It is significant to note that the surface area derived from BET measurements agrees extremely well with the area calculations based on the volume of carbon fibres present. This implies that the fibres do not possess many surface features which are smaller than the dimension of the diffusion layer and are not electrochemically active. In segment m

$$\begin{aligned} Z_m &= 1{\cdot}35 \times 10^{-5}\,\frac{V}{V_m} \\ &= \frac{1{\cdot}35 \times 10^{-5}\,V}{7\pi(r_m - r_{m-1})(r_m + r_{m-1})} = \frac{3{\cdot}70 \times 10^{-4}}{(r_m + r_{m-1})}\,\Omega. \end{aligned} \tag{4}$$

In order for R_m and P_m to even approach Z_m only the most conductive conditions should be considered. Thus, the comparison is made for mat 32 (i.e., $m > 3$) and for a polysulphide melt in the one phase region. This situation is fairly well approximated by assuming resistivities of 4 Ω cm for each [6].

$$R_m = P_m \doteq \frac{4}{14\pi}\ln\left(\frac{r_m}{r_{m-1}}\right) = \frac{4}{14\pi}\ln\left(1+\frac{0{\cdot}04}{r_{m-1}}\right).$$

Since $\ln(1+y) \sim y$ for small y

$$R_m = \frac{3{\cdot}64 \times 10^{-3}}{r_{m-1}}\,\Omega$$

the ratio Z_m/R_m becomes

$$\frac{Z_m}{R_m} = \frac{3{\cdot}70 \times 10^{-4}}{3{\cdot}64 \times 10^{-3}}\,\frac{r_{m-1}}{(r_m + r_{m-1})}$$

$$= 0{\cdot}10\left[\frac{1}{(r_m/r_{m-1}) + 1}\right].$$

By inspection it is clear that the term in square brackets is virtually equal to 1/2 regardless of m. In fact, the value ranges from 0·48 ($m = 1$) to 0·49 ($m = 16$). Thus, Z_m is only 5% the value of R_m or P_m.

These small calculated polarization resistances are supported by the results of a.c. impedance measurements on Na/S cells during cycling. In the first experiment a small a.c. signal was superimposed upon the d.c. current, and the a.c. impedance was determined by a phase sensitive detector between 10 and 10 000 Hz [12]. The impedance was ohmic within the error limits of the technique. A small capacitive component appeared to exist close to the end of both discharge and charge and this intriguing result led us to repeat the experiment using more sensitive apparatus. A network analyzer (Hewlett-Packard 3042 A) was subsequently employed and frequencies from 100 Hz to 10^5 Hz were scanned at various states of charge for nearly 100 cycles. In this two-probe measurement the d.c. and a.c. circuits were separated by a large ohmic resistor. Lead contributions were small and easily subtracted from experimental values. Once again the corrected impedance was ohmic and independent of frequency with cell impedance dependent upon the state of charge (see Section 4). The results, however, gave no evidence of any capacitive contribution. In addition to these measurements a four-probe technique involving a lock-in amplifier (PAR 5204) was developed to eliminate the lead contribution. The frequency range was 30–30 000 Hz. A complex plane impedance plot at the end of the charge cycle is shown in Fig. 3. The ohmic nature is clear.

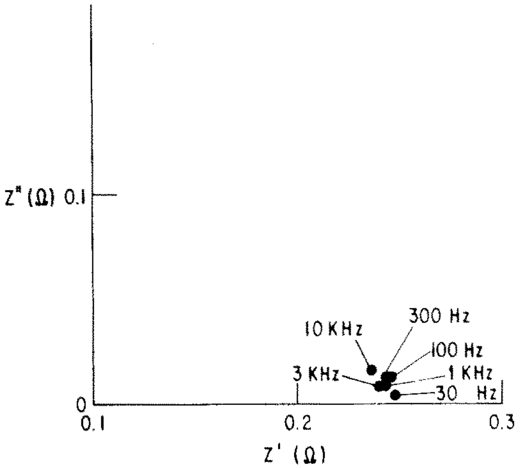

Fig. 3. Complex plane impedance plot for Na/S cell at the end of charge.

The a.c. impedance work supports the conclusions reached by the calculations: the absence of a measurable capacitive component during discharge or charge strongly indicates that polarization impedances are negligible. This is entirely consistent with the calculated maximum of 5% for the Z_m/R_m ratio. Thus, to a first approximation Z_m may be neglected and cell impedance is determined by the ohmic resistance of each of its components.

2.3. *Distribution of reactants and products*

The following assumptions are incorporated in the model in order to account for the influence of compositional changes and permit calculation of the sulphur electrode resistance.

(a) In the two-phase region Na_2S_5 initially forms at the beta-alumina/sulphur electrode interface and moves as a front through the sulphur electrode. The reverse process occurs during charge.

(b) In the one phase region the polysulphide composition is relatively constant over a large portion of the sulphur electrode.

(c) The high resistive carbon fibre layer remains nearly filled with Na_2S_5 when charging in the two-phase region.

(d) Polysulphide density is nearly constant in the one phase region, but the height of this molten phase is a function of composition.

Most of these conditions were either observed experimentally or were obtained analytically; (b) reflects both characteristics. The chemical analysis reported by Piercy and Sudworth [13] is supported by the results of the mathematical model presented by Jacquelin and Pompon [7] for the entire one-phase region. The presence of Na_2S_5 in the high resistance carbon fibre layer (c) was shown in a prior analysis [6]. Assumption (a) is likely because all sulphur must be converted to Na_2S_5 before other polysulphides are formed [16]. Experimental data concerning polysulphide density indicates relatively little change (< 3%) in the one phase region [14]. However, the volume increase which occurs as Na is added to the melt is sizeable and is considered in the calculations.

3. Calculation of sulphur electrode resistance

3.1. *The one-phase region*

Composition uniformity in the one-phase region has been experimentally observed [13], analytically observed [7] and utilized in previous models [5, 6]. The sulphur electrode resistance is approximated by considering the carbon mat and polysulphide resistances to be in parallel with each other for both the conductive mat and resistive mat segments (Fig. 2). The height of the polysulphide is a function of composition and must be considered in the equation.

$$V_p = \pi h_p(r_c^2 - r_0^2) = \frac{W_p}{D_p} \tag{7}$$

where V_p, h_p, W_p and D_p are the polysulphide volume, height, weight and density, respectively. The height may subsequently be expressed as a function of the state of charge, Q

$$h_p = \frac{W_S + QK_{Na}}{\pi D_p(r_c^2 - r_0^2)} \tag{8}$$

where W_S is the weight of sulphur and K_{Na} is the weight of Na (in grams) discharged per ampere-hour. The sulphur electrode resistance becomes

$$R_{sul} = \frac{\rho_1\rho_p}{2\pi(\rho_1 h_p + \rho_p h)}\ln\frac{r_2}{r_0} + \frac{\rho_2\rho_p}{2\pi(\rho_2 h_p + \rho_p h)}\ln\frac{r_c}{r_2} \tag{9}$$

where ρ_p designates the specific resistivity of the melt in the one-phase region, ρ_1 and ρ_2 are resistivities of mats 31 and 32 respectively and h is the mat height. In general the first term may be simplified because $\rho_1 \gg \rho_p$ [6]. This is shown in Equation 14.

3.2. *The two-phase region*

The lack of data in the two-phase region requires that certain approximations be used to describe melt resistivity over this range. Compositional changes in the electrode are accounted for by the motion of an Na_2S_5 front, and the residual melt at the end of charge is taken to be considerably more resistive than the carbon mat (the Na/S cell is not charged to 100% and there is always some Na_2S_5 remaining in the sulphur electrode at the conclusion of the charge cycle). Although these approximations present certain restrictions, they do enable the analysis to be extended to the two-phase region. Since the extent of two-phase operation essentially determines the degree of reactant utilization in a Na/S cell, it is important that one identifies the factors contributing to sulphur electrode resistance over this composition range.

The position of the Na_2S_5 front is obtained by assuming it is related to the state of charge of the cell.

$$\frac{V_x}{V} = \frac{Q_x}{Q_{1/2}} \tag{10}$$

where V_x is the volume fraction of the sulphur electrode filled with Na_2S_5 which occurs at state of charge Q_x, V is the total melt volume and $Q_{1/2}$ is the state of charge at the one phase–two phase boundary. Using x_f as the distance from the solid electrolyte to the front (Fig. 4) Equation 10 becomes

$$\frac{(x_f + r_0)^2 - r_0^2}{r_c^2 - r_0^2} = \frac{Q_x}{Q_{1/2}}$$

$$\text{or } (x_f + r_0)^2 = \frac{Q_x(r_c^2 - r_0^2)}{Q_{1/2}} + r_0^2 \tag{11}$$

$$x_f = \left[\frac{Q_x(r_c^2 - r_0^2)}{Q_{1/2}} + r_0^2\right]^{1/2} - r_0. \tag{12}$$

These equations imply that the melt height is constant throughout the electrode.

The distance, x_f, is evaluated for various states of charge as shown later. It is also used below in the quantity r_f, as the radius in the sulphur elec-

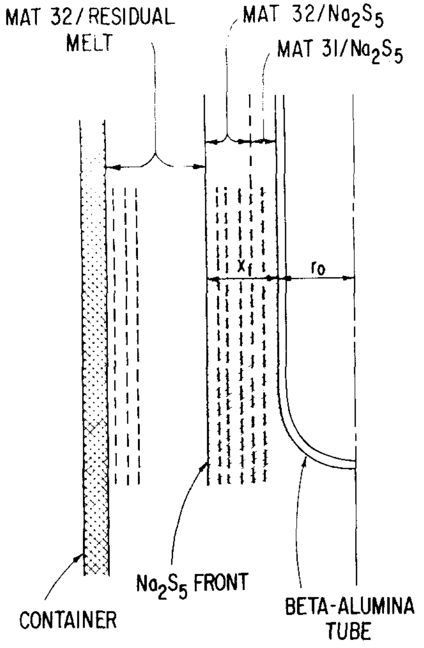

Fig. 4. Schematic of sulphur electrode with composition in the two-phase region.

trode where the Na_2S_5 front ends, $r_f = r_0 + x_f$. The sulphur electrode resistance in the two-phase region thus contains parallel mat/melt resistances for three segments which are in series; (a) high resistance mat/Na_2S_5, (b) low resistance mat/Na_2S_5 front and (c) low resistance mat/residual melt.

$$R_{sul} = \frac{\rho_1\rho_5}{2\pi(\rho_1 h_5 + \rho_5 h)}\ln\frac{r_2}{r_0} + \frac{\rho_2\rho_5}{2\pi(\rho_2 h_5 + \rho_5 h)}\ln\frac{r_f}{r_2} + \frac{\rho_3\rho_2}{2\pi(\rho_2 h_3 + \rho_3 h)}\ln\frac{r_c}{r_f} \tag{13}$$

where ρ_5 is the resistivity of Na_2S_5 and ρ_3 is the resistivity of the residual melt. The first and last terms may be simplified because $\rho_1 \gg \rho_5$ and $\rho_3 \gg \rho_2$. The latter condition is apparent because only 1·2 A h remains in the electrode at the conclusion of charge for the cycle of interest (see Section 4). This implies that the sulphur electrode consists of roughly 88% sulphur and only 12% Na_2S_5. Under these conditions the Na_2S_5 is discontinuously distributed in the sulphur and a large resistivity, approaching that of pure sulphur is expected [17].

$$R_{sul} = \frac{\rho_5}{2\pi h_5}\ln\frac{r_2}{r_0} + \frac{\rho_2\rho_5}{2\pi(\rho_2 h_5 + \rho_5 h)}\ln\frac{r_f}{r_2} + \frac{\rho_2}{2\pi h}\ln\frac{r_c}{r_f} \tag{14}$$

The total cell resistance is composed of several parts as evident in Fig. 1.

$$R_{cell} = R_\beta + R_{sul} + R_0 \tag{15}$$

Equations 14 or 9 are employed for R_{sul} depending upon whether two-phase or one-phase compositions are involved.

4. Calculations and discussion

All calculations were based on dimensions and resistivities actually used in our 16 A h laboratory cell: $r_0 = 0{\cdot}5$ cm, $r_c = 1{\cdot}16$ cm, $h = 7$ cm, $r_2 = 0{\cdot}58$ cm, $\rho_1 = 2500\ \Omega$ cm, $\rho_2 = 4\ \Omega$ cm, $W_s = 31$ g.

The measurements of ρ_1 and ρ_2 were reported previously [6]. Values for ρ_p, ρ_5 and D_p were obtained from Cleaver [14]. For the latter, 1·92 g cm^{-3} was chosen as an average density in the one-phase region. R_{sul} was computed for various states of charge and cell resistance was experimentally determined by a current interruption method [1] for the 64th cycle of cell 330 (Table 1).

The results shown in Table 1 yield interesting

Table 1. Sulphur electrode calculations; cell 330, cycle 64

Q (A h)	R_{sul} (Ω)	R_{cell} (Ω)	R_{cell}–R_{sul} (Ω)
Discharge, two-phase region			
1·8	0·077	0·180	0·103
3·6	0·069	0·167	0·098
5·4	0·064	0·157	0·093
7·2	0·060	0·150	0·090
Discharge, one-phase region			
8·8	0·057	0·151	0·094
11.0	0·046	0·150	0·104
Charge, one-phase region			
2·8	0·046	0·150	0·104
5·0	0·057	0·151	0·094
Charge, two-phase region			
6·0	0·059	0·154	0·095
7·8	0·063	0·165	0·102
9·6	0·068	0·177	0·109
11·4	0·074	0·187	0·113

information concerning the sulphur electrode and its role in Na/S cells. Sulphur electrode resistance is a function of the state of cell charge and accounts for the observed variation of cell resistance. In general the sulphur electrode contributes $1{\cdot}2\ \Omega\ \mathrm{cm}^2$ ($\pm 0{\cdot}3\ \Omega\ \mathrm{cm}^2$) which represents approximately 40% of the total cell resistance. The difference, $R_{\text{cell}} - R_{\text{sul}}$, is the sum of the beta-alumina and contact resistances and provides the remaining $2{\cdot}0\ \Omega\ \mathrm{cm}^2$. This quantity is relatively independent of charge and apparently unaffected by physical changes (e.g., volume) occurring within the melt. Partitioning this sum into the respective components is difficult because of ambiguities in assessing the precise value of R_β. Four-probe a.c. measurements in air at elevated temperatures consistently display a lower resistance than the one obtained by d.c. methods during the electrolytic filling of sodium from the molten nitrate. Nonetheless, there is little doubt that a finite contact resistance similar to the one proposed by Gibson [15] exists.

The ability of the model to calculate the sulphur electrode resistance at various states of charge is extremely useful. The extent of two-phase operation essentially determines cell capacity. Resistance in the two-phase region is characterized by the increasing involvement of the carbon mat and the electrode now contributes $1{\cdot}5\ \Omega\ \mathrm{cm}^2$ to the total cell resistance. If the cell resistance rises above this increment, other factors must be responsible. The observed time-dependent rise of cell resistance is frequently associated with loss in cell capacity because of high resistances in the two-phase region. The model intimates that such behaviour may be caused by either R_0, R_β, or both. Current studies in our laboratory are aimed at identifying these effects.

Acknowledgements

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