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A model for internal pressurization in cationic solid electrolytes

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The possibility of internal pressurization in a cationic solid electrolyte is examined by analysing a three-compartment cell consisting of two solid electrolyte membranes with different ionic and electronic conductivities. The pressure generated in the central chamber is related to the ionic and electronic conductivities of the membranes, the thicknesses of the membranes as well as the current density. By identifying the appropriate equivalent circuit for the three-compartment cell, the transient problem of pressurization is also solved. Finally, the probability of degradation of sodium-β''-alumina used in Na–S cells is assessed using published values of electronic conductivity. The calculations indicate that the pressure generated can be large if the electronic conductivity of sodium-β''-alumina in contact with molten sodium is greater than 10^{-3} (ohm m)$^{-1}$. Published work, however, indicates that the electronic conductivity at 350° C is $\sim 8 \times 10^{-5}$ (ohm m)$^{-1}$. Therefore, degradation due to internal pressurization is unlikely. However, on the other hand, it is conceivable that certain impurities or stabilizing elements may impart higher electronic conductivities. Consequently, the chemical composition of sodium-β''-alumina may be an important factor in relation to long-term operation.

1. Introduction

Recently, DeJonghe [1] has proposed that internal precipitation and subsequent pressurization of a metal can occur in cationic conductors provided a gradient in transport properties exists in the solid electrolyte. DeJonghe [1] has further proposed that pressures in excess of the failure strength of the electrolyte may be generated with modest levels of electronic conductivity (with spatial gradient). If this indeed is true, long-term reliability of electrochemical systems such as the sodium–sulphur battery may depend upon the gradient in electronic conductivity which can develop over a prolonged period of time. For example, in the sodium–sulphur battery, possible interaction of sodium-β''-alumina or sodium-β-alumina, the electrolyte, with molten sodium may lead to an increase in electronic conductivity in the part of the solid electrolyte in contact with sodium. This could establish a gradient in electronic conductivity requisite for pore pressurization.

From the point of view of degradation, however several important questions must be addressed. Firstly, a mechanism by which an initially empty pore may be filled must be identified. It is easy to demonstrate that while a metal-filled pore may pressurize owing to a gradient in electronic conductivity, an empty pore cannot be filled regardless of the existence of gradient in electronic conductivity. A finite solubility of the metal in the solid electrolyte may provide the requisite mechanism for pore filling if the solubility increases with increase in temperature. Secondly, the time required for pressure to reach some prescribed value must be estimated to determine if pressure of sufficient magnitude to cause degradation can be generated. Finally, fracture mechanical calculations of reasonable accuracy must be made to assess the role of pressurized pores on degradation.

The purpose of this paper is first to present a one-dimensional calculation of pore pressurization, similar to the one given by DeJonghe [1]. The approach given here will directly lead to the pressure generated in terms of the various

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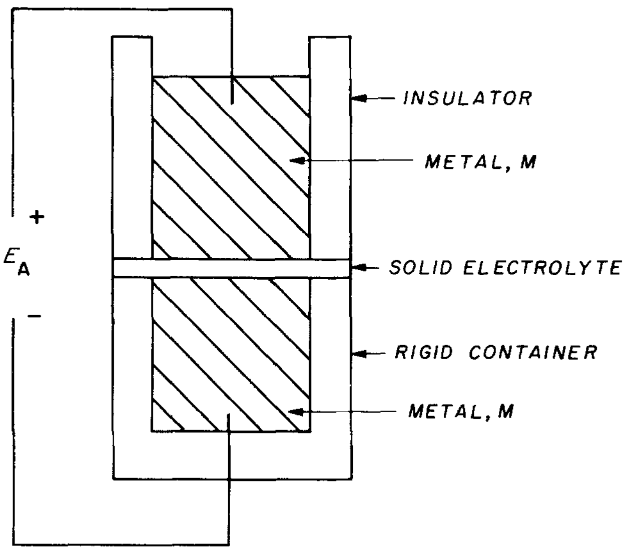

Figure 1 A schematic drawing of an electrolyte pressure cell.

parameters. Furthermore, by identifying the appropriate equivalent circuit for the process, time required to pressurize the pore will be determined. Finally, the failure of β''-alumina will be examined as a consequence of internal pressurization.

2. Theory

Although the analysis presented below is applicable to any cationic conductor, calculations will be presented for sodium-β''-alumina owing to its application in the sodium–sulphur battery. First we will consider the pressurization of a metal in an electrochemical cell with a cationic solid electrolyte and the corresponding equivalent circuit. Subsequently, we will examine a three-compartment cell employing two solid electrolyte membranes having different ionic and electronic conductivities and determine the pressure generated in the central chamber as well as the time required for pressurization.

2.1. Electrochemical cell with sealed rigid container as one of the compartments

Consider a cell of the type shown in Fig. 1. A solid electrolyte membrane, which is predominantly a cationic conductor (with M^{z+} as the mobile species, z being the valence) with low electronic conductivity is sealed to a rigid container filled with metal M. The upper chamber is also filled with metal M. Initially, the pressure in both of the chambers is the same, zero. An external voltage, E_A, is applied such that the upper chamber is connected to a positive terminal. The electrochemical potential of M^{z+} in the upper chamber is given by

$$\eta^{U}_{M^{z+}} = \mu^{0}_{M^{z+}} + zFE_A, \qquad (1)$$

while that of M^{z+} in the lower chamber is given by

$$\eta^{L}_{M^{z+}} = \mu^{0}_{M^{z+}}, \qquad (2)$$

in which $\mu^{0}_{M^{z+}}$ is the chemical potential of M^{z+} in the standard state, $\eta_{M^{z+}}$ is the electrochemical potential of M^{z+} and F is the Faraday constant. Thus, initially, a flux of M^{z+} is established from the upper chamber into the lower chamber. The electronic flux is predominantly in the outer circuit although a very low level electronic flux will occur through the electrolyte on account of its electronic conductivity. As more and more M enters the lower chamber, the chamber becomes pressurized. After some time if the pressure in the lower chamber is $P(t)$, then the electrochemical potential of M^{z+} in the lower chamber will be given by

$$\eta^{L}_{M^{z+}} = \mu^{0}_{M^{z+}} + V^{m}_{M^{z+}}P(t) \qquad (3)$$

where $V^{m}_{M^{z+}}$ is the partial molar volume of M^{z+} in M. As the $\eta^{L}_{M^{z+}}$ has now increased, the rate of flux of M^{z+} will have decreased. After a long time (mathematically infinite), the electrochemical potential of M^{z+} in both the upper and the lower chambers will be equal and the flux of ions will stop. The electrochemical potential of electrons in the upper chamber is given by

$$\eta^{U}_{e} = \mu^{0}_{e} - FE_A \qquad (4)$$

(where μ^{0}_{e} is the chemical potential of electrons, Fermi level and F is the Faraday constant) while

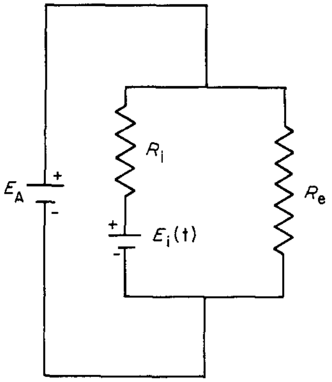

Figure 2 The equivalent circuit for the cell shown in Fig. 1. R_i and R_e are the ionic and the electronic resistances of the solid electrolyte membrane respectively. E_A is the applied d.c. voltage and $E_i(t)$ is the time-dependent internal emf generated which opposes the ionic flux.

that in the lower chamber at all times will be given by

$$\eta_e^L = \mu_e^0. \tag{5}$$

Since the partial molar volume of electrons is negligible, the effect of pressure on the electrochemical potential of electrons is negligible. Therefore, low-level electronic flux will continue through the circuit. The appropriate equivalent circuit for the cell is shown in Fig. 2. R_i and R_e denote the ionic and the electronic resistances, respectively, with $R_i \ll R_e$. $E_{i(t)}$ denotes the internal emf source which tends to oppose only the ionic flux. From Equations 1 and 3 it is seen that in steady state when the ionic flux is completely stopped,

$$\eta^U_{M^{z+}} = \eta^L_{M^{z+}}, \tag{6}$$

and therefore

$$E_A = \frac{V^m_{M^{z+}}P(\infty)}{F}, \tag{7}$$

where $P(\infty)$ is the steady state pressure. With reference to the equivalent circuit, then in the steady state

$$E_i(\infty) = E_A = \frac{V^m_{M^{z+}}P(\infty)}{zF}. \tag{8}$$

At any time t,

$$E_i(t) = \frac{V^m_{M^{z+}}P(t)}{zF}. \tag{9}$$

With the aid of the equivalent circuit we can now estimate the time required to pressurize the lower chamber. The instantaneous ionic current at any time, t, is given by

$$I_i(t) = \frac{E_A - E_i(t)}{R_i}. \tag{10}$$

The volume of M that arrived in time, t, in the lower chamber is given by

$$\Delta V(t) = \frac{V^m_M}{zF}\int_0^t I_i(t)\mathrm{d}t, \tag{11}$$

where V^m_M is molar volume of M. For simplicity, let us now assume that the materials of construction of the cell are rigid. Then, if the compressibility of M is given by κ and the volume of the lower chamber as V_L, then

$$P(t) = \frac{\Delta V(t)}{\kappa V_L}. \tag{12}$$

Therefore,

$$P(t) = \frac{V^m_M E_A t}{\kappa z F R_i V_L} - \frac{V^m_M}{\kappa z F R_i V_L}\int_0^t E_i(t)\mathrm{d}t. \tag{13}$$

Now since $P(t)$ is related to $E_i(t)$ via Equation 9, we can show by substitution in Equation 13 that

$$E_i(t) = \frac{(V^m_M)^2 E_A t}{\kappa z^2 F^2 R_i V_L} - \frac{(V^m_M)^2}{\kappa z^2 F^2 R_i V_L}\int_0^t E_i(t)\mathrm{d}t, \tag{14}$$

or in differential form

$$\frac{\mathrm{d}E_i(t)}{\mathrm{d}t} = \frac{(V^m_M)^2}{\kappa z^2 F^2 R_i V_L}[E_A - E_i(t)]. \tag{15}$$

Thus, integrating and substituting initial condition

$$E_i(t) = E_A\left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \tag{16}$$

or expressed in terms of pressure:

$$P(t) = P(\infty)\left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \tag{17}$$

in which the relaxation time, τ, is given by

$$\tau = \frac{\kappa z^2 F^2 R_i V_L}{(V^m_M)^2}. \tag{18}$$

The above analysis shows that the relaxation time for pressurization is proportional to the compressibility of M and the volume, V_L, of the lower chamber. The purpose of the above analysis is to demonstrate the use of the equivalent circuit approach in estimating the time required to pressurize the cell. This approach will be used for analysing the three-compartment cell described in the following section.

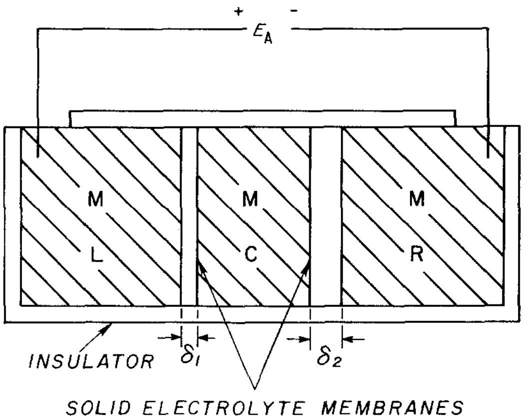

Figure 3 A three-compartment cell with two solid electrolyte membranes having different ionic and electronic conductivities. Upon application of an external d.c. voltage, E_A, the flux of metal ions is established from the left chamber (L) through the middle chamber (M) to the right chamber (R).

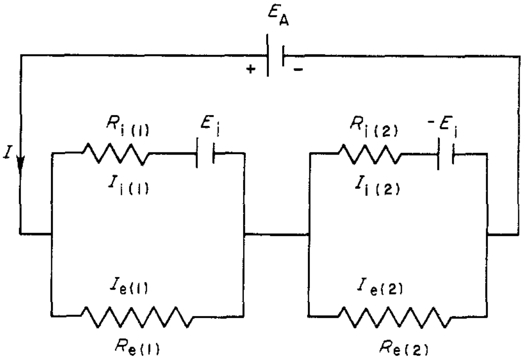

Figure 4 The equivalent circuit for the three-compartment cell shown in Fig. 3. $R_{i(1)}$, $R_{i(2)}$, $R_{e(1)}$, and $R_{e(2)}$ are the ionic and the electronic resistances of the two solid electrolyte membranes, respectively. E_A is the applied voltage while E_i is the internally generated emf which in one circuit element opposes the ionic current but in the other circuit element augments the ionic current.

2.2. Pressurization in a three-compartment cell

The three-compartment cell shown in Fig. 3 is a one-dimensional approximation to the pore pressurization problem. The problem examined by DeJonghe [1] was also one dimensional. With reference to Fig. 3, the left (L) and the right (R) chambers are unconstrained infinite reservoirs containing metal M. The central chamber (C) of finite size filled with M is constrained (i.e. the separating membranes 1 and 2 are sealed to the insulating tube). The separating membranes are made of solid electrolytes which are predominantly cationic conductors of M^{z+} with low level electronic conductivities. Furthermore, the absolute values of the ionic and the electronic conductivities of the two membranes are different. We wish to determine the pressure generated in the steady state upon application of an external voltage, E_A, as shown in Fig. 3. In the following we first present an analysis using Wagner's approach. In the subsequent subsection, equivalent circuit approach will be presented.

Let the ionic and the electronic conductivities of membranes 1 and 2 be $\sigma_{i(1)}$, $\sigma_{i(2)}$ and $\sigma_{e(1)}$, $\sigma_{e(2)}$, respectively. The thicknesses of the two membranes are δ_1 and δ_2, respectively. The electric potentials in L, C and R are Φ_L, Φ_C and Φ_R, respectively, with $\Phi_L - \Phi_R = E_A$.

In steady state, the pressure generated in the central chamber is $P(\infty)$. As the pressure does not change with time, it implies that the ionic fluxes in and out of the central chamber are the same. Furthermore, the potential in the central chamber is also invariant with time. Thus, the electronic fluxes in and out of the central chamber are also same. Therefore, equating the electron flux in and out of the central chamber, we get

$$\frac{\sigma_{e(1)}(\Phi_C - \Phi_L)}{\delta_1} = \frac{\sigma_{e(2)}(\Phi_R - \Phi_C)}{\delta_2}. \quad (19)$$

Therefore,

$$\Phi_C = \frac{[\sigma_{e(1)}\delta_2\Phi_L + \sigma_{e(2)}\delta_1\Phi_R]}{[\sigma_{e(1)}\delta_2 + \sigma_{e(2)}\delta_1]}. \quad (20)$$

The ionic fluxes are also equal. Therefore,

$$\sigma_{i(1)}\left[\frac{(\Phi_L - \Phi_C)}{\delta_1} - \frac{V^m_{M^{z+}}P(\infty)}{zF\delta_1}\right] = \sigma_{i(2)}\left[\frac{(\Phi_C - \Phi_R)}{\delta_2} + \frac{V^m_{M^{z+}}P(\infty)}{zF\delta_2}\right] \quad (21)$$

Rearranging terms,

$$P(\infty) = \{\delta_1\delta_2 zF[\sigma_{i(1)}\sigma_{e(2)} - \sigma_{i(2)}\sigma_{e(1)}]E_A\}/\{V^m_{M^{z+}}[\sigma_{e(1)}\delta_2 + \sigma_{e(2)}\delta_1][\sigma_{i(1)}\delta_2 + \sigma_{i(2)}\delta_1]\}, \quad (22)$$

in which we have replaced $\Phi_L - \Phi_R = E_A$.

2.3. Equivalent circuit approach for the three-compartment cell*

The equivalent circuit for the three compartment cell shown in Fig. 3, is given in Fig. 4. In steady

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*Wagner's approach and the equivalent circuit approach are essentially the same. The equivalent circuit approach is particularly useful in analysing the transient pressurization problem.

state, the ionic and the electronic currents in both segments are the same, i.e.

and
$$\left.\begin{aligned} I_{i(1)} &= I_{i(2)} = I_i \\ I_{e(1)} &= I_{e(2)} = I_e \end{aligned}\right\}. \tag{23}$$

The emf, E_i, generated by the pressure in the central chamber is of opposite polarities in the two segments of the circuit since the pressure (>0) in the central chamber enhances the ionic flux from the central chamber to the right chamber while it suppresses the ionic flux from the left chamber into the central chamber. In steady state, the pressure in the central chamber is $P(\infty)$ and the corresponding emf is $E_i(\infty)$. In steady state, Equations 23 are valid. Therefore,

$$I_e[R_{e(1)} + R_{e(2)}] = E_A$$

$$[I_iR_{i(1)} + E_{i(\infty)} + I_iR_{i(2)} - E_{i(\infty)}] = E_A \tag{24}$$

i.e.

$$I_i(R_{i(1)} + R_{i(2)}) = E_A.$$

Also,

$$\begin{aligned} I_eR_{e(1)} &= I_iR_{i(1)} + E_{i(\infty)} \\ I_eR_{e(2)} &= I_iR_{i(2)} - E_{i(\infty)}. \end{aligned} \tag{25}$$

Therefore,

$$E_{i(\infty)} = \frac{[R_{i(2)}R_{e(1)} - R_{i(1)}R_{e(2)}]E_A}{[R_{i(1)} + R_{i(2)}]\,[R_{e(1)} + R_{e(2)}]}. \tag{26}$$

Noting that

$$R_{i(1)} = \frac{\delta_1}{A\sigma_{i(1)}}, \quad R_{i(2)} = \frac{\delta_2}{A\sigma_{i(2)}}$$

$$R_{e(1)} = \frac{\delta_1}{A\sigma_{e(1)}}, \quad R_{e(2)} = \frac{\delta_2}{A\sigma_{e(2)}},$$

where A is the cross-sectional area, it is easily shown that

$$E_{i(\infty)} = \{\delta_1\delta_2[\sigma_{i(1)}\sigma_{e(2)} - \sigma_{i(2)}\sigma_{e(1)}]E_A\}/ \{[\sigma_{e(1)}\delta_2 + \sigma_{e(2)}\delta_1]\,[\sigma_{i(1)}\delta_2 + \sigma_{i(2)}\delta_1]\}, \tag{27}$$

and

$$P(\infty) = \{\delta_1\delta_2 zF[\sigma_{i(1)}\sigma_{e(2)} - \sigma_{i(2)}\sigma_{e(1)}]E_A\}/ \{V^m_{M^{z+}}[\sigma_{e(1)}\delta_2 + \sigma_{e(2)}\delta_1]\,[\sigma_{i(1)}\delta_2 + \sigma_{i(2)}\delta_1]\}, \tag{28}$$

which is the same as Equation 22 thereby confirming the equivalent circuit. With the aid of Equation 22 or 28, it is instructive to estimate the pressure that can be generated. For the sake of illustration, let us assume the membranes to be made of sodium-β''-alumina. Let $\delta_1 = \delta_2 = 10^{-3}$ m,

$$\sigma_{i(1)} = \sigma_{i(2)} = 25\ (\text{ohm m})^{-1}$$

$$\sigma_{e(1)} = 10^{-5}\ (\text{ohm m})^{-1},\ \sigma_{e(2)} = 10^{-3}\ (\text{ohm m})^{-1}$$

and let the applied voltage, E_A, be equal to 0.4 V (which corresponds to the current density of $5000\ \text{A m}^{-2}$ or $500\ \text{mA cm}^{-2}$). The steady state pressure generated electrolytically is found to be 814 MPa or 118 100 psi. For the specific case of $\sigma_{i(1)} = \sigma_{i(2)}$ and $\delta_1 = \delta_2$, Equation 28 reduces to

$$P(\infty) = \frac{zF[\sigma_{e(2)} - \sigma_{e(1)}]E_A}{V^m_{M^{z+}}[\sigma_{e(2)} + \sigma_{e(1)}]}, \tag{29}$$

indicating that when $\sigma_i \gg \sigma_{e(2)} \gg \sigma_{e(1)}$,

$$P(\infty) \approx \frac{zF E_A}{V^m_{M^{z+}}}, \tag{30}$$

i.e. the maximum pressure generated is independent of the actual magnitudes of $\sigma_{e(1)}$ and $\sigma_{e(2)}$, as long as $\sigma_{e(2)} \gg \sigma_{e(1)}$ (for $\delta_1 = \delta_2$). However, the time required to pressurize may depend upon the absolute values of the conductivities. The equivalent circuit approach can be used to estimate the relaxation time.

2.4. Estimation of relaxation time for the three-compartment cell

With reference to the equivalent circuit shown in Fig. 4, prior to reaching the steady state, at any time t, $I^{(t)}_{i(1)} \neq I^{(t)}_{i(2)}$ and $I^{(t)}_{e(1)} \neq I^{(t)}_{e(2)}$. That is, the ionic and the electronic currents (which are time-dependent) in and out of the central chamber are not equal. However, from Kirchoff's laws, we know that

$$\left.\begin{aligned} I^{(t)}_{i(1)}R_{i(1)} + E_i(t) &= I^{(t)}_{e(1)}R_{e(1)} \\ I^{(t)}_{i(2)}R_{i(2)} - E_i(t) &= I^{(t)}_{e(2)}R_{e(2)} \\ I^{(t)}_{e(1)}R_{e(1)} + I^{(t)}_{e(2)}R_{e(2)} &= E_A \\ \text{and} \qquad & \\ I^{(t)}_{i(1)}R_{i(1)} + I^{(t)}_{i(2)}R_{i(2)} &= E_A. \end{aligned}\right\} \tag{31}$$

The volume of M^{z+} entering the central chamber in time t is given by

$$\Delta V(t) = \frac{V^m_{M^{z+}}}{zF}\left[\int_0^t I^{(t)}_{i(1)}\mathrm{d}t - \int_0^t I^{(t)}_{i(2)}\mathrm{d}t\right]. \tag{32}$$

Assuming the components of the cell to be rigid, and assuming the initial pressure to be zero, the pressure in the central chamber after time t is given by

$$P(t) = \frac{\Delta V(t)}{\kappa V}, \tag{33}$$

with κ as the compressibility of M, and V being the volume of the central chamber. In terms of $E_i(t)$, the pressure is given by

$$P(t) = \frac{zFE_i(t)}{V^{m}_{M^{z+}}}. \tag{34}$$

From Equations 32, 33 and 34,

$$E_i(t) = \frac{(V^{m}_{M^{z+}})^2}{z^2F^2\kappa V}\int_0^t (I^{(t)}_{i(1)} - I^{(t)}_{i(2)})\,dt. \tag{35}$$

Finally, it is to be noted that at all times Kirchoff's rules are obeyed. Thus,

$$I^{(t)}_{i(1)} + I^{(t)}_{e(1)} = I^{(t)}_{i(2)} + I^{(t)}_{e(2)}. \tag{36}$$

Using Equations 31 to 36, it can be shown, by writing Equation 35 in a differential form, that

$$\frac{dE_i(t)}{\left[\dfrac{E_A[R_{i(2)}R_{e(1)} - R_{i(1)}R_{e(2)}]}{[R_{e(1)} + R_{e(2)}][R_{i(1)} + R_{i(2)}]} - E_i(t)\right]} = \frac{dt}{\tau} \tag{37}$$

where

$$\tau = (\kappa Vz^2F^2\{[R_{e(2)} - R_{i(2)}]R_{i(1)}R_{e(1)} + [R_{e(1)} - R_{i(1)}]R_{i(2)}R_{e(2)}]\}/\{(V^{m}_{M^{z+}})^2 \times [R_{e(1)} + R_{e(2)}][R_{i(1)} + R_{i(2)}]\}. \tag{38}$$

In terms of conductivities and thicknesses, the relaxation time is given by

$$\tau = \frac{\kappa Vz^2F^2\delta_1\delta_2}{A(V^{m}_{M^{z+}})^2} \times \left\{\frac{[\sigma_{i(2)} - \sigma_{e(2)}]\delta_1 + [\sigma_{i(1)} - \sigma_{e(1)}]\delta_2}{[\sigma_{i(2)}\delta_1 + \sigma_{i(1)}\delta_2][\sigma_{e(2)}\delta_1 + \sigma_{e(1)}\delta_2]}\right\} \tag{39}$$

in which A is the cross-sectional area in the direction of the current.

Integration of Equation 37 gives

$$E_i(t) = \frac{E_A[R_{i(2)}R_{e(1)} - R_{i(1)}R_{e(2)}]}{[R_{e(1)} + R_{e(2)}][R_{i(1)} + R_{i(2)}]} \times \left[1 - \exp\left(-\frac{t}{\tau}\right)\right], \tag{40}$$

so that in steady state

$$E_i(\infty) = \frac{E_A[R_{i(2)}R_{e(1)} - R_{i(1)}R_{e(2)}]}{[R_{e(1)} + R_{e(2)}][R_{i(1)} + R_{i(2)}]} \tag{41}$$

or in terms of conductivities and thicknesses,

$$E_i(\infty) = \frac{\delta_1\delta_2[\sigma_{i(1)}\sigma_{e(2)} - \sigma_{i(2)}\sigma_{e(1)}]E_A}{[\sigma_{e(2)}\delta_1 + \sigma_{e(1)}\delta_2][\sigma_{i(2)}\delta_1 + \sigma_{i(1)}\delta_2]} \tag{42}$$

which is identical with Equation 27 as required. If we choose $\sigma_{i(1)} = \sigma_{i(2)} \gg \sigma_{e(2)} \gg \sigma_{e(1)}$, and choose $\delta_1 = \delta_2$ the relaxation time is given by

$$\tau = \frac{\kappa Vz^2F^2\delta}{A(V^{m}_{M^{z+}})^2\sigma_{e(2)}}. \tag{43}$$

Therefore, although the maximum pressure generated does not depend upon the absolute conductivites as long as $\sigma_{i(1)} \simeq \sigma_{i(2)} \gg \sigma_{e(2)} \gg \sigma_{e(1)}$ (Equation 30), the relaxation time for pressurization does depend upon the electronic conductivity. Specifically, the higher the value of $\sigma_{e(2)}$, the shorter will be the relaxation time. Choosing $V/A = 4/3 \times 10^{-5}$ m, $\delta_1 = \delta_2 = 7.5 \times 10^{-5}$ m, for the case of a cell made with sodium-β''-alumina.

$\tau \approx 7590$ sec if $\sigma_{e(2)} = 10^{-3}$ (ohm m)$^{-1}$, while $\tau \approx 75900$ sec if $\sigma_{e(2)} = 10^{-4}$ (ohm m)$^{-1}$. The analysis presented above shows that extremely large magnitudes of pressure can be created with modest levels of electronic conductivity under certain conditions.

3. Numerical results and discussion

For the three-compartment cell consisting of two cationic solid electrolytes, it has been shown that high pressures can be generated in the central chamber provided the two membranes exhibit different values of ionic and electronic conductivities. This result is in agreement with that of DeJonghe [1] who examined the effect of gradient in transport number of internal pressurization. In the foregoing analysis, we have examined the discrete case, instead of a spatial variation in electronic conductivity. However, using a discrete case (three-compartment cell), it has been possible to calculate pressure generated explicitly in terms of various parameters. More importantly, however, the problem of transient pressurization has been modelled by identifying an appropriate equivalent circuit for the three-compartment cell. From the point of view of degradation, however, several questions need to be answered. Perhaps, the most important is the three-dimensional problem, i.e. pressurization of a spherical pore. It would appear that the pressure generated in a spherical pore will be considerably smaller since the flux of ions away from the pore can be established in all directions unlike the unidirectional problem. This problem will be addressed in a separate communication. Using the three-compartment cell and its transient solution, however, it is possible to assess semi-quantitatively the possibility of electrolyte degradation due to internal pressurization. In this case, then, the central chamber of the three-compartment cell represents a metal-filled pore situated within a solid electrolyte at the boundary across which the transport properties of the solid electrolyte discontinuously change. In the following analysis, the probability of degradation due to internal pressurization for sodium-β''-alumina in a sodium–sulphur battery is assessed.

The sodium–sulphur battery, which uses sodium-β''-alumina as the solid electrolyte, is generally operated at a temperature between 300 and 350° C. Typical wall thickness of tubular geometry of the sodium-β''-alumina electrolyte membrane is of the order of 2×10^{-3} m. The ionic conductivity at 300° C is of the order of 25 $(\text{ohm m})^{-1}$. Let us assume that the electronic conductivity of pristine β''-alumina at 300° C is of the order of 10^{-5} $(\text{ohm m})^{-1}$. It is known that over a period of time, the part of β''-alumina in contact with liquid sodium becomes dark in colour. It has been suggested [2] that electronic conductivity is higher than that of the pristine β''-alumina, in the darkened region. Consider that a sodium-filled pore exists at the boundary between darkened and pristine (in contact with sulphur) regions. It is assumed here that the boundary is sharp. Furthermore, it has been assumed that the pore is somehow filled to begin with. This point will be discussed later. Let us examine the charging step of the battery. During charging, sodium-ions transport through β''-alumina from the "S" (sodium–polysulphide) chamber to the sodium reservoir. The thickness of the pristine region of β''-alumina will be denoted by δ_1 while that of the darkened region will be denoted by δ_2. The total thickness, δ, is given by $\delta = \delta_1 + \delta_2 = 2 \times 10^{-3}$ m. The electronic conductivity of the pristine region is assumed to be $\sigma_{e(1)} = 10^{-5}$ $(\text{ohm m})^{-1}$. The electronic conductivity of the darkened region, $\sigma_{e(2)}$, is assumed to be greater. Consider that the charging current density imposed is of the order of 5×10^3 A m^{-2} (500 mA cm^{-2}). This corresponds to a potential drop of 0.4 V across β''-alumina. (This means that the externally applied voltage exceeds the open circuit potential which opposes the applied voltage, by 0.4 V, neglecting polarization at the β''-alumina/sulphur electrode interface.) Using Equation 22, steady state pressure in the pore can be calculated as a function of the thickness of the region with enhanced electronic conductivity, i.e. as a function of δ_2. In Fig. 5, steady state pressure has been plotted as a function of δ_2 for three assumed values of $\sigma_{e(2)}$; namely, $\sigma_{e(2)} = 10^{-4}$ $(\text{ohm m})^{-1}$, $\sigma_{e(2)} = 10^{-3}$ $(\text{ohm m})^{-1}$ and $\sigma_{e(2)} = 10^{-2}$ $(\text{ohm m})^{-1}$. It is observed that for $\sigma_{e(2)} = 10^{-2}$ $(\text{ohm m})^{-1}$, the maximum steady state pressure generated is on the order of 1400 MPa (2×10^5 psi). The pressure generated at $\delta_1 = \delta_2$ is nearly independent of σ_e as long as $\sigma_{e(2)} \gg \sigma_{e(1)}$ (Equation 29). Furthermore, maximum pressure shifts towards larger δ_2 with increasing $\sigma_{e(2)}$. This implies that if δ_2 is small, the pressure generated will also be small, in agreement with DeJonghe [1].

Equation 22 indicates that if the polarity is reversed, the pore will depressurize. This implies that during discharging, the pores will tend to depressurize and during charging the pores will tend to pressurize. Consider that pores are filled with sodium but under negligible pressure in the discharged state. When the battery is being charged, the pores will pressurize but may not achieve maximum attainable pressure depending upon the time of charging in relation to the relaxation time. Using Equation 39, an estimate the relaxation time, τ, can be made.

Let us assume that the solid electrolyte contains a sodium-filled pore of radius 10^{-5} m. Thus, we may choose V/A to be of the order of $(4\pi r^3/3)/\pi r^2 = 4r/3 = 1.33 \times 10^{-5}$ m. Using the isothermal compressibility of sodium at 300° C as $\kappa = 2.289 \times 10^{-10}$ m^2 N^{-1} [3], the relaxation time can be calculated for various values of $\sigma_{e(1)}$ and $\sigma_{e(2)}$ as a function of δ_2. The relaxation times for $\sigma_{e(1)} = 10^{-5}$ $(\text{ohm m})^{-1}$, $\sigma_{e(2)} = 10^{-4}$ $(\text{ohm m})^{-1}$, and $\sigma_{e(1)} = 10^{-5}$ $(\text{ohm m})^{-1}$, $\sigma_{e(2)} = 10^{-3}$ $(\text{ohm m})^{-1}$ are shown in Fig. 6. Note that the relaxation time also exhibits a maximum at some value of δ_2. The relaxation time for $\sigma_{e(1)} = 10^{-5}$ $(\text{ohm m})^{-1}$, $\sigma_{e(2)} = 10^{-2}$ $(\text{ohm m})^{-1}$ is not shown in the figure since it is too small to be indicated on the same scale. The question of interest is what is the pressure generated in a given charging time as a function of the volume

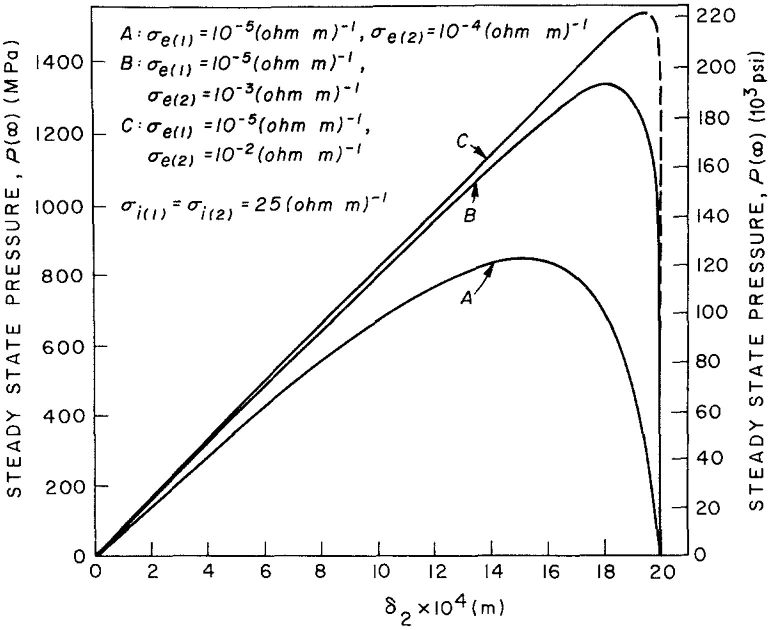

Figure 5 Steady state pressure generated in the central chamber as a function of δ_2 as well as a function of the electronic conductivity of the second membrane. The solid electrolytes are of sodium-β''-alumina and the metal is liquid sodium. The applied voltage $E_A = 0.4$ V and the total thickness of the solid electrolyte, $\delta = \delta_1 + \delta_2 = 2 \times 10^{-3}$ m.

of the pore as well as δ_2. By analogy with Equation 40, the transient pressure can be given by

$$P(t) = P(\infty)\left[1 - \exp\left(-\frac{t}{\tau}\right)\right]. \qquad (44)$$

At 5×10^3 A m^{-2} (500 mA cm^{-2}) as the charging current density, typical charging time is on the order of 1 h or 3600 sec. In Fig. 7, we have shown $P(t)$ with $t = 3600$ sec for two values of $\sigma_{e(2)}$; namely 10^{-3} (ohm m)$^{-1}$ and 10^{-2} (ohm m)$^{-1}$. The magnitude of $P(t)$ generated with $\sigma_{e(2)} = 10^{-4}$ (ohm m)$^{-1}$ is too small to be shown on the same scale and as such is not shown. For $\sigma_{e(2)} = 10^{-3}$ (ohm m)$^{-1}$, the transient pressure generated is more or less independent of δ_2 and is on the order of 50 MPa. This is in contrast with the steady state pressure which indicates that maximum pressure occurs for $\delta_2 \gg \delta_1$. For $\sigma_{e(2)} = 10^{-2}$ (ohm m)$^{-1}$, on the other hand, the transient pressure shown does increase with increasing δ_2. This is not surprising since for $\sigma_{e(2)} = 10^{-2}$ (ohm m)$^{-1}$, the relaxation time is much shorter.

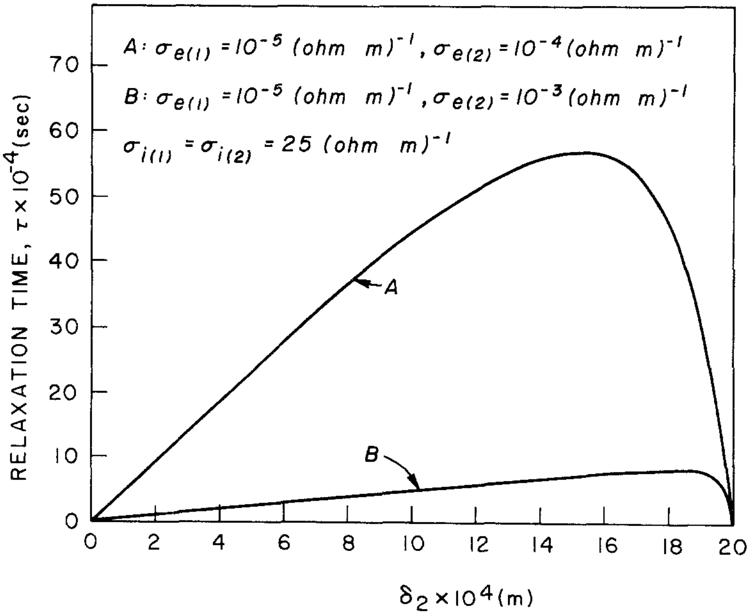

Figure 6 Relaxation time for the three compartment cell as a function of δ_2 for two values of $\sigma_{e(2)}$. Total electrolyte thickness, $\delta = \delta_1 + \delta_2 = 2 \times 10^{-3}$ m.

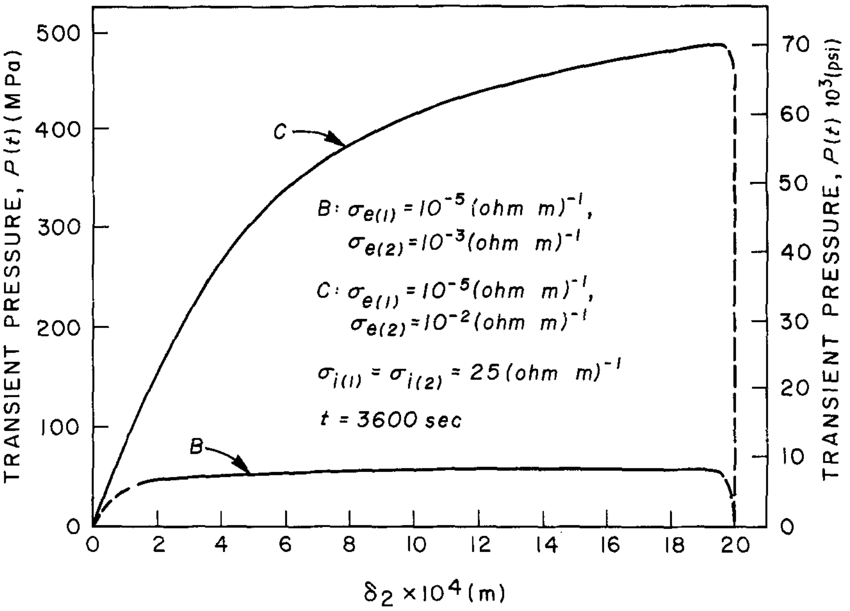

Figure 7 Transient pressure in the central chamber as a function of δ_2 for two values of $\sigma_{e(2)}$ in 1 h of electrolysis under an applied voltage of 0.4 V. Total electrolyte thickness, $\delta = \delta_1 + \delta_2 = 2 \times 10^{-3}$ m.

In sodium–sulphur batteries, typical charging current densities are of the order of 1000 A m^{-2} (100 mA cm^{-2}) instead of 5000 A m^{-2} assumed in the foregoing calculations. Since the objective is to charge the battery to a given level of charge, the smaller the current density, the longer will be the time. To achieve the same level of charge, charging current density × charging time = constant. One would expect, however, that the pressure generated in a pore for differing charging current densities for the same level of charge will be different. To illustrate this point, the transient pressure for same level of charge is plotted against δ_2 at three charging current densities; namely 5000, 3000 and 1000 A m^{-2} in Fig. 8. Clearly, the lower the charging current density, the lower is the pressure generated.

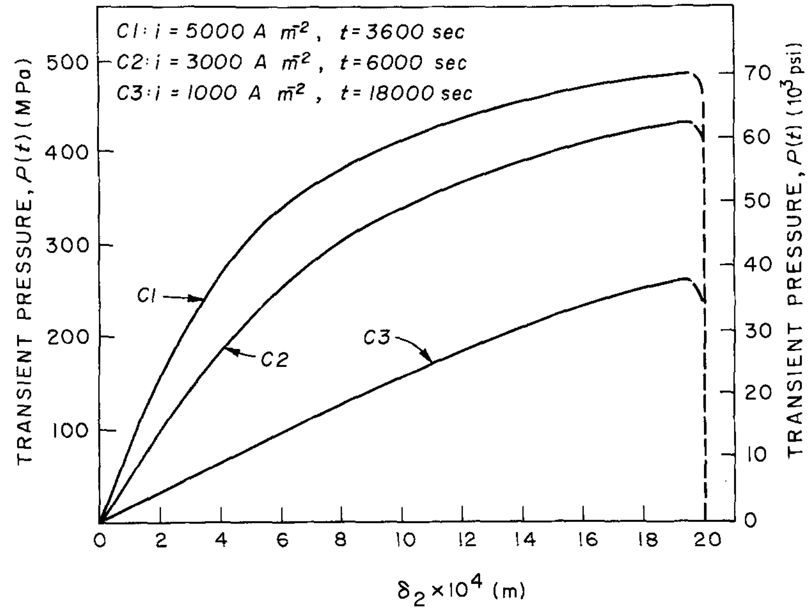

Figure 8 Transient pressure generated as a function of δ_2 for three charging current densities but for a fixed level of charge. Total electrolyte thickness, $\delta = \delta_1 + \delta_2 = 2 \times 10^{-3}$ m.

Finally, it is of interest to estimate pressure generated (transient) as a function of the pore size. Within the one-dimensional approximation, the steady state pressure is not a function of pore size but the transient pressure will depend upon the pore size as the relaxation time is a function of the pore size. Clearly, the smaller the pore size, the larger is the transient pressure with $P(\infty)$ being the upper limit.

During the charging state of the sodium–sulphur battery, generation of large internal pressures are possible, provided certain conditions are satisfied. The principal one is the existence of a significant increase of electronic conductivity over a substantial part of the thickness of the electrolyte. The analysis presented here explicitly permits the calculation of the pressure if the electronic and the ionic conductivities as well as other parameters are known. The analysis also shows that the pressure generated during the charging step will depend in a very sensitive manner on the electronic conductivity of β''-alumina. The application of the above analysis for assessing degradation can be made only if the information on electronic conductivity is accurately known. In what follows, the possibility of degradation by internal pressurization will be assessed and important factors in relation to electrolyte fabrication are outlined.

The factor of paramount importance in relation to internal pressurization is the existence of pores. A mere gradient in electronic conductivity will not necessarily lead to the precipitation of sodium. For example, consider that for a given set of conditions, the steady state pressure is given as 200 MPa. Let us imagine that in a dense specimen, sodium under pressure precipitates out. As soon as some sodium precipitates, the surrounding matrix of β''-alumina must elastically deform to accommodate the sodium droplet. Assuming that an atom of sodium is incompressible, the shape of the first droplet of sodium consisting of one atom will be spherical. The elastic stresses in the immediate vicinity will be of the order of shear modulus of β''-alumina (10^5 MPa). But the steady state pressure is only 200 MPa. Thus, the sodium precipitated would have a tendency to go back into solution. Therefore, for moderate applied voltage, sodium precipitation should not occur despite the presence of a gradient in electronic conductivity, if the β''-alumina is devoid of porosity. If there exists some porosity, internal pressurization can occur at moderate applied voltages. It appears that an empty pore cannot fill regardless of the gradient in electronic conductivity since the equipotential surfaces intersect the pores orthogonally. Therefore, the flux lines will be tangential to the pores and the ionic as well as electronic fluxes will bypass the empty pores. However, if sodium can dissolve in β''-alumina to some extent and if the solubility increases with increasing temperature, it would be possible to precipitate sodium in pores if β''-alumina that was heated to a high temperature in contact with sodium is subsequently cooled to a lower temperature. Such pores may be able to pressurize to a significant extent if the enhancement in electronic conductivity is significant. The level of pressure generated is a function of the time of charging. For example, if the magnitude of the electronic conductivity in the darkened region is less than 10^{-3} (ohm m)$^{-1}$, the value of pressure generated in a pore of 10^{-5} m radius in 1 h (with charging current density of 5000 A m^{-2} is only on the order of 50 MPa – probably not sufficient to cause significant damage. Also, as the typical charging current densities are generally even lower (~ 1000 A m^{-2}), the pressure created would be even lower. If the electronic conductivity is on the order of 10^{-2} (ohm m)$^{-1}$ or greater, however, it is conceivable that large pressures can be generated in sodium-filled pores under certain conditions. If it can be assumed that chemical composition in some manner would dictate the magnitude of electronic conductivity, then it implies that one must strive to achieve a composition such that the highest value of electronic conductivity generated is less than 10^{-4} to 10^{-3} (ohm m)$^{-1}$. For example, it is possible that stabilizing elements such as magnesium of lithium may impart different levels of electronic conductivities. Thus, long-term life of sodium–sulphur cells may depend upon the composition. Recently, Kennedy *et al.* [4] have shown that electronic conductivity of sodium-β-alumina can be significantly altered if doped with iron. Experiments of Weber [5], however, indicate that the electronic conductivity of lithia-stabilized sodium-β''-alumina (at 350° C), which had been in contact with sodium for a prolonged period of time, is of the order of 8×10^{-5} (ohm m)$^{-1}$ e.g. $\sigma_{e(2)} \approx 8 \times 10^{-5}$ (ohm m)$^{-1}$. The present calculations would indicate that the maximum pressure generated in a pore of 10^{-5} m radius in 1 h under a charging current density of 5000 A m^{-2} is only on the order of 600 psi (4 MPa). Pressure of this magnitude would not cause any damage to the solid electrolyte. Thus, it would appear that degradation of sodium-β''-alumina by internal pressurization in sodium–sulphur cells will not occur under normal conditions provided the electronic conductivity is of the order of 10^{-4} (ohm m)$^{-1}$. Since the electronic conductivity may be sensitive to impurities, identification and subsequent control of such impurities is vital.

DeJonghe [1] has suggested that abnormal operation of the sulphur electrode may lead to enhanced pressure. Our calculations indicate that this should not be so since the pressure generated in the pore will be related to the charging current density (or potential drop across the β''-alumina excluding polarization losses at the β''-alumina/sulphur interface).

In conclusion, large internal pressures may be generated if electronic conductivity in excess of 10^{-3} (ohm m)$^{-1}$ is developed in that part of β''-alumina in contact with sodium. Since impurities in β''-alumina may affect the magnitude of electronic conductivity, identification of the detrimental impurities and their control is necessary. For example, the work of Kennedy *et al.* [4] would suggest that iron may be detrimental. The results of Weber [5], however, indicate that the electronic conductivity in lithia stabilized β''-alumina, is of the order of 8×10^{-5} (ohm m)$^{-1}$. As such, internal pressurization should not be a serious problem. Furthermore, efforts should be made to fabricate ceramics with near theoretical density so that pores which could serve as precipitation sites are absent.

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