ELECTRICAL SCREENING PROCEDURE
FOR SOLID IONIC CONDUCTORS

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An electrical screening method has been developed for preliminary evaluation of polycrystalline specimens of candidates for use as solid ionic conductive electrolytes in batteries. The procedure measures dielectric loss and capacitance, from which are calculated an ac conductivity attributed provisionally to ions and an activation energy for that conductivity. Electronic conductivity is directly measured. The screening procedure applied to sodium beta-alumina yielded acceptable values for conductivity and activation energy.
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SUMMARY

An electrical screening method has been developed for preliminary evaluation of polycrystalline specimens of candidates for use as solid ionic conductive electrolytes in batteries. The procedure measures dielectric loss and capacitance, from which are calculated an ac conductivity attributed provisionally to ions and an activation energy for that conductivity. Electronic conductivity is directly measured. The screening procedure applied to sodium beta-alumina yielded acceptable values for conductivity and activation energy.

INTRODUCTION

A number of solids have been reported to be ionic conductors. Investigation in this area has recently been stimulated by the discovery, and development for battery applications, of solid ionic conductors with conductivities of the order of that of liquid electrolytes (ref. 1).

For example, a class of Ag⁺ conductors is based on modified silver iodides as exemplified by RbAg₄I₅, which has a conductivity of approximately 0.2 (Ω cm)⁻¹ at room temperature (refs. 2 and 3). Beta-alumina and structurally related compounds demonstrate surprisingly large Na⁺ ion conductivities of the order of 0.05 (Ω cm)⁻¹ for single crystals and 0.005 (Ω cm)⁻¹ for practical polycrystalline membranes at 25°C. Lower conductivities are observed for other alkali ions in the structures (refs. 4 to 8). Practical applications of this material in high-energy-density secondary batteries require temperatures of approximately 300°C for sufficient conductivity to be attained unless very thin polycrystalline or single-crystal membranes can be developed. This high-temperature requirement is a handicap both for space satellite applications and for terrestrial uses. It is therefore important to identify and develop a wider range of materials which may provide lower temperature operation and wider choice of conducting ions. Materials of interest are ions of the low-equivalent-weight metals, with emphasis
on the alkalis and the halogens. At the Lewis Research Center, work has been done on a series of Group II and Group III fluorides to elucidate the mechanism of F⁻ ion conduction (refs. 9 to 11). Recently, the program has emphasized alkali ion conductors. Selection of compounds has been based on crystal-chemical criteria, as described in reference 12. This report describes an electrical method used for screening candidate materials and validates the method with sodium beta-alumina.

ELECTRICAL SCREENING METHOD

It is convenient to use ac methods for preliminary evaluation of candidate ionic conductors because specimen preparation is simpler than for transport measurements. The latter require single crystals or impermeable compacts. However, ionic transport must be proved by dc methods.

The application of dielectric loss measurements and the calculation of ac conductivity from these data, as used in this work for indicating ionic mobility, are based on standard dielectric relaxation theory (ref. 13). A condensed version appears in reference 14. From observations of the capacitance, loss, and loss peaks as functions of temperature and frequency, the theory permits derivation of the following parameters of interest: a calculated ac conductivity $\sigma_{ac}$ and an activation energy $\Delta E$. The calculated ac conductivity is, in effect, that which would be observed at the high-frequency limit of the polarization process involved. It is given by

$$\sigma_{ac} = \frac{\epsilon_S - \epsilon_{\infty}}{\tau}$$

where $\tau$ is the relaxation time obtained from the loss peak where the condition $\omega \tau = 1$ exists, and $\omega$ is the frequency in radians per second. The quantity $\epsilon_S - \epsilon_{\infty}$ is the difference between the static dielectric constant $\epsilon_S$ and that for infinite frequency $\epsilon_{\infty}$; it is obtained from the Cole-Cole plot (ref. 15). In this analysis it is assumed that the observed polarization is a space charge caused by mobile ions being blocked at internal impedances in the sample. The internal impedances are dominant in imperfect polycrystalline samples. Effectively, the resistance-capacitance (RC) time constant of the circuit $\tau$ is assumed to be caused by the sample.

An activation energy $\Delta E$ is obtained from the temperature dependence of the calculated conductivity $\sigma_{ac}$ according to

$$\sigma_{ac} = \frac{A}{T} e^{-\Delta E/RT}$$

(2)
where A is the usual pre-exponential factor in conductivity expressions, containing the charge density and constants of the lattice (ref. 16) with the special condition that the density of carriers is independent of temperature. This condition means that \( \Delta E \) obtained by this method is the same activation energy which appears in the temperature dependence of the relaxation time (ref. 14, eq. (117)).

The preceding treatment of dielectric loss data is, in principle, the same as that employed in reference 5. In practice, however, the theory of reference 5 could not be used as a screening technique for any material prepared as a sintered compact in an early form of the material development. For those materials, calculation of conductivity \( \sigma_{ac} \) is based on the space charge polarization theory of Maxwell-Wagner applied to conducting domains embedded in an insulating matrix (ref. 13, pp. 203-208).

In the equation

\[
\sigma_{ac} = \text{Constant} \times \frac{\epsilon_i}{\tau}
\]

\( \epsilon_i \) is the intrinsic high-frequency limit of the dielectric constant of the substance; it is not directly measurable either in loose-powder specimens or in the compacted specimen used here. The value of \( \epsilon_i \) must be determined by optical or electrical measurements on a single crystal or by analogy with a similar substance. Radzilowski, Yao, and Kummer (ref. 5) measured the value of \( \epsilon_i \) for sodium beta-alumina to be 10. Their "constant" for equation (3), in reference 5 the analogous equation is numbered (4), is a geometrical factor derived from the observed anisotropy of the powder particles, as in reference 13 (pp. 203-208).

The advantages of the present method for preliminary screening, then, are (1) a polycrystalline compact of only a preliminary development nature may be used, thus avoiding both the extensive ceramic development required for direct measurement and the powder preparation required for the method of reference 5; (2) knowledge of \( \epsilon_i \) is not required.

A disadvantage of the present method is that the conductivity, being calculated at the high-frequency limit of a polycrystalline sample, is actually a lower limit to the intrinsic value. This occurs because grain boundaries, voids, and anisotropy diminish the effective density of ionic charge carriers. It must be emphasized that observation of relaxation phenomena in response to ac may reflect any of several types of relaxations which, separately or together, may have parameters resembling those to be expected from ionic motion (ref. 17). This screening method therefore discloses a necessary but not sufficient condition for ionic mobility in the solid.
EXPERIMENT

Electrical Measurements

Alternating-current measurements. - Capacitance and loss measurements were made at first with a manual balancing type of bridge having a frequency range of 20 to $10^5$ hertz. This bridge was replaced by an automatically balancing bridge providing the discrete frequencies $\nu$ of $10^3$, $10^4$, $10^5$, and $10^6$ hertz. Both bridges employed a guard circuit to minimize the effects of stray lead capacitances.

Aluminum contacts were evaporated on the sample; platinum wires were attached to the contacts by conducting epoxy and then connected to the end of the probe. The sample was suspended in a cryostat or in a vertical tube furnace by means of a three-lead coaxial probe.

A calibrated copper-constantan thermocouple junction was placed so as to make contact with the sample surface during measurement. The thermocouple signal was amplified and read from a digital voltmeter. The temperature of the sample was changed by heat exchange through a dry nitrogen atmosphere with either a liquid nitrogen reservoir or a resistance heater. With this arrangement, measurements could be carried out from 80 K to about 500 K.

Background capacitance and loss, obtained with Teflon disks in place of the compacted sample, varied less than 1 percent over the range of temperature and frequency employed.

The empty powder sample holder, designed after that used in reference 6, exhibited similar behavior.

Thermocouple readings were estimated to be precise to $\pm 1$ K, capacitance measurements to $\pm 0.2$ picofarad, loss tangents to $\pm 0.005$, and frequencies to $\pm 0.1$ percent.

Direct-current polarization measurements. - The screening procedure employed in reference 12 also includes ion blocking dc polarization measurements using the Hebb-Wagner technique (refs. 18 and 19). These measurements were made for the usual purposes: (1) to obtain the relative values of ionic and electronic conductivity; (2) to seek qualitative confirmation of the existence of ionic conduction by extrapolation of the current to zero time after application of the dc field. This part of the procedure was not applied to beta-alumina.

Sodium Beta-Alumina Specimen

A dense (~95 percent theoretical) polycrystalline compact was synthesized from $\text{Na}_2\text{CO}_3$ and $\text{Al}_2\text{O}_3$ in the starting ratio $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ of 9. Final reaction sintering was
done under hot working conditions to obtain preferred orientation (ref. 20). X-ray diffraction disclosed that parallel to the pressed disk faces the specimen had about three times the random intensity for basal planes. The sample used in this work was cut transversely to the oriented disk face so that electrodes could be placed perpendicular to the partially oriented basal planes within which the sodium ions are mobile.

RESULTS

The results of the electrical measurements on the sodium beta-alumina specimen are shown in figures 1 and 2. In figure 1 the dielectric loss $e''$ is plotted against reciprocal absolute temperature at several frequencies. In figure 2 the real part $e'$ of the dielectric constant is plotted against the imaginary part of the loss $e''$ at a single frequency. We observe in figure 1 that the resonance peak for $\nu$ of $10^3$ hertz occurs at the temperature given by $1/T = 4.1 \times 10^{-3}$ K$^{-1}$. The relaxation time, then, at this temperature, given by $\tau = 1/\omega_{\text{res}}$, is $1/2\pi \times 10^3$ seconds, where $\omega_{\text{res}}$ is the resonance frequency. This value of $\tau$ is used to calculate the presumed ionic conductivity $\sigma_{\text{ac}}$ by equation (1). The value of $\epsilon_S - \epsilon_\infty$ is $3.65 \times 10^5$ for $10^3$ hertz; it is obtained from the Cole-Cole plot shown in figure 2. The quantity $\epsilon_S - \epsilon_\infty$ is a pure number in the cgs system; for $\sigma_{\text{ac}}$ to be obtained in $(\Omega \text{ cm})^{-1}$, $\epsilon_S - \epsilon_\infty$ must be multiplied by the permittivity of free space $\epsilon_0$, which equals $8.85 \times 10^{-14}$ coulomb per volt per centimeter. Substituting into equation (1):

$$\sigma_{\text{ac}} = \frac{(3.65 \times 10^5)(8.85 \times 10^{-14})}{(2\pi \times 10^3)^{-1}} = 2.03 \times 10^{-4} \text{ (}\Omega \text{ cm})^{-1}$$

This is the calculated conductivity at $1/T = 4.1 \times 10^{-3}$ K$^{-1}$. The conductivity can be computed in a similar way for the other resonance peaks. Values of $\sigma_{\text{ac}} T$ are plotted against $1/T$, as shown in figure 3, to obtain the activation energy $\Delta E$ and the pre-exponential factor $A$ from equation (2). In the case of the sodium beta-alumina specimens, $\Delta E = 20.5 \pm 0.8$ kilojoules per mole ($4.9 \pm 0.2$ kcal/mole), $A = 1.3 \pm 0.3 \times 10^3$ K $(\Omega \text{ cm})^{-1}$, and $\sigma_{27^\circ C} = 1.1 \pm 0.3 \times 10^{-3}$ $(\Omega \text{ cm})^{-1}$. It should be noted that equation (3) differs from the equation used in previous dielectric loss work (ref. 5), where the activation energy was obtained from the temperature dependence of the resonance frequency $\omega_{\text{res}}$ and the equation

$$\omega_{\text{res}} = \omega_0 e^{-\Delta E/RT}$$

This difference in the pre-exponential term of the temperature dependence results
in different values of $\Delta E$. Equation (2) as used here results in a $\Delta E$ that is 2 to 4 kilo-
joules per mole larger than would be obtained with equation (4).

DISCUSSION

The value of $1.1 \times 10^{-3} \, (\Omega \text{ cm})^{-1}$ calculated for the ac conductivity at $27^\circ \text{C}$ for the
moderately oriented sodium beta-alumina compares favorably with values determined
directly. For example, data of reference 6 extrapolate to about $10^{-3} \, (\Omega \text{ cm})^{-1}$ at $27^\circ \text{C}$. The several points of difference between the present sample and the intensively devel-
oped ceramics used for transport measurements prevent useful comparisons. It is
regarded as sufficient validation of this screening method that a compacted sample, pre-
pared in a preliminary type of procedure, has given clear indication of promise as an
ionic conductor.

The value of $\Delta E$ obtained in the present work, 20.5 kilojoules per mole (4.9 kcal/
mole), is higher than has been reported, 15 kilojoules per mole (ref. 6). Again, al-
though the differences between the materials prevent useful comparison, it is consid-
ered adequate to the purpose at hand that the value found would have been taken as evi-
dence of unusually high mobility of the conducting species.

CONCLUSIONS

The screening method developed here has been found to yield sufficiently accurate
values of ionic conductivity and activation energy of the mobile species to be useful in
preliminary screening of materials as candidates for further study as ionic conductors.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, November 29, 1972,
502-05.

REFERENCES

no. 1, Jan. 1969, pp. 13C-22C.


Figure 1. - Dielectric loss of sodium beta-alumina oriented compact.

Figure 2. - Cole-Cole plot for sodium beta-alumina oriented compact. Frequency, $10^3$ hertz; $\varepsilon_s = 3.65 \times 10^5$; $\varepsilon_\infty = 0$; $\varepsilon_s - \varepsilon_\infty = 3.65 \times 10^5$. 
Figure 3. - Calculated conductivity curve for sodium beta-alumina oriented compact.
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