Electrical Polarization of Lead Bromide Crystals. I

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An attempt was made to measure electronic conductivity in lead bromide in equilibrium with lead, since experimental data on the cell $-Pb/PbBr_2/C+$ in the literature are not consistent with existing theories. Combination of our results with published data for bromine-induced hole conduction in lead bromide shows that neither our data, nor the published conduction data obtained with the afore-mentioned cell arrangement, are in agreement with electronic currents. It turned out that complete steady-state ion-discharge blockings has not been achieved, and that ionic currents have dominated.

1. Introduction

In studies of the polarization of solids complete steady-state ion-discharge blocking can be achieved in solid electrolyte systems of the type Me/MeX/C, where MeX is a solid with predominant ionic conduction. If a dc potential is applied to this cell with the negative pole at the metal electrode and small compared to the decomposition potential of MeX, the ionic conduction will be suppressed and the resultant current can be used to determine the electronic conductivity in MeX (*1, 2*).

Wagner and Wagner (*3*) have used this type of cell to determine the electronic conductivity in $PbCl_2$ and $PbBr_2$ doped with 1% KCl and 1% KBr, respectively. The experimental results are similar to those reported for the cuprous halides, measured in the same cell arrangement, and suggest hole conduction (*4*). Their results on $PbCl_2$–KCl and $PbBr_2$–KBr, however, are not amenable to a theoretical analysis, because the experimental slopes of the log*i* versus *E* plots are about four times smaller than suggested by Wagner's theory (*1*). This behaviour is to be expected if the hole concentration becomes comparable to the concentration of the mobile ionic defects (*5*). In that case the slope is lowered by a factor of 2, with respect to the value predicted by Wagner's theory (*1, 6*), still leaving a discrepancy between existing theories and experimental results.

We have tried to measure the electronic conductivity in lead bromide single crystals in equilibrium with lead, and have compared the data with bromine-induced hole conduction in lead bromide (*7, 8*).

2. Experimental

Measurements were carried out on nominally pure lead bromide single crystals. The crystals were grown in a zone-refining apparatus (*9*). Flat disks up to about 3 mm thick and with a surface area of about 0.5 cm² were cleaved from the single crystal boules. The samples were mounted in a pyrex polarization cell, which was basically of the same type as was previously published (*8*). Several types of lead contacts were used in this study:

(a) Evaporated lead films; lead was evaporated on freshly cleaved surfaces in a Speedivac Coating Unit (model 6.E.2 Edwards). The electrode area was smaller than the crystal surface area, whereas the blocking electrode (Pt covered with Aquadag) covered the entire anodic sample surface. Contact with Pt electrode and lead films was established by means of Aquadag. In order to obtain the cell constant, the ac conductivity was measured as a function of temperature. These data were compared to the known specific conductivity of lead bromide (*8*).

(b) In some experiments one of the platinum electrodes was covered with a flat disk of lead;

(c) The lower electrode was replaced by a small copper cupel, in which some lead was molten. The sample, attached to the upper Pt electrode be means of Aquadag, was gently lowered, until the sample surface contacted the molten lead. After cooling the lead content of the cupel adhered firmly to the sample surface.

All experiments including electrode preparation (c) were carried out in a nitrogen atmosphere. The lead was cut from Lead Rods 6N (Kochlight Laboratories Ltd.), which was kindly supplied by Mr. J. M. L. Kerbusch of this laboratory.

Measurements were started after annealing the crystal at a temperature in the range 200–300°C for one day. Currents were measured as a function of decreasing voltage. Thereafter current measurements were performed on increasing voltage. One current–voltage run in the voltage region 0.1–1 V usually lasted about six weeks, since it took about two days for the current to reach a constant value. After each measurement the interface $Pb/PbBr_2$ showed a damage which could be most clearly observed on contacts c. A thin brownish-red powder-like film had grown on the lead electrodes. The lead disk electrodes were covered with spots of the powder, indicating a rather incomplete contact with the sample surface. Evaporated lead films had even disappeared partially after very long runs. For this reason most of the experiments were carried out with electrode contact c. It must be pointed out, however, that the three types of electrode contacts yielded the same shape for the current–voltage characteristics.

Technical and purified nitrogen were used as an ambient. The nitrogen was passed over a B.T.S. catalyst (BASF) to remove oxygen. The gas was dried with Union Carbide molecular sieves. In both ambients a cathode damage was observed. In purified nitrogen a white film with brownish-red dots developed. X-Ray diffraction studies[1] showed that the films consisted of a mixture of lead bromide and lead monoxide (red tetragonal form). After each current–voltage run a new sample with freshly prepared electrode contacts was mounted in the polarization cell.

The determination of the current through the

crystal was made by measuring the voltage drop (Electrometer Keithly 610 BR) across a decade resistor (0–40 MΩ Bleeker) in series with the crystal.

The temperature was measured with a calibrated chromel–alumel thermocouple. The temperature control and stability of the cell furnace was better than 1°C over the period of one current–voltage run.

3. Theory

The magnitude of the electronic conductivity can be estimated by determining current–voltage curves for the cell

$$-Pb/PbBr_2/C,N_2 +. \qquad (I)$$
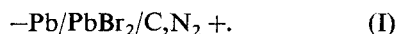
The electrochemical potentials of electrons and ions at the interface $Pb/PbBr_2$ are related to the thermodynamic potential of lead as a consequence of the equilibrium between Pb in the electrode and in the crystal. The reaction involved can be represented by

$$Pb + V''_{Pb} \rightleftharpoons Pb^{\times}_{Pb} + 2e', \quad K_{Pb} \qquad (1)$$
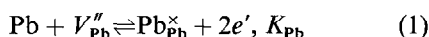
It is well known that lead bromide is an anionic conductor, so we prefer a reaction expressed in terms of dominant mobile structure elements (5)

$$Pb \rightleftharpoons Pb^{\times}_{Pb} + 2V^{\cdot}_{Br} + 2e', \quad K^{*}_{Pb}. \qquad (2)$$
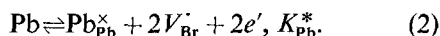
On applying a voltage with polarity as indicated, and small compared to the decomposition potential $E_d(= \Delta G(PbBr_2)/F$, where ΔG denotes the free energy of formation of lead bromide from the elements) bromide ion vacancies migrate initially towards the lead cathode and are discharged according to reaction (2). Since bromide ions are not discharged at the anode the concentration of the anion vacancies at the $PbBr_2/C$ interface decreases. A concentration gradient is built up. Under steady-state conditions, migration of bromide ion vacancies due to the electric field is balanced by diffusion due to the concentration gradient: the cell is polarized. The polarization current is then carried exclusively by electrons, moving either as excess electrons, or via electron holes. It is known that in lead bromide holes are much more mobile than electrons (9, 11). The result of Wagner and Wagner (3) suggests that holes are introduced from the anode.

Wagner and Wagner (4) first pointed out that in a polarization cell the applied voltage E defines the steady-state activity of each elemental

component of the solid electrolyte at the blocking interface. In cell arrangement I, the surface of the blocking electrode is in the same condition as if it was simultaneously in contact with reservoirs of lead and bromine with activities (10) $a_{Pb} = \exp(-2eE/kT)$ and $P_{Br_2} = \exp[-2(E_d - E)e/kT]$, where the activities refer to the conventional standard states Pb(s) and Br$_2$ (g, 1 atm).
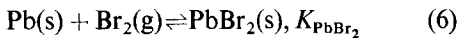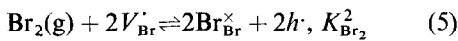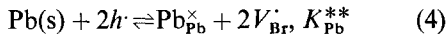
The relation between thermodynamic potential and electrochemical potentials was used by several authors to derive an expression for the total electronic current (polarization current), i_t, through an ionic crystal with one reversible and one inert, electronically conducting electrode (1, 5, 12).

The expression is represented by

$$i_t = i_n + i_p =$$
$$= \frac{kT}{eL}[\sigma_n^0(1 - e^{-eE/kT}) + \sigma_p^0(e^{eE/kT} - 1)]. \quad (3)$$

L denotes the cell constant (ratio of crystal thickness and electrode contact area). σ_n^0 and σ_p^0 are the specific electron and hole conductivities, respectively, for lead bromide in contact with Pb($a_{Pb} = 1$).

σ_p^0 and the specific hole conductivity, σ_p, of lead bromide equilibrated in bromine vapour ($P_{Br_2} = 1$ atm) are related through the formation of lead bromide from the elements:

$$Pb(s) + 2h^{\cdot} \rightleftharpoons Pb_{Pb}^{\times} + 2V_{Br}^{\cdot}, \quad K_{Pb}^{**} \quad (4)$$

$$\underline{Br_2(g) + 2V_{Br}^{\cdot} \rightleftharpoons 2Br_{Br}^{\times} + 2h^{\cdot}, \quad K_{Br_2}^2 \quad (5)}$$

$$Pb(s) + Br_2(g) \rightleftharpoons PbBr_2(s), \quad K_{PbBr_2} \quad (6)$$

with

$$K_{PbBr_2} = K_{Pb}^{**} \times K_{Br_2}^2 \quad \text{and} \quad K_{Pb}^{**} = (K_{sch}/K_i^2)K_{Pb}.$$

Here K_i denotes the intrinsic electronic excitation constant, and K_{sch} denotes the Schottky constant. K_{Br_2} is the equilibrium constant, describing the bromination of lead bromide (8). The hole mobility does not depend on the hole concentration, so we can write in accordance with reaction (5) (8, 17).

$$\sigma_p^0 = P_{Br_2}^{\pm}(I)\sigma_p. \quad (7)$$

From conductivity experiments on lead bromide in a bromine atmosphere (8) we could estimate an expression for σ_p ($P_{Br_2} = 1$ atm) in the intrinsic region of the ionic conductivity

$$\sigma_p = 1.2 \exp(-0.74 \text{ eV}/kT)\Omega^{-1}\text{cm}^{-1}, \quad (8)$$

If it was assumed that the hole mobility has a uniform temperature dependence in the region 25–350°C.

From thermodynamic data (13) we calculated for the decomposition of lead bromide into solid lead and gaseous bromine

$$K_{PbBr_2}^{-1} = 5.6 \times 10^7 \exp(-3.20 \text{ eV}/kT) \text{ atm} \quad (9)$$

Now in cell I $a_{Pb} = 1$, and therefore $P_{Br_2}^{\pm}$ (I) = $K_{PbBr_2}^{-\pm}$. Introducing this, and Eq. (9) into relation (7) gives

$$\sigma_p^0 = 9 \times 10^3 \exp(-2.34 \text{ eV}/kT)\Omega^{-1}\text{cm}^{-1}. \quad (10)$$

Equation (3) is valid under the condition that the ionic current is completely blocked, and that thermodynamic equilibrium is established. An upper limit of the current for decomposition according to equilibrium (6) can be obtained by calculating partial bromine pressures, P_{Br_2}, at the PbBr$_2$/C interface for a given value of the applied voltage, E, using $P_{Br_2} = \exp[-2(E_d - E)e/kT]$. The decomposition current, i_{Br_2}, is given by (4)

$$i_{Br_2} = e\dot{n}\frac{P_{Br_2}}{P}, \quad (11)$$

if the experiment is carried out in a stream of inert gas with a flow rate $\dot{n}$ atoms/s, and a pressure P. It is assumed that equilibrium between the crystal and the ambient is established very rapidly, so that equilibrium is maintained. Expressions for i_p (viz. Eq. (3)), and i_{Br_2} were calculated as a function of applied voltage at constant temperature. The temperatures chosen correspond to some experimental temperatures. A flow rate of nitrogen of 10 l/hr was used in the experiments.

The calculated expressions for the currents (in amperes) are

$$i_p(477K) = 1.5 \times 10^{-(21-10.5E)} \quad (12)$$

$$i_p(541K) = 1.34 \times 10^{-(18-9.4E)} \quad (13)$$

$$i_{Br_2}(477K) = 1.5 \times 10^{-(25-21E)} \quad (14)$$

$$i_{Br_2}(541)K = 1.21 \times 10^{-(21-18.7E)}. \quad (15)$$

A machine calculation of the current–voltage curve, described by Eq. (3) shows that a plateau type current–voltage curve will be obtained if $\sigma_n^0 > 10^3\sigma_p^0$. The electron current reaches its limiting value at $eE/kT \gg 1$. In the case that excess electron conduction is negligible we can write as an approximation

$$\log i_p \simeq \frac{eE}{2.3kT} + \log\left[\frac{eL}{kT}\sigma_p^0\right], \quad (16)$$

if $eE/kT \gg 1$.

4. Experimental Results

Current–voltage characteristics of cell I were measured in the temperature region 25–300°C. Use was made of evaporated lead contacts, lead disks, and contacts established with molten lead (Section 2). With these types of electrodes we obtained in the afore-mentioned temperature region $i - E$ plots in which no saturation plateau was found. They present, however, exponential functions of E. In Fig. 1 we have plotted some current–voltage curves [electrode contact (c)] as $\log[(eL/kT)i_t]$ versus E, together with the estimated unblocked ionic, i_0, specific hole, i_p, and thermodynamically defined decomposition currents, i_{Br_2}, at 477 and 541K. The slope of all $\log i_t$ versus E curves is about one-third of the value $e/(2.3kT)$ for applied voltages $E > 0.3$ V. A similar result was obtained by Wagner and Wagner (3) as was mentioned in the introduction. The experimental slope of their $\log i_t$ versus E curve at 573K was about four times smaller than the theoretical slope in Eq. (16): moreover,
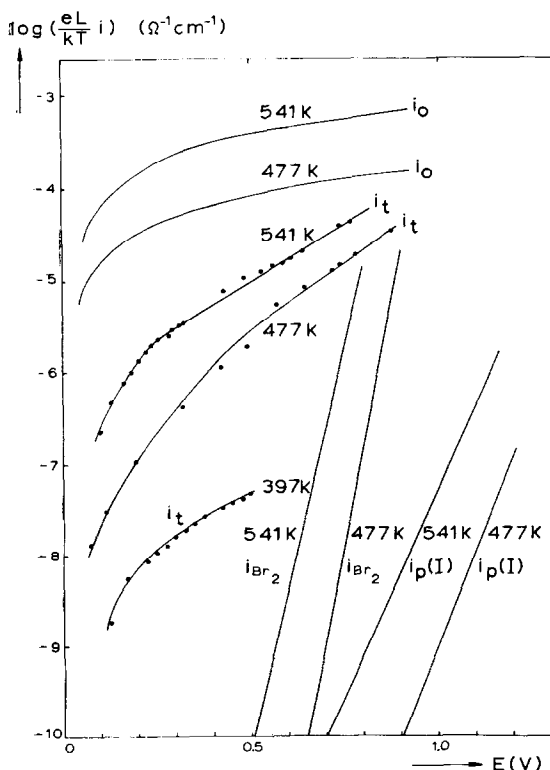
$\log i_t$ showed a linear dependence on E over the entire voltage range (0.1–0.8 V).

The initial rise of the $\log i_t$ versus E plots is in better agreement with the theoretical slope. Extrapolated σ_p^0 values for four runs in the intrinsic region of ionic conductivity can be represented by

$$\sigma_p^0 = 1.6 \exp(-0.8 \text{ eV}/kT)\,\Omega^{-1}\text{cm}^{-1}, \quad (17)$$

a remarkable result, since this expression is almost identical with the intrinsic hole conduction in lead bromide in contact with bromine vapour $(P_{Br_2} = 1 \text{ atm})$ (cf. Eq. (8)).

In order to obtain information on the cathodic damage a pressed tablet of tetragonal lead oxide powder was mounted in the polarization cell: $-Pb/PbO/C+$. It is known that tetragonal lead monoxide is an n-type conductor (14, 15). This feature is clearly demonstrated by the current–voltage curve presented in Fig. 2.

5. Discussion

The experimental results obtained with the cell $-Pb/PbBr_2/C+$ cannot be correlated to Wagner's general theory, as will be demonstrated for both electron and hole currents.

In a previous paper (8) we predicted the equilibrium constant K_{Pb} of reaction (1)

$$K_{Pb} = 2.5 \times 10^{+6} \exp(-3.8 \text{ eV}/kT) \text{ mole fraction.} \quad (18)$$

In the intrinsic region of ionic conductivity we found (8)

$$[V''_{Pb}]_0 = \tfrac{1}{2}[V_{Br}^\cdot]_0$$
$$= 10 \exp(-0.57 \text{ eV}/kT) \text{ mole fraction.} \quad (19)$$

FIG. 1. The total current, i_t, the unblocked current, i_0, the decomposition current, i_{Br2}, and the predicted hole current, i_p, in lead bromide, plotted as $\log(eL/kT)i$ versus E.
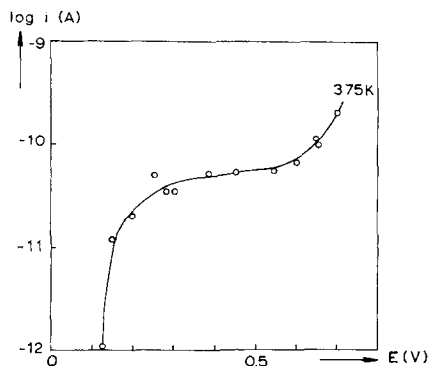

FIG. 2. The electronic current in a pressed tablet of tetragonal lead monoxide: $d = 0.26$ cm, electrode area 0.26 cm^2; $\sigma_n^0 = 1.7 \times 10^{-9}\,\Omega^{-1}$ cm^{-1}.

The concentration of electrons in lead bromide in contact with metallic lead ($a_{Pb} = 1$) can be predicted from Eqs. (18) and (19)

$$n = 5.0 \times 10^{+3} \exp\left(-2.2 \text{ eV}/kT\right) \text{ mole fraction.} \tag{20}$$

It must be pointed out, however, that the preexponential factor in Eq. (18) and, therefore, also in Eq. (20), is a rough estimate (8). The shape of the experimental current–voltage curves exclude without doubt an interpretation in terms of electron currents. In addition, Eq. (20) shows that electron currents in cell arrangement I will be extremely small, since $\mu_n < \mu_p (\simeq 10^{-2}$ cm^2 V^{-1} s^{-1}) (8, 9). From Eq. (10) and $\mu_p \simeq 10^{-2}$ cm^2 V^{-1} s^{-1} (8) we conclude that the hole concentration in cell arrangement I is also very small. In the introduction we mentioned the feature that the theoretical slope of the $\log i_t$ versus E curve is lowered by a factor of 2 in the case that the hole concentration becomes comparable to the concentration of the mobile ionic defects: $[V_{Br}^{\cdot}]$. In view of Eq. (10), the hole mobility and Eq. (19) we calculate $p \ll [V_{Br}^{\cdot}]_0$. If the PbBr$_2$/C interface is only partially blocking we can use a modified expression

$$i_p = \frac{kT}{eL} \sigma_p{}^0 \exp\left[\frac{eE}{kT}\left(1 - \frac{i_a}{i_0}\right) - 1\right] \tag{21}$$

suggested by Kröger and coworkers (16). Here i_a denotes an ionic contribution: $i_a \ll i_0$.
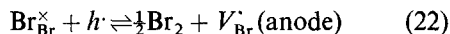
From our experimental curves we obtain for i_a/i_0 values of about 0.7. These values for i_a/i_0 are so large that it is doubtful whether Eq. (21) may be used at all, since the validity of this equation is based on the condition $i_a \ll i_0$: moreover a comparison between i_t and i_0 values indicates lower i_a values. Both modifications on Wagner's theory mentioned so far imply the basic applicability of this theory. A comparison of Eq. (10) and (17) shows that the experimental $\sigma_p{}^0$ values exceed the hole currents to be expected by orders of magnitude.

We now turn to the fact that we observed the formation of lead monoxide in between the lead and lead bromide. Let us, therefore, consider the following cell
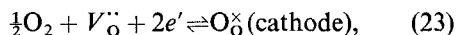
$$-\text{Pb}/\text{PbO}/\text{PbBr}_2/\text{C}+. \tag{II}$$
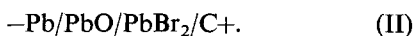
Lead monoxide is a mixed conductor, whereas lead bromide is practically a pure ionic conductor, since n and p are extremely small. In cell arrangement II electrons are blocked a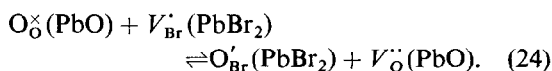t the PbO/PbBr$_2$ interface. Lead ions are neither mobile in lead bromide, nor mobile in lead monoxide. In lead monoxide it is assumed that $V_O^{\cdot\cdot}$ is mobile (15), in lead bromide $V_{Br}^{\cdot}$. In cell arrangement II one may assume, therefore, the next electrode reactions

$$\text{Br}_{Br}^{\times} + h^{\cdot} \rightleftharpoons \tfrac{1}{2}\text{Br}_2 + V_{Br}^{\cdot} \text{ (anode)} \tag{22}$$

and

$$\tfrac{1}{2}\text{O}_2 + V_O^{\cdot\cdot} + 2e' \rightleftharpoons \text{O}_O^{\times} \text{ (cathode)}, \tag{23}$$
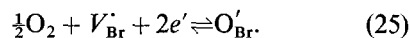
since there is undoubtedly some presence of oxygen. The boundary reaction at the PbO/PbBr$_2$ interface in accordance with these electrode reactions is given by

$$\text{O}_O^{\times}(\text{PbO}) + V_{Br}^{\cdot}(\text{PbBr}_2)$$
$$\rightleftharpoons \text{O}_{Br}^{\cdot}(\text{PbBr}_2) + V_O^{\cdot\cdot}(\text{PbO}). \tag{24}$$

The initial formation of lead monoxide can be represented by

$$\tfrac{1}{2}\text{O}_2 + V_{Br}^{\cdot} + 2e' \rightleftharpoons \text{O}_{Br}'. \tag{25}$$

The phenomenon of photooxidation of lead colloids in lead halides as described by Verwey (9) shows that reaction (25) can proceed very fast. Cell arrangement II represents an idealized configuration with respect to the situation built up during our measurements: the cathodic damage had a powder-like structure. Nevertheless, as a consequence of the lead monoxide formation the thermodynamically defined i_{Br_2} is drastically disturbed, in such a way that ionic conduction had prevailed.

Wagner and Wagner (3) measured at 573K for $\sigma_p{}^0$ the value 10^{-6} Ω^{-1} cm^{-1}. From Eq. (17) we obtain for $\sigma_p{}^0$ at 573K the value 1.6×10^{-7} Ω^{-1} cm^{-1}. We are, therefore, inclined to believe that the results of Wagner and Wagner cannot be interpreted in terms of hole conduction. In their experiments ionic conduction had prevailed too. The build-up of their PbX$_2$/Pb (X = Cl, Br) electrode makes this assumption more obvious, since in fact a PbX$_2$/C,Pb contact was used (18). In the cell arrangement +C/PbBr$_2$/C– we measured steady-state ionic currents as a function of applied voltage (19). The experimental slopes observed are always lower than the slopes of the $\log i_t$ versus E plots presented here: moreover, the magnitude of these steady-state currents is of the same order of magnitude as compared to the currents presented by Wagner and Wagner (3). It is reasonable for lead chloride to behave similarly in the cell arrangement +C/PbCl$_2$/C–, since the ionic conductivity in both lead chloride and lead bromide stems from anion vacancies formed according to a Schottky mechanism. For the

deviation from stoichiometry in AgBr in contact with silver at 550K Wagner (2) has calculated $Ag/Br = 1 + 10^{-12}$. In his calculations he used plateau-type i_t versus E curves, measured by Ilschner (20). The relevant thermodynamic and defect parameters for AgBr (21) show that in AgBr in equilibrium with silver n is orders of magnitude larger than our predicted n in lead bromide in contact with lead. The deviation from stoichiometry in lead bromide in contact with lead is, therefore, negligibly small.

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