Br^- Ionic Conductivity for $PbBr_2$-Based Solid Electrolyte

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The electrical conductivity of $(1 - x)PbBr_2 \cdot xKBr$ solid electrolytes is enhanced on increasing x to $x = 0.02$. The maximum conductivity, 2.7×10^{-6} S·cm^{-1} at 298 K was obtained for $x = 0.02$. The transference number for the Br^- ion is almost equal to 1, which was determined by the Tubandt's method, dc conductivity with Au electrodes, and the electromotive force of a Br_2 gas concentration cell. The Ba-based system, $(1 - x)BaBr_2 \cdot xKBr$ solid electrolyte, has a lower conductivity compared with that for the Pb-based system.

Introduction

Anion conducting solid electrolytes have been investigated for applications in gas sensors and fuel cells.[1–3] O^{2-} ions have been well-known to migrate in stabilized zirconia. Zr^{4+} ions in ZrO_2 were partially substituted by M^{2+} or M^{3+} cations such as Ca^{2+} or Y^{3+} in the stabilized zirconia to produce O^{2-} ion vacancies. The most promising way to obtain a high conductivity is to produce vacancies for a mobile ion. However, the divalent O^{2-} ions hardly migrate in the solid at low temperature (<700 K). A high conductivity at room temperature has been obtained for a monovalent F^- or Cl^- carrier ion.[4–9] For the F^- ionic conductor, many materials have been extensively investigated and have exhibited a high conductivity at room temperature.[4–6] In the case of the Cl^- ionic conductor, only $PbCl_2$-based materials show ionic conduction at room temperature.[7–9] Before the 1930s, Tubandt reported that $PbCl_2$ is a pure Cl^- ion conductor.[10,11] Although pure $PbCl_2$ has a low conductivity, it is greatly increased by doping with MCl (M = Na, K, etc.) to give $(1 - x)PbCl_2 \cdot xMCl$.[7–9] The formation of anion vacancies with M^+ doping is also effective for obtaining high Cl^- ion conductivity. This Cl^- conductor has already been applied to a Cl_2 gas sensor.[12,13] For a Br^- conducting electrolyte, however, high conductivity at room temperature had not been reported.[14] It is commonly accepted that Br^- ions are too large to migrate in a solid electrolyte. We have briefly reported that the $(1 - x)PbBr_2 \cdot xKBr$ system has a high Br^- ionic conductivity even at room temperature.[15]

In this paper, the electrical properties of the $(1 - x)PbBr_2 \cdot xKBr$ solid electrolyte were investigated in detail.

Experimental Section

Sample Preparation. $PbBr_2$ (99.99%) and KBr (>99%) were used as the starting materials for the $(1 - x)PbBr_2 \cdot xKBr$ system. The stoichiometric mixture was dried at 573 K for 1 h in a quartz glass tube, which was then evacuated and sealed. The sealed sample was melted at 773 K for 1 h to yield a solid solution. The sample was then ground and pressed into a pellet (13 mm diameter and ca. 1 mm thickness) at a pressure of 1×10^8 Pa. The porosity for the pressed samples is 7–10%, which was determined by the ratio of a measured density (from pellet volume and weight) and a theoretical density. The pressed samples were used for the conductivity measurements.

Measurements. X-ray powder diffraction analysis was conducted using a Rigaku Geigerflex from Rigaku Corp. The electrical conductivity was determined by means of a complex impedance method ($100-10^6$ Hz) using Hewlett-Packard Model 4276A and 4277A impedance analyzers. Au electrodes were deposited on both surfaces of the pellet using an ion coater (Shimadzu IC-50). Before every measurement, the pellet was heated to 523 K in a stream of dried N_2 to eliminate adsorbed water. The measurements were carried out in the same atmosphere. Dc conductivity was measured after sample polarization at 1 V for 1 h each time the measuring temperature was changed. Au electrodes were sputtered or Pb metal disk electrodes were pressed on both surfaces of the pellet for the dc conductivity measurement.

Results and Discussion

Conductivity and Phase. The resistivity of the solid electrolyte is obtained by summing the bulk and the grain boundary resistivities, which is determined by the complex impedance plot (Cole–Cole plot). Monosemicircle which corresponding to the total (bulk and grain boundary) resistivity σ_{g+gb} was obtained at a higher frequency region for all the samples examined. The straight line of the internal resistance between the Au blocking electrodes and the solid electrolyte was appeared at lower frequency region. The conductivity of the solid electrolyte was obtained from the reciprocal of the total resistivity $[1/\sigma_{g+gb}]$. Figure 1 presents the

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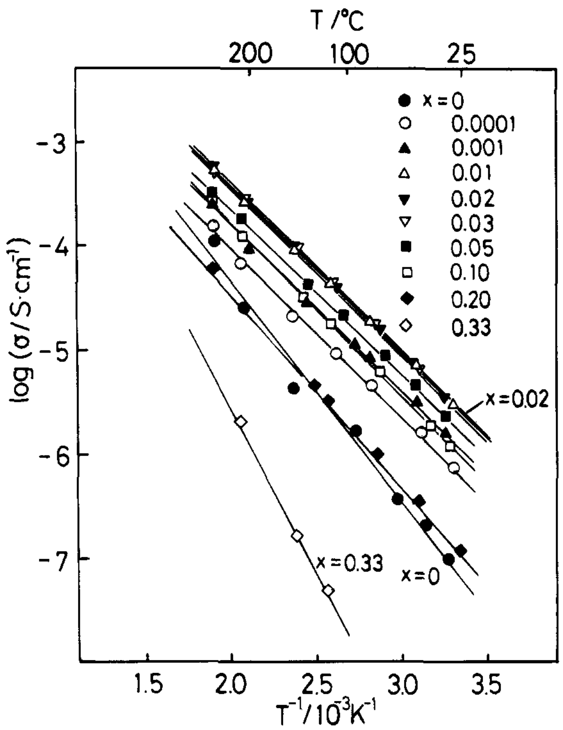

Figure 1. Temperature dependence of the electrical conductivity for the (1 − x)$PbBr_2$·xKBr system.

temperature dependence of the obtained conductivity for the (1 − x)$PbBr_2$·xKBr system with Au electrodes. Although pure $PbBr_2$ shows a low conductivity, the conductivity is greatly enhanced by KBr addition. The conductivity enhancement occurs even at $x = 0.0001$. The maximum conductivity was obtained for $x = 0.02$, which gave 2.7×10^{-6} $S \cdot cm^{-1}$ at 298 K. The activation energy for carrier migration is 0.42 eV for pure $PbBr_2$, and the activation energy is decreased to ca. 0.36 eV by increasing x. This conductivity enhancement is attributed to the formation of Br^- ion vacancies with KBr doping. However, the conductivity was decreased with KBr addition when x was larger than 0.02. Figure 2 presents the X-ray diffraction patterns to determine the reason for the conductivity decrement for $x > 0.02$. The peaks for a second phase appeared, and its intensity increased with an increase in the x value. The peaks for the second phase agreed with that for $x = 0.33$. No $PbBr_2$ peaks were obtained for $x = 0.33$. On the basis of these results, the second phase may be estimated to be KPb_2Br_5. The conductivity above $x = 0.02$ was decreased by the presence of the low conductive KPb_2Br_5 second phase (see $x = 0.33$ in Figure 1).

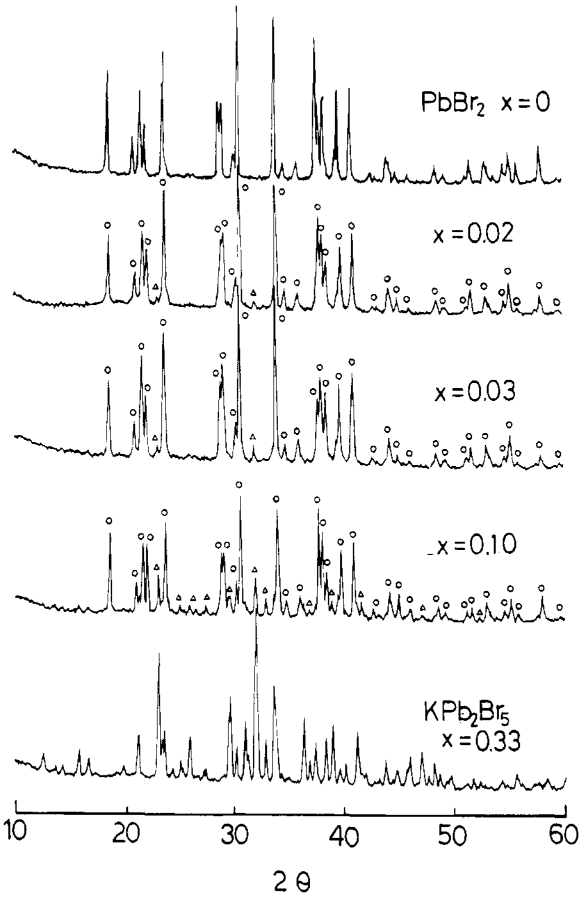

Figure 2. X-ray diffraction patterns for the (1 − x)$PbBr_2$·xKBr system: (○) $PbBr_2$; (△) KPb_2Br_5.

Table 1. Electrical Properties for the $PbBr_2$-Type Solid Electrolyte

sample	conductivity ($S \cdot cm^{-1}$) 298 K	conductivity ($S \cdot cm^{-1}$) 573 K	activation energy (eV)	ref
$0.98PbBr_2-0.02KBr$	2.7×10^{-6}	1.1×10^{-3}	0.36	this study
$0.98BaBr_2-0.02KBr$		2.5×10^{-5}	0.66	this study
$0.98PbCl_2-0.02KCl$	8.0×10^{-6}	2.5×10^{-3}	0.33	this study
$0.98BaCl_2-0.02KCl$		5.6×10^{-5}	0.65	18

$BaBr_2$, $PbCl_2$, and $BaCl_2$ also have a $PbBr_2$-type orthorhombic structure (space group *Pmnb*).[16] We also prepared the Ba-based electrolytes, because the ionic radius for the Ba^{2+} ion is larger than that of the Pb^{2+} ion.[17] The conductivity data for these $BaBr_2$-type solid electrolytes are summarized in Table 1. The conductivity of the Ba-based solid electrolytes is appreciably lower than that of the Pb-based materials for both samples. The electrical properties for $0.98PbBr_2-0.02KBr$ are similar to those for $0.98PbCl_2-0.02KCl$, despite the ionic radius of the Br^- ion being larger than that of the Cl^- ion.[17] These results suggest that the lattice size hardly influences the ionic conductivity. The high conductivity of the Pb-based electrolytes may be attributed to the lower $Pb^{2+}-X^-$ bonding energy than that of $Ba^{2+}-X^-$.

Tubandt's Method. The carrier ions were determined using Tubandt's method illustrated in Figure 3. Electrolytes I–III have the same composition of $0.98PbBr_2 \cdot 0.02KBr$ and are superimposed on each other. Gold as a cathode was sputtered on the surface of electrolyte III, while a Pb metal anode was pressed on electrolyte I. The samples were heated to 473 K for 2 h in a stream of dried N_2 before the measurements and were then electrolyzed at 10 μA for 453 h at 413 K in same atmosphere. The imposed voltage to the cell is 5–10 V, which is higher than a calculated decomposition voltage of 1.28 V for $PbBr_2$.[19] Theoretical weight changes of the three electrolytes expected for the transport by a given species alone are shown in Table 2. The weight changes for electrolyte I with Pb anode, electrolyte II, and electrolyte III with Au cathode were measured after the electrolysis. Two cells were measured to clarify the reproducibility of weight changes. If $0.98PbBr_2 \cdot 0.02KBr$ is a cation conductor for Pb^{2+} or K^+, whose ions at the electrolyte I with the Pb anode is migrated to electrolyte III with an Au cathode, and then

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Table 2. Weight Changes by the Tubandt's Method

	theoretical weight change (mg)				experimental result (mg)	
electrolyte	electron	K^+	Pb^{2+}	Br^-	cell 1	cell 2
I	±0	−6.6	−17.5	+13.5	+13.6	+12.9
II	±0	±0	±0	±0	−0.4	+0.6
III	±0	+6.6	+17.5	−13.5	−12.3	−14.1

Pb or K metal is deposited on the Au cathode. In the case of Br^- ionic migration, the $PbBr_2$ for electrolyte III on Au cathode is decomposed to Pb metal and Br^- ions. These Br^- ions migrate from the electrolyte III to electrolyte I, and the Pb metal remains on the Au cathode. The migrated Br^- ions react with the Pb anode to form $PbBr_2$. No weight change for the three electrolytes obtain when the main carrier is electron. It was found that the weight changes in our experiment were close to the theoretical weight changes for Br^- ion migration. This result proves that the main carrier for this system is the Br^- ion.

Dc Conductivity. Figure 4 shows the dc conductivity with Au or Pb electrodes for the sample of $0.98PbBr_2-0.02KBr$. The calculated decomposition potentials are 1.2−1.4 V at 298−523 K for $PbBr_2$.[19] The applied potential for dc conductivity measurement was fixed to 1.0 V, which is lower than the calculated decomposition potential. Dc conductivity was measured after the sample polarization at 1 V for 1 h each time the measuring temperature was varied. In the case of Pb electrodes, the current flowed continuously after potential application. The dc conductivity nearly agreed with that determined by the complex impedance method. The reactions at the cathode and the anode with Br^- migration are summarized as follows:

$$Pb + 2Br^- \underset{\text{cathode}}{\overset{\text{anode}}{\rightleftharpoons}} PbBr_2 + 2e^- \qquad (1)$$

In the case of Au electrodes, the current flowed momentarily after potential application, and then it greatly decreased by ion polarization of the solid electrolyte. The current showed a constant value after around 1 h, since the migrable ions were polarized. The dc conductivity showed a lower value compared with that by the complex impedance method. This dc conductivity would be attributed to electron conductivity. The dc conductivity of the sample with Au electrodes also suggests that the transport number of electrons was less than 10^{-5} at room temperature and was increased with elevated temperature.

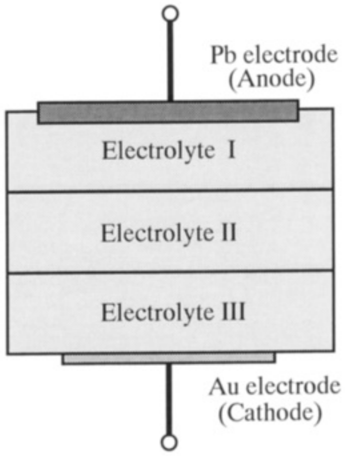

Figure 3. Tubandt's method.

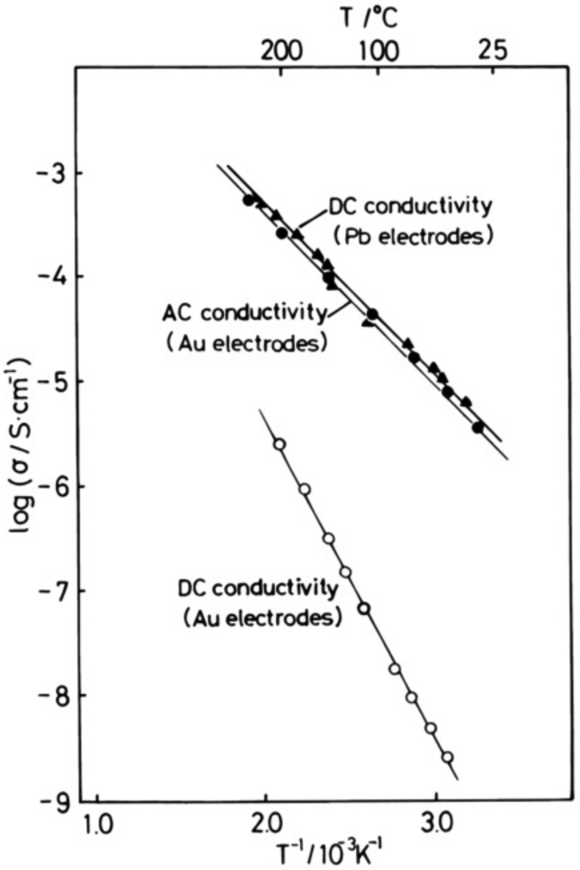

Figure 4. Ac and dc conductivities for the $(1-x)PbBr_2-xKBr$ system: (●) ac conductivity with Au electrodes; (▲) dc conductivity with Pb electrodes; (○) dc conductivity with Au electrodes.

Br_2 Concentration Cell. A Br_2 concentration cell was prepared by a melting method.[18,20] This method has been already utilized by us to prepare a sensor probe for Cl_2 gas using $0.97BaCl_2-0.03KCl$ electrolyte. Pb metal and $0.98PbBr_2 \cdot 0.02KBr$ were used for the solid reference electrode and the solid electrolyte. The solid electrolyte was melted at once at ca. 800 K to obtain a high density. The Br_2 gas concentration for the reference electrode was fixed by the equilibrium of the $PbBr_2$ formation from Pb and Br_2. RuO_2 paste as a measuring electrode was painted on and then dried at 473 K for 1 h. The RuO_2 electrode is thermodynamically stable to Br_2 gas. Figure 5 shows the apparatus for the emf (electromotive force) measurements. The prepared cell was fixed in a glass tube and an Au lead as a terminal was attached to the RuO_2 electrode. Br_2 vapor was prepared by heating liquid Br_2 (99%) and passing it through the glass tube. The EMF between the RuO_2 electrode and the Pb reference electrode obeys the Nernst equation

$$\text{emf} = \frac{RT}{2F} \ln \frac{P_{Br_2}}{P'_{Br_2}} \qquad (2)$$

where R, T, F, P_{Br_2}, and P'_{Br_2} are the gas constant, the

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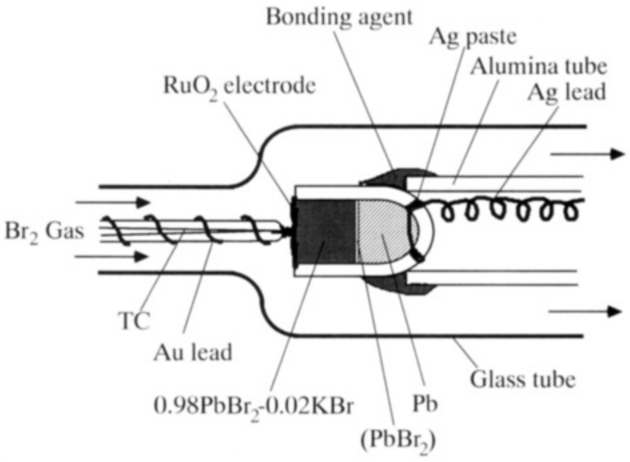

Figure 5. Apparatus of the EMF measurement for the Br_2 concentration cell.

absolute temperature, the Faraday constant, the Br_2 partial pressure at the measuring electrode ($P_{Br_2} = 1$), and the Br_2 partial pressure at the reference electrode. For the reference electrode, the following equilibrium exists

$$Pb + Br_2 \rightleftarrows PbBr_2 \tag{3}$$

$$K = \frac{a_{PbBr_2}}{a_{Pb}(P'_{Br_2})} \tag{4}$$

Because the activities of a_{Pb} and a_{PbBr_2} are equal to 1, eq 5 is given as

$$K = (P'_{Br_2})^{-1} = \exp(-\Delta G^\circ/RT) \tag{5}$$

where ΔG° is standard Gibbs energy of the formation of $PbBr_2$ (eq 3). From eq 2 and 5, eq 6 is modified to give

$$\mathrm{emf} = -\Delta G^\circ/2F \tag{6}$$

Using eq 6, the theoretical EMF was calculated.[19] The ion transference number t_{ion} was calculated by

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{electron}} = \frac{\mathrm{emf}_{experimental}}{\mathrm{emf}_{theoretical}} \tag{7}$$

Table 3. EMF Results for Br_2 Concentration Cell

temp (K)	EMF_{theor} (V)	EMF_{exptl} (V)	t_{ion}
373	1.306	1.284	0.983
423	1.270	1.250	0.984
473	1.233	1.210	0.981
523	1.197	1.180	0.986

Table 3 presents the EMF results. The experimental results nearly agreed with theoretical EMF. The ion transference numbers obtained from the EMF method were 0.98−0.99 for all the experimental temperatures. Although the transference number for electrons is increased with an increase in temperature in Figure 4, the t_{ion} value was slightly increased at 523 K. The reactivity between the Br_2 vapor and the RuO_2 electrode may be improved by the elevated temperature. The calculated ion transference number from dc and ac results in Figure 4 is almost 1.00. The t_{ion} value from the Br_2 concentration cell may be approach to 1.00 when the reactivity between the Br_2 vapor and the RuO_2 electrode is improved. This result also suggests that the sole carrier is the Br^- ion for this solid electrolyte.

Conclusion

The electrical properties of the solid electrolyte of the $(1 - x)PbBr_2-xKBr$ system were investigated. The maximum conductivity was 2.7×10^{-6} S·cm^{-1} at 298 K for $0.98PbBr_2-0.02KBr$ sample. A KPb_2Br_5 phase was formed as a second phase with an increase in the x value. The Br^- transference number for the $0.98PbBr_2 \cdot 0.02KBr$ sample is almost 1, as clarified by Tubandt's method, dc conductivity with Au electrodes, and the EMF method. A Br^- conducting electrolyte having a measurable conductivity even at room temperature has not reported until now. This $PbBr_2$-based electrolyte will become one of the new materials in the field of the material chemistry.

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