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An Investigation of the Hebb-Wagner's d-c Polarization Technique I. Steady-state Chemical Potential Profiles in Solid Electrolytes

Jun-ichiro Mizusaki, Kazuo Fueki, and Takashi Mukaibo

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Using an electrochemical cell, Ag/AgX (X=Br or I)/C, the steady-state chemical potential profiles of silver in AgX were determined under d-c polarization conditions. Several Pt probes were attached to the AgX specimens, and the potential differences between the Ag electrode and the Pt probes were measured. It was found that, in order to obtain the correct chemical potential profiles, the Pt probes must be embedded in the specimen to avoid influences of the degradation of AgX at the surface of the specimen. The results obtained by the cell with carefully assembled probes revealed that Wagner's theory holds for AgX.

Hebb-Wagner's d-c polarization technique[1,2] is generally used for the determination of electronic transport numbers of mixed conductors. The cell arrangements employed in this technique are as follows:

⊖ cation reversible electrode/mixed conductor/ion-blocking electrode ⊕ (I)

or;

⊖ ion-blocking electrode/mixed conductor/anion reversible electrode ⊕ (II)

The theory of this technique, originated by Wagner,[2] is based on the assumption that there is no gradient of the electrochemical potential of blocked ions in the steady state; in other words, the driving force due to the electrical potential gradient is cancelled by that due to the chemical potential gradient. The chemical potential profiles in the steady state were calculated theoretically and illustrated graphically by Choudhury and Patterson.[3,4]

Direct measurements of the chemical potential profile in mixed conductors of predominantly electronic conduction were carried out by Hebb (Ag_2S[1]), Miyatani (Ag_2S,[5] Ag_2Te[6]), and Yokota (Cu_2S[7]). The observed results agreed well with those calculated in a similar manner.

As to the mixed conductors of a predominantly ionic conduction, the electrical potential profile of $PbBr_2$[8] has previously been measured. However, no explanation has been given to correlate the observed potential profiles with Wagner's theory.

The purpose of the present study is to measure the chemical potential profiles in ionic conductors, such as AgBr and AgI, using a cell of the (I) type to reveal whether or not Wagner's theory holds in these systems.

Experimental

Circut and Experimental Procedures. The circuit employed for the measurement is shown in Fig. 1. AgX (X=Br or I) was placed between Ag and graphite electrodes to construct a Hebb-Wagner's d–c polarization cell. Several Pt wires were attached to AgX as probes. This cell was placed in an electric furnace, the temperature of which was controlled by means of an electronic controller to within ±1 °C. The potential difference between the Ag and graphite electrodes was kept constant by means of a potentiostat. When the current flowing through the circuit reached a stationary value, the chemical potential profile in a steady-state was determined by measuring the potential differences between the Ag electrode and the Pt probes by means of a high impedance d–c digital voltmeter.

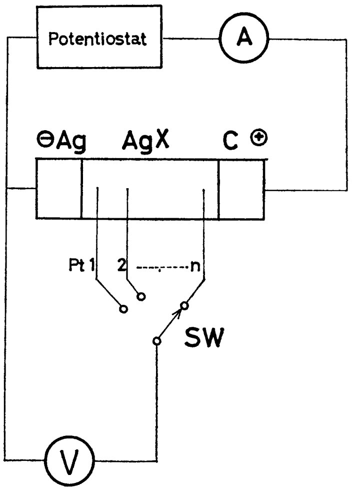

Fig. 1. Circuit diagram for the measurement.

The measurement was performed in a purified nitrogen flow of 2 cm s^{-1} at 350 and 400 °C for AgBr, and 500 °C for AgI.

Cells. Three types of cell arrangements were employed. In the first and second types, Pt probes were embedded in the specimen, while in the third type, Pt probes were in contact with the surface of the specimen.

The first type, Cell (i), is illustrated in Fig. 2. Reagent-grade AgBr was purified 50 times by zone refining and then solidified in a rod-shaped single crystal, 15 mm in length and 10 mm in diameter, by the Bridgeman method. Holes 0.8 mm in diameter were drilled from the side surface to the axis of the AgBr rod. In these holes, Pt wires (0.2 mm in diameter) protected by an alumina tube (0.8 mm in outer diameter and 0.4 mm in inner diameter) were buried as probes so that only the tips of the wires were in contact

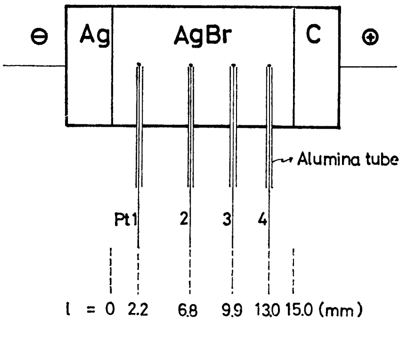

Fig. 2. Arrangement of Cell (i).

with the AgBr rod. The AgBr rod was then sandwiched by Ag and graphite electrodes and pressed by means of a spring to ensure contact.

As AgI experiences a phase transformation at 146 °C, the rod-shaped specimen prepared from the solidification of the molten AgI is quite brittle at room temperature and can not endure mechanical treatment such as the drilling of holes from the side surface. Therefore, instead of the first type, the second type, Cell (ii), was employed for the measurement of AgI. Figure 3 shows the arrangement of Cell (ii). Three pellets, 10 mm in diameter and *a*, *b*, and *c* mm thick respectively, were prepared by pressing reagent-grade AgI in a die. An Ag electrode, three AgI pellets, and a graphite electrode were assembled in series. The Ag and graphite electrodes and two of the AgI pellets, *a* and *c* mm thick, have holes, 0.8 mm in diameter, along the axis. Pt wires protected by an alumina tube were inserted in the holes from both ends, so that their tips were in contact with the end surfaces of the middle AgI pellet, *b* mm thick. In Cell (ii-A), the thicknesses of the AgI pellets employed were $a=3.0$ mm, $b=5.7$ mm and $c=1.1$ mm, and in Cell (ii-B), $a=1.1$ mm, $b=6.0$ mm, and $c=3.0$ mm.

The third type, Cell (iii-A) or Cell (iii-B), consists of an AgBr or AgI rod, 10 mm in diameter, solidified from the melt. Pt probes were wound around the rod at appropriate intervals. The rod was then sandwiched between Ag and graphite electrodes. The arrangement of Cell (iii-B) is shown in Fig. 4.

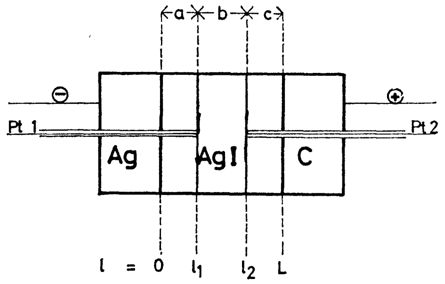

Fig. 3. Arrangement of Cell (ii).

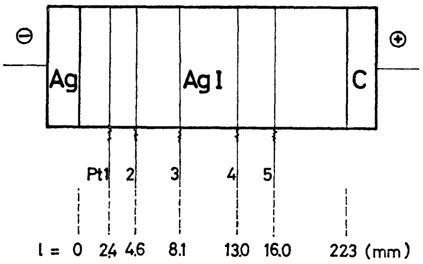

Fig. 4. Arrangement of Cell (iii-B).

Results and Discussion

The experimental results obtained by the use of Cell(i) and Cell(iii-A) are shown in Fig. 5. Those obtained by the use of Cell (ii) and Cell(iii-B) are shown in Fig. 6. The steady-state was attained within 48 hours.

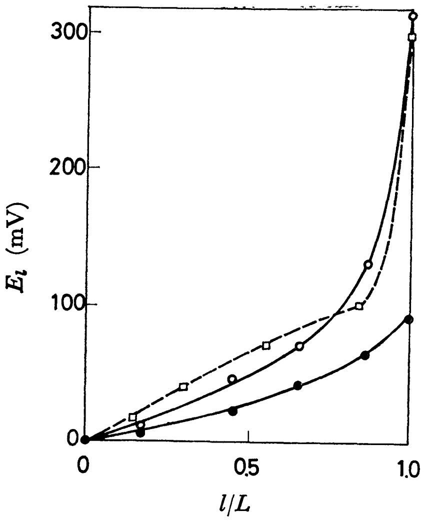

Fig. 5. Steady-state potential profiles of AgBr at 400 °C. ●; Cell(i), $E_L=93$ mV, $i=1.0$ μA cm^{-2}, $L=15.0$ mm. ○; Cell(i), $E_L=318$ mV, $i=1.4$ μA cm^{-2}. □; Cell(iii-A), $E_L=300$ mV, $i=2.3$ μA cm^{-2}, $L=10.8$ mm.

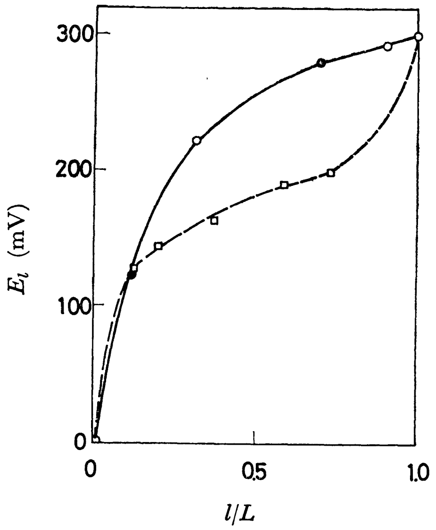

Fig. 6. Steady-state potential profiles of AgI at 500 °C. ○; Cell(ii-A), $E_L=300$ mV, $i=57$ μA cm^{-2}, $L=9.8$ mm. ●; Cell(ii-B), $E_L=300$ mV, $i=38$ μA cm^{-2}, $L=10.3$ mm. □; Cell(iii-B), $E_L=300$ mV, $i=45$ μA cm^{-2}, $L=22.3$ mm.

Chemical Potential Profiles in the Steady-state. When AgX shows an n-type electronic conduction, μ_{Ag}, the chemical potential of silver in AgX in a steady-state, is represented in the same manner as is used in Wagner's theory, by this equation;

$$il = \frac{\sigma_e^0 RT}{F}\left\{1-\exp\left(\frac{\mu_{Ag}(l)-\mu_{Ag}^0}{RT}\right)\right\} \qquad (1)$$

where μ_{Ag}^0 is the μ_{Ag} of metallic silver, $\mu_{Ag}(l)$ is μ_{Ag} distance of l from the Ag/AgX interface, and σ_e^0 is the electronic conductivity of AgX at the Ag/AgX interface. At the AgX/C interface, $l=L$; therefore,

$$iL = \frac{\sigma_e^0 RT}{F}\left\{1-\exp\left(\frac{\mu_{Ag}(L)-\mu_{Ag}^0}{RT}\right)\right\} \qquad (2)$$

From Eqs. (1) and (2), we obtained:

$$\frac{l}{L}=\frac{1-\exp\left(\dfrac{\mu_{\mathrm{Ag}}(l)-\mu_{\mathrm{Ag}}{}^{0}}{RT}\right)}{1-\exp\left(\dfrac{\mu_{\mathrm{Ag}}(L)-\mu_{\mathrm{Ag}}{}^{0}}{RT}\right)} \tag{3}$$

In the case of p-type AgX

$$il=\frac{\sigma_{\mathrm{h}}{}^{0}RT}{F}\left\{\exp\left(\frac{\mu_{\mathrm{Ag}}{}^{0}-\mu_{\mathrm{Ag}}(l)}{RT}\right)-1\right\} \tag{4}$$

where $\sigma_{\mathrm{h}}{}^{0}$ is the conductivity due to hole conduction at the Ag/AgX interface. Therefore,

$$\frac{l}{L}=\frac{\exp\left(\dfrac{\mu_{\mathrm{Ag}}{}^{0}-\mu_{\mathrm{Ag}}(l)}{RT}\right)-1}{\exp\left(\dfrac{\mu_{\mathrm{Ag}}{}^{0}-\mu_{\mathrm{Ag}}(L)}{RT}\right)-1} \tag{5}$$

Eqs. (3) and (5) represent the relationship between $(\mu_{\mathrm{Ag}}(l)-\mu_{\mathrm{Ag}}{}^{0})$ and l/L for n-type and p-type AgX respectively.

Comparison of the Experimental Results with the Theoretical Results. Under the present experimental conditions, the Ag electrode at the Ag/AgX interface acts as a reversible electrode for both silver ions and electrons, while at the Pt/AgX or C/AgX interface, the Pt or graphite electrode is chemically inert in effect and reversible only for electrons. Therefore, the electrical potential difference, E_l, between the Pt electrode at l and the Ag electrode is written as:

$$E_lF=\eta_{\mathrm{e}}{}^{0}-\eta_{\mathrm{e}}(l) \tag{6}$$

where $\eta_{\mathrm{e}}{}^{0}$ and $\eta_{\mathrm{e}}(l)$ are the electrochemical potentials of electrons in AgX at the Ag/AgX interface and that at l respectively. Under the ion-blocking conditions, the electrochemical potential of silver ions is constant throughout the cell; therefore,

$$\eta_{\mathrm{Ag}^{+}}{}^{0}=\eta_{\mathrm{Ag}^{+}}(l) \tag{7}$$

Therefore, we can obtain from Eqs. (6) and (7):

$$E_lF=\mu_{\mathrm{Ag}}{}^{0}-\mu_{\mathrm{Ag}}(l) \tag{8}$$

In the same manner, the potential difference, E_L, between the Ag electrode and the graphite electrode located at L is:

$$E_LF=\mu_{\mathrm{Ag}}{}^{0}-\mu_{\mathrm{Ag}}(L) \tag{9}$$

The insertion of Eqs. (8) and (9) into (3) and (5) yields:

$$\frac{l}{L}=\frac{1-\exp\left(-\dfrac{E_lF}{RT}\right)}{1-\exp\left(-\dfrac{E_LF}{RT}\right)} \tag{10}$$

and:

$$\frac{l}{L}=\frac{\exp\left(\dfrac{E_lF}{RT}\right)-1}{\exp\left(\dfrac{E_LF}{RT}\right)-1} \tag{11}$$

The experimntal results for AgBr are represented in Fig. 7 as a plot of l/L *vs.* $\dfrac{1-\exp\left(-\dfrac{E_lF}{RT}\right)}{1-\exp\left(-\dfrac{E_LF}{RT}\right)}$, while those for AgI are given in Fig. 8 as a plot of l/L *vs.* $\dfrac{\exp\left(\dfrac{E_lF}{RT}\right)-1}{\exp\left(\dfrac{E_LF}{RT}\right)-1}$. In the Figure, the results obtained by the use of Cells(i) and (ii), in which the Pt probes embedded in the specimens show a good linearity. This indicates that Eq. (10) holds in Cell(i) and Eq. (11) in Cell(ii). Therefore, it may be concluded that AgBr and AgI are n-type and p-type conductors respectively under the present experimental conditions, as was found by Ilschner[9] and Raleigh,[10] and that Wagner's theory holds for the mixed conductors of a predominantly ionic conduction.

However, the results obtained by using Cell(iii),

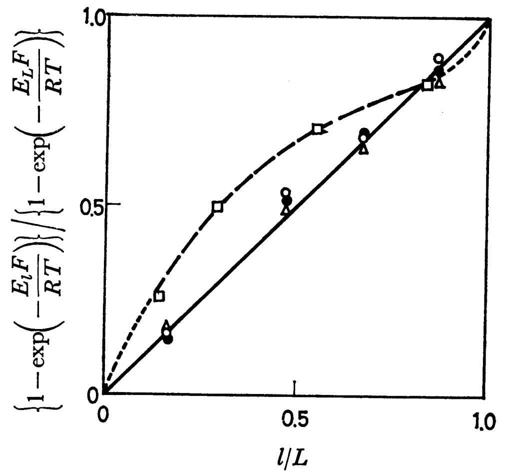

Fig. 7. Comparison of experimental results with theoretical one about AgBr.
Solid line; theoretical result
○; Cell(i), E_L=318 mV, 400 °C.
●; Cell(i), E_L=93 mV, 400 °C.
△; Cell(i), E_L=300 mV, 350 °C, i=0.1 μA cm^{-2}.
□; Cell(iii-A), E_L=300 mV, 400 °C.

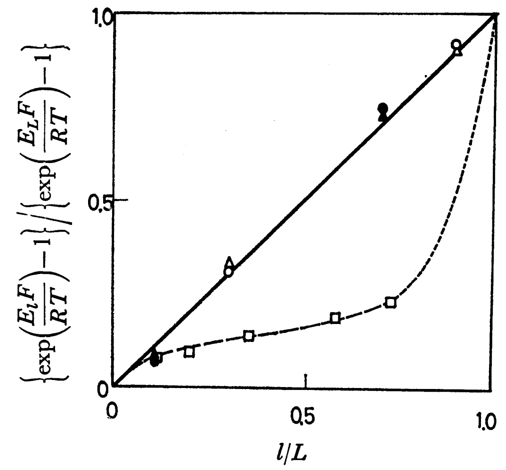

Fig. 8. Comparison of experimental results with theoretical one about AgI, 500 °C.
Soild line; theoretical result
○; E_L=300 mV, Cell(ii-A).
△; E_L=350 mV, Cell(ii-A).
●; E_L=300 mV, Cell(ii-B).
▲; E^{L}=350 mV, Cell(ii-B).
□; E_L=300 mV, Cell(iii-B).

in whish Pt probes are placed in contact with the surface of a specimen, do not agree with Wagner's theory.

Electronical Conductivity of AgBr. Inserting the values of a steady-state current, the applied potential difference, E_L, and the sample length, L, of Cell(i) into Eqs. (2) and (8), one obtains $3.0\times10^{-6}\ \mho\ \mathrm{cm}^{-1}$ (350 °C) and $4.0\times10^{-5}\ \mho\ \mathrm{cm}^{-1}$ (400 °C) as the $\sigma_\mathrm{e}{}^0$ of AgBr. These values are in good agreement with the results obtained by Ilschner.

The Effect of the Degradation of AgI at the AgI/C Interface on the Potential Profiles. Using Eqs. (3) and (8), the $\sigma_\mathrm{h}{}^0$ of AgI at 500 °C was calculated. The result obtained from Cell(ii-A) was $9.5\times10^{-6}\ \mho\ \mathrm{cm}^{-1}$. However, this value is about one order of magnitude larger than the value obtained by the extrapolation of Ilschner's data.[9] This fact suggests that the current passed through AgI might be an ionic current due to the degradation of AgI at the AgI/C interface.

When the ionic current is predominant in AgI, the ionic current, i_ion, correlates with the electrochemical potential difference of Ag^+ between Ag and graphite electrodes as follows:

$$\eta_{\mathrm{Ag}^+}(L) - \eta_{\mathrm{Ag}^+}{}^0 = \frac{i_\mathrm{ion}LF}{\sigma_\mathrm{i}} \tag{12}$$

where σ_i represents the ionic conductivity of AgI. The length of the AgI specimen used in this work is less than 2.23 cm, the current density is less than 180 $\mu\mathrm{A/cm}^2$, and the σ_i of AgI at 500 °C is $2.5\ \mho\ \mathrm{cm}^{-1}$.[11] Therefore, $i_\mathrm{ion}L/\sigma_\mathrm{i} < 0.16$ mV. It is evident that the drop of the electrochemical potential of silver ions in the AgI specimen is negligibly small compared to the observed potential differences. Therefore, Eq. (7) holds in the present system and the observed potential profiles coincide with those under the complete ion-blocking conditions.

The Effect of the Degradation of AgX at the Side Surface of the Specimen on the Potential Profile. The equilibrium halogen vapor pressure with regard to each observed silver chemical potential can be calculated from the standard free energy of the formation of AgX and the equilibrium constant of the $\mathrm{X}_2 = 2\mathrm{X}$ reaction. As for AgBr in Fig. 5, the chemical potential near the AgBr/C interface corresponds to the bromine vapor pressure of the order of 10^{-8} atm, whereas those of the other part of the AgBr rod corresponds to the order of 10^{-10}—10^{-11} atm; as for AgI in Fig. 6, most of the AgI rod corresponds to the iodine vapor pressure of the order of 10^{-4}—10^{-5} atm. Therefore, a large difference in equilibrium halogen-vapor pressure exists between the nitrogen atmosphere and the AgX rod, resulting in the degradation of AgX at the surface of the rod.

As in Cells(i) and (ii), Pt probes were embedded in the specimen, whereas in Cell(iii) Pt probes were attached to the surface of the specimen; the disagreement of the results obtained by the use of Cell(iii) with the theoretical values may be due to this degradation of the AgX surface.

In conclusion, we must embed the Pt probes in the specimen in order to observe the correct chemical potential profiles in a solid electrolyte.

Summary

(i) Using an electrochemical cell, Ag/AgBr (or AgI)/C, the steady-state chemical potential profiles in AgBr and AgI were measured under the d-c polarization conditions.

(ii) It was found that Wagner's theory holds for mixed conductors of a predominantly ionic conduction.

(iii) It was concluded that Pt probes must be embedded in AgX in order to obtain the correct chemical potential profile.

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