Transport Properties of the Mixed-Conductivity Compound Ag$_{1.92}$Te at 160°C

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The transport properties of the mixed-conductivity compound Ag$_{1.92}$Te have been investigated within its homogeneity range at a temperature of 160°C. The composition dependence of the chemical diffusion coefficient has been obtained from galvanostatic polarization experiments on the asymmetric cell Ag | AgI | Ag$_{1.92}$Te | Pt employing coulometric titrations for composition variation. Evaluation formulas for mixed conductors with arbitrary electronic transport numbers permit the determination of the chemical diffusion coefficient of Ag$_{1.92}$Te. The electronic transport numbers needed for the calculations have been obtained from separate measurements of the partial conductivities. The chemical diffusion coefficient decreases slightly with decreasing silver content with typical values around 0.004 cm^2 s^{-1}. The electronic conductivity increases with decreasing silver content with values in the range of 4–10 S cm^{-1}, while the ionic conductivity is independent of silver activity, with typical values around 0.9 S cm^{-1}. The electronic properties have been interpreted in terms of a simple model considering nondegenerate electrons and nondegenerate holes. © 1997 Academic Press

1. INTRODUCTION

The transport properties of mixed ionic–electronic conductors like transition metal oxides or chalcogenides were discussed in several fundamental contributions in the past; see for example Refs. (1–6). The dependence of the transport properties (chemical diffusion coefficient, ionic and electronic conductivity) on the nonstoichiometry of mixed conductors was investigated in detail (2, 7, 8). The concepts of irreversible thermodynamics concerning mass transport in mixed conductors were discussed by Wagner (2); additionally, transport phenomena in the presence of internal defect reactions were considered by Maier (9).

The high-temperature modifications of the silver chalcogenides are typical examples for mixed-conductivity compounds. These compounds show simple defect chemistry, as no internal defect reactions occur which would lead to ionic defects with variable charges. In general, the silver cations of

the high-temperature phases are randomly distributed, leading to structural cationic disorder and to high ionic conductivities. According to the phase diagram of silver and tellurium (10) three intermetallic compounds, viz. Ag$_2$Te, Ag$_{1.92}$Te, and Ag$_5$Te$_3$, exist in this binary system above 120°C. Ag$_2$Te shows fairly small deviations from the ideal stoichiometric composition, while Ag$_{1.92}$Te and Ag$_5$Te$_3$ are stable in relatively broad composition ranges. Among others, Miyatani *et al.* (11–13), Kellers *et al.* (14), and Sitte *et al.* (15–18) studied the transport properties of Ag$_2$Te. A detailed investigation of the transport properties of Ag$_5$Te$_3$ can be found in Ref. (19).

Recently, we have investigated the theory of galvanostatic processes in mixed conductors with arbitrary electronic transport numbers. Hence, we have been motivated in performing experimental studies on the transport properties of Ag$_{1.92}$Te, which can be regarded as a typical example of a mixed conductor with comparable ionic and electronic conductivities. The chemical diffusion coefficients are determined by galvanostatic polarization experiments on an asymmetric electrochemical cell using formulas derived for the general case of mixed conductors with comparable ionic and electronic conductivities (20, 21). The ionic and electronic conductivities are measured independently, using the van der Pauw technique (22–24) in a recently developed cell (18). The composition of the mixed-conductivity compound is varied in situ by application of coulometric titration (25) with high stoichiometric resolution. In addition, the conductivity data will be interpreted by using a simple model introduced by Valverde (7, 8).

2. APPLICATION OF CHRONOPOTENTIOMETRY TO THE DETERMINATION OF THE CHEMICAL DIFFUSION COEFFICIENT

Galvanostatic polarization experiments on the asymmetric electrochemical cell

$$\text{Ag} \mid \frac{\text{AgI}}{\text{Ag}_{\text{ref}}} \mid \text{Ag}_{1.92}\text{Te} \mid \text{Pt} \qquad [\text{I}]$$
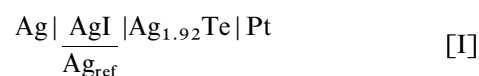
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containing an electronically blocking electrode at position $x = 0$ (Ag|AgI) and an ionically blocking electrode (Pt) at position $x = L$ are performed to determine the chemical diffusion coefficient of the mixed-conductivity compound $Ag_{1.92}Te$ as a function of composition. As the electronic transport number of $Ag_{1.92}Te$ is expected to deviate from unity (1, 11), the evaluation formulas for the determination of chemical diffusion coefficients by means of galvanostatic polarization experiments must be modified (20, 21). Since the theory of galvanostatic processes in mixed conductors with arbitrary electronic transport numbers is beyond the scope of this work, only a short summary of the derivation of the pertinent evaluation formulas for the determination of the chemical diffusion coefficient will be given here.

According to Refs. (20, 21) the relationship between the voltage response U of cell [I] due to a galvanostatic current step and the deviation of the diffusant concentration from the equilibrium value $c_{Ag, 0}$ at the ionic electrode $\Delta c_{Ag}(0)$ and the electronic electrode $\Delta c_{Ag}(L)$ reads

$$U = -\frac{jL}{\sigma} - \frac{t_e}{F}\frac{RT\vartheta}{c_{Ag, 0}}\Delta c_{Ag}(0) - \frac{t_i}{F}\frac{RT\vartheta}{c_{Ag, 0}}\Delta c_{Ag}(L) \quad [1]$$

with $j, L, \sigma, t_e, t_i, F, R, T,$ and ϑ denoting the total current density, the length of the bar-shaped sample, the total conductivity, the electronic and ionic transport number, the Faraday constant, the gas constant, the absolute temperature, and the thermodynamic factor of the mobile neutral species ($\vartheta = d \ln a_{Ag}/d \ln c_{Ag}$, with a_{Ag} being the activity of silver) (4), respectively. The deviation of the diffusant concentration from its equilibrium value is found by solving Fick's second law of diffusion

$$\frac{\partial c_{Ag}}{\partial t} = \tilde{D}\frac{\partial^2 c_{Ag}}{\partial x^2}, \quad [2]$$

where $\tilde{D}$ is the chemical diffusion coefficient. In the case of a mixed conductor with comparable ionic and electronic conductivities the direct current fed through cell [I] will stimulate chemical diffusion processes at the electronically as well as at the ionically blocking electrode. Therefore, the boundary conditions for the *polarization process* can be written as

$$\frac{\partial c_{Ag}}{\partial x} = -\frac{t_e j}{F\tilde{D}} \quad [3a]$$

at the ionic (electronically blocking) electrode, and

$$\frac{\partial c_{Ag}}{\partial x} = \frac{t_i j}{F\tilde{D}} \quad [3b]$$

at the electronic (ionically blocking) electrode, respectively. Inserting the short-time approximation of the solution to Eqs. [2] and [3] into Eq. [1] results in

$$U = -\frac{jL}{\sigma} - \frac{2jRT\vartheta\sqrt{t}}{F^2 c_{Ag, 0}\sqrt{\pi\tilde{D}}}(t_e^2 + t_i^2). \quad [4]$$

For sufficiently long polarization times ($t \gg L^2/4\tilde{D}$) the long-time approximation of the polarization voltage is given by

$$U = -\frac{jLRT\vartheta}{F^2\tilde{D}c_{Ag, 0}}\left(\frac{\tilde{D}t}{L^2} + \frac{1}{3}\right). \quad [5]$$

According to Eq. [4] the voltage response varies linearly with the square root of time for short polarization times as illustrated in Fig. 1. The experimental data of Fig. 1 were obtained from polarization experiments on cell [I] at an emf of 174 mV and a polarization current of 0.5 mA. The slope k of this straight line can be expressed as

$$k = -\frac{2jRT\vartheta}{F^2 c_{Ag, 0}\sqrt{\pi\tilde{D}}}(t_e^2 + t_i^2). \quad [6]$$

A plot of the voltage response versus time is shown in Fig. 2. In agreement with Eq. [5], a straight line is observed at quite long polarization times with the slope k' being

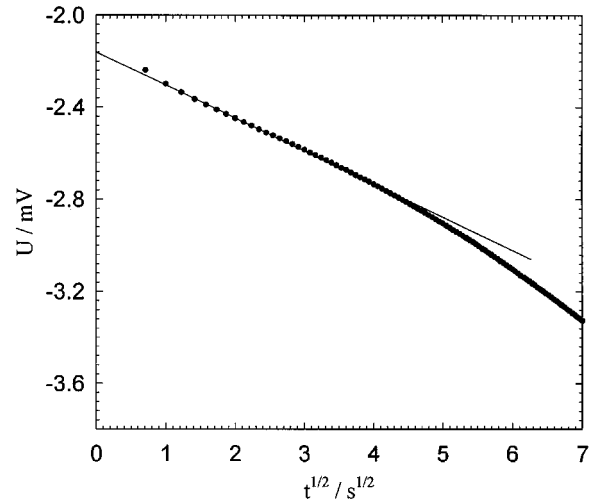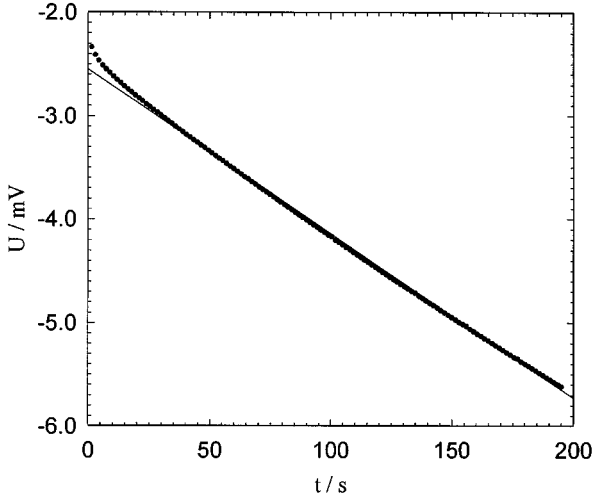$$k' = -\frac{jRT\vartheta}{(zF)^2 L c_{Ag, 0}}. \quad [7]$$

FIG. 1. Voltage response of the cell $Ag|AgI|Ag_{1.92}Te|Pt$ versus square root of time for a polarization experiment ($E = 174\,mV$, $I = 0.5\,mA$, $T = 160°C$); $k = -0.1457\,mV\,s^{-1/2}$.

FIG. 2. Voltage response of the cell Ag | AgI | Ag$_{1.92}$Te | Pt versus time; same conditions as those described in the legend of Fig. 1: $k' = -0.01593\,\mathrm{mV\,s^{-1}}$.

FIG. 3. ΔU plotted as a function of $t^{1/2}$ for a depolarization process ($E = 174\,\mathrm{mV}$, $I = 0.5\,\mathrm{mA}$, $T = 160°\mathrm{C}$); $k = -0.150\,\mathrm{mV\,s^{-1/2}}$.

The chemical diffusion coefficient is given by the ratio of the slopes k' and k

$$\tilde{D} = \left[2\,\frac{k'L}{k\sqrt{\pi}}(t_e^2 + t_i^2) \right]^2. \qquad [8]$$

After switching off the current, the cell voltage relaxes until a new thermodynamic equilibrium is established. Thus, the boundary condition for the *depolarization process* at both electrodes reads
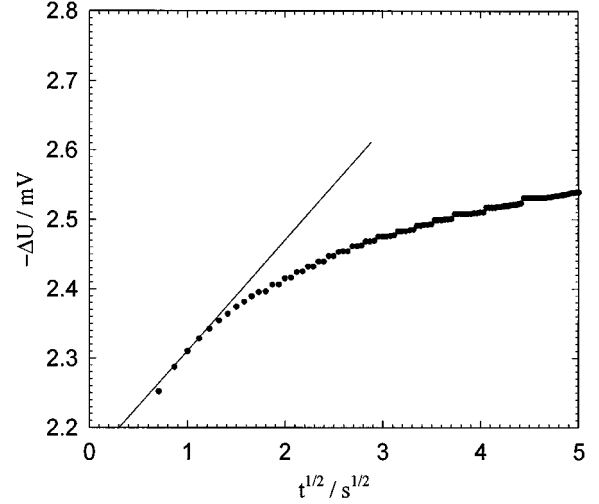
$$\frac{\partial c_{Ag}}{\partial x} = 0. \qquad [9]$$

The exact solution for the depolarization process can be found in Ref. (20), whereas only the short-time approximation is presented here

$$U(t) = -\frac{jLRT\vartheta}{F^2\tilde{D}c_{Ag,0}} \left[\left(\frac{\tilde{D}t}{L^2} + \frac{\tilde{D}t_p}{L^2} + \frac{1}{3} - \frac{2\sqrt{\tilde{D}t}}{L\sqrt{\pi}} \right)(t_e^2 + t_i^2) \right.$$

$$\left. + \left(\frac{\tilde{D}t}{L^2} + \frac{\tilde{D}t_p}{L^2} - \frac{1}{6} \right) 2t_e t_i \right], \qquad [10]$$

t_p being the polarization time. The difference between the polarization voltage at the end of the polarization process (Eq. [5]) and the short-time depolarization voltage (Eq. [10]) is

$$\Delta U = -\frac{jL}{\sigma} - \frac{jLRT\vartheta}{F^2\tilde{D}c_{Ag,0}} \left[\frac{2\sqrt{\tilde{D}t}}{L\sqrt{\pi}}(t_e^2 + t_i^2) - \frac{\tilde{D}t}{L^2} \right], \quad [11]$$

noting that $\sigma = (zF)^2\tilde{D}c_{Ag,0}/(RT\vartheta t_e t_i)$ (1). A plot of the difference ΔU as a function of $t^{1/2}$ is shown in Fig. 3 for a depolarization experiment on cell [I] at an emf of 174 mV and a current of the preceding polarization experiment of 0.5 mA. Figure 3 confirms the linear behavior of the ΔU versus $t^{1/2}$ plot at very short times, as the linear term in t of Eq. [11] can be neglected. Again, the slope k of this straight line is given by Eq. [6]. If one plots the difference between $kt^{1/2}$ and ΔU versus t, a straight line is expected yielding the slope k' given by Eq. [7]. Experimental results for the determination of the slope k' are shown in Fig. 4 and analogously to the polarization experiment the chemical diffusion coefficient is obtained from Eq. [8].
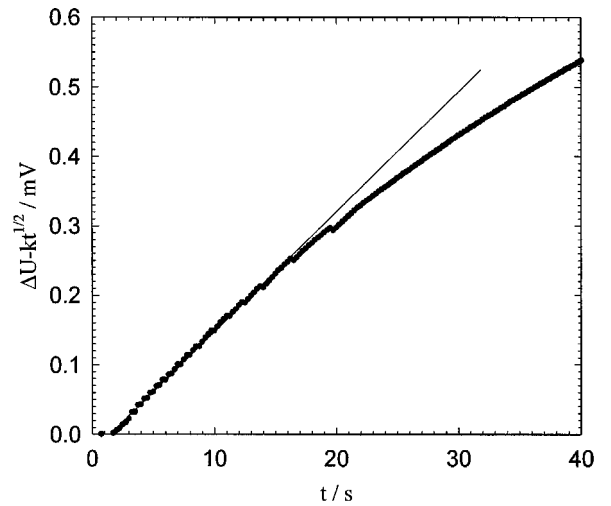
FIG. 4. $(\Delta U - kt^{1/2})$ vs t plot; same conditions as those described in the legend of Fig. 3; $k' = -0.01733\,\mathrm{mV\,s^{-1}}$.

Obviously, the electronic and ionic transport numbers must be known in order to determine the chemical diffusion coefficient using Eq. [8]. If the electronic transport number is close to $t_e \approx 1$, the evaluation formula (Eq. [8]) reduces to the well-known expression

$$\tilde{D} = \left(\frac{2k'L}{k}\right)^2 \Big/ \pi \qquad [12]$$

which was successfully applied to many mixed conductors with predominantly electronic conduction (26, 27).

3. EXPERIMENTAL

Polycrystalline samples of $Ag_{1.92}Te$ were prepared by solid-state coulometric titration at a temperature of 160°C using the same cell as described for the polarization measurements. Commercially available Ag_2Te (99.99%, Johnson Matthey) was used as the starting material. At the desired composition ($Ag_{1.920}Te$ at an emf of 150.6 mV) the material was ground and pressed into disk-shaped samples for the subsequent conductivity or diffusion measurements.

The ionic and electronic conductivities of $Ag_{1.92}Te$ were measured simultaneously at a temperature of 160°C by applying a dc four-point van der Pauw technique (18). Here a disk-shaped powder compact of a thickness of 0.924 mm, a diameter of 10 mm, and a weight of 0.52545 g served as sample. Four peripheral ionic electrodes ($Ag|AgI$) positioned at the bottom of the sample were used for the ionic conductivity measurements, while four peripheral electronic electrodes (Pt) mounted at the upper surface of the sample were applied to the determination of the electronic conductivities. The composition of the sample was changed by coulometric titration. The ionic current fed through the ionic electrodes was typically amounted to 50 μA and the electronic current amounted to 250 μA resulting in typical probe voltages of 50–150 μV. More details about the simultaneous measurements of the ionic and electronic conductivities as a function of composition can be found in Ref. (18).

The specimen used for the polarization experiments on the asymmetric cell [I] at 160°C was prepared by pressing 1.3623 g of $Ag_{1.92}Te$ into a tablet of 6-mm diameter and 6.090-mm length. The ionic electrode was composed of a silver iodide tablet serving as solid electrolyte and a silver bar as silver source or sink. A silver wire was wound around the electrolyte, representing the reference electrode. The electronic electrode was simply a platinum plate and all compartments of the cell were held together by light spring action. The polarization current applied to cell [I] typically amounted to 0.5 mA and the voltage response measured between the platinum plate and the reference electrode (silver wire) was around 3–5 mV at the end of the polariza-

tion process. In addition, this cell was applied to the determination of the coulometric titration curve of $Ag_{1.92}Te$, as the composition of the sample was modified *in situ* by performing coulometric titrations.

All experiments were carried out in a sealed quartz apparatus under a constant helium flow in order to exclude traces of moisture and oxygen. The emf as well as the time-dependent cell voltage were measured by a high-impedance multimeter (Keithley 199). The coulometric titrations as well as the polarization experiments were performed using a precision current source (Knick J152). The electronic and ionic conductivity measurements were carried out by means of a multimeter with scanner (Keithley 199) connected to a dc voltage amplifier (Knick C3050) and a direct current source (Knick J152). The temperature was controlled by means of a precision temperature controller (Eurotherm 818) within 0.2 K, employing chromelalumel thermocouples. A personal computer served as data acquisition system connecting the measuring instruments by means of IEEE interfaces.

4. RESULTS AND DISCUSSION

The ionic and electronic conductivities of $Ag_{1.92}Te$ measured as a function of the emf E of cell [I] at a temperature of 160°C are illustrated in Fig. 5. The electronic conductivity σ_e (filled squares) increases with decreasing silver activity of the specimen (increasing emf of cell [I]), while the ionic conductivity σ_i (filled circles) is almost independent of the silver content of the sample. Our results obtained from simultaneous dc measurements applying the van der Pauw method are in satisfactory agreement with results found in the literature (1, 11, 24). The coulometric titration curve E versus y of Ag_yTe ($1.912 < y < 1.920$) at 160°C is shown in

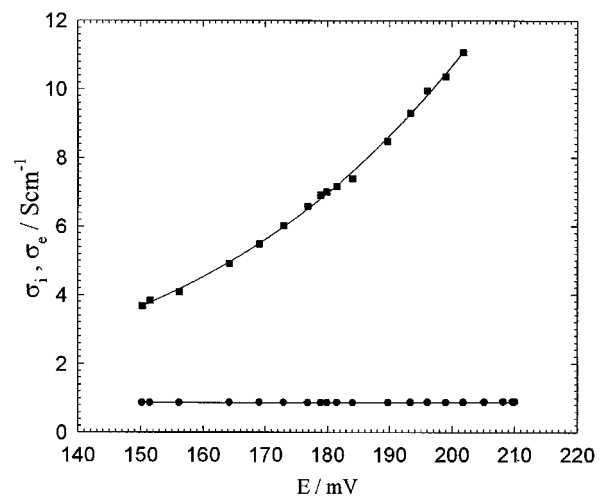**FIG. 5.** Electronic (filled squares) and ionic (filled circles) conductivities as a function of the emf of the cell $Ag|AgI|Ag_{1.92}Te|Pt$ at 160°C.

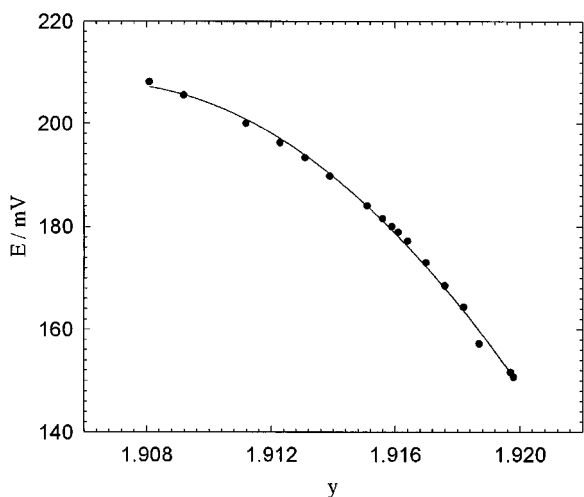**FIG. 6.** Coulometric titration curve E versus y of $Ag_{1.92}Te$ at 160°C.

Fig. 6. As the emf is given by

$$-FE = \mu_{Ag} - \mu_{Ag}^{\ominus}, \qquad [13]$$

the equilibrium cell voltage decreases with increasing silver activity (silver content) of the sample, see Fig. 6.

The chemical diffusion coefficient of $Ag_{1.92}Te$ at 160°C as determined by application of chronopotentiometry to cell [I] is plotted as a function of the emf of cell [I] in Fig. 7. The electronic transport number results from the partial conduc-
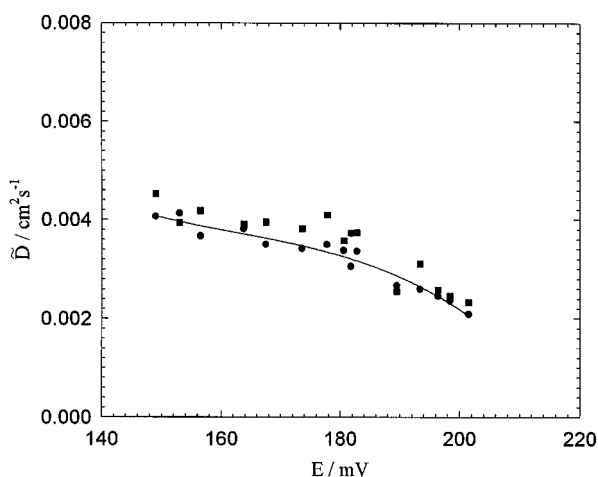

FIG. 7. Variation of the chemical diffusion coefficient as a function of the emf of the cell $Ag|AgI|Ag_{1.92}Te|Pt$ at 160°C. Filled circles and filled squares correspond to polarization (switching on) and depolarization (switching off) experiments, respectively. The solid line is a least-square fit as a guide to the eye.

tivities given in Fig. 5

$$t_e = \frac{\sigma_e}{\sigma}; \quad \sigma = \sigma_e + \sigma_i, \qquad [14a]$$

while the ionic transport number is obviously given by

$$t_i = \frac{\sigma_i}{\sigma}; \quad t_e + t_i = 1. \qquad [14b]$$

As the electronic transport number is in the range 0.80–0.91, correct values of the chemical diffusion coefficient can be obtained only by using Eq. [8] instead of Eq. [12]. The filled circles in Fig. 7 refer to the results obtained from polarization (switching on) experiments and the filled squares represent the depolarization (switching off) experiments. In contrast to structurally disordered Ag_2Te (16, 17) or Ag_5Te_3 (19) the chemical diffusion coefficient of $Ag_{1.92}Te$ at 160°C decreases slightly with decreasing silver activity of the sample and shows no maximum. Structural cationic disorder can also be expected in the case of $Ag_{1.92}Te$ due to the composition independent and fairly high values of the ionic conductivity (0.9 S cm^{-1}). As a maximum in a $\tilde{D}$ versus E plot corresponds to an inflection point of the coulometric titration curve at the same emf value (15), the absence of both an inflection point of the coulometric titration curve (Fig. 6) and a maximum in Fig. 7 confirms the reliability of our results.

The variation of the electronic conductivity with composition of the mixed conductor can be interpreted in terms of a simple model introduced by Valverde (7, 8) involving nondegenerate electrons in the conduction band and nondegenerate holes in the valence band. According to Valverde, the shape of the coulometric titration curve (plot of emf E versus y of Ag_yTe) is given by

$$y = y^0 - 2x_e^0 \sinh\left[\frac{F(E - E^0)}{RT}\right] \qquad [15]$$

with x_e^0 denoting the mole fraction of the electrons at the stoichiometric point. The superscript refers to the stoichiometric composition of the compound $Ag_{1.92}Te$. When the holes are nondegenerate, a plot of y versus $\exp(FE/RT)$ will yield a straight line at emf values satisfying the condition $E \gg E^0$, see Eq. [15]. Figure 8 represents such a plot obtained from the coulometric titration curve shown in Fig. 6. The straight line in Fig. 8 provides evidence for the nondegenerate nature of the holes. Additionally, the holes are the dominating electronic defects in almost the whole stability range of the compound, as the influence of the electrons will lead to a deviation from linearity. The intercept of the straight line at the ordinate axis yields the parameter $y^0 = 1.9225$ and the slope $x_e^0 \exp(-FE^0/RT)$ amounts to
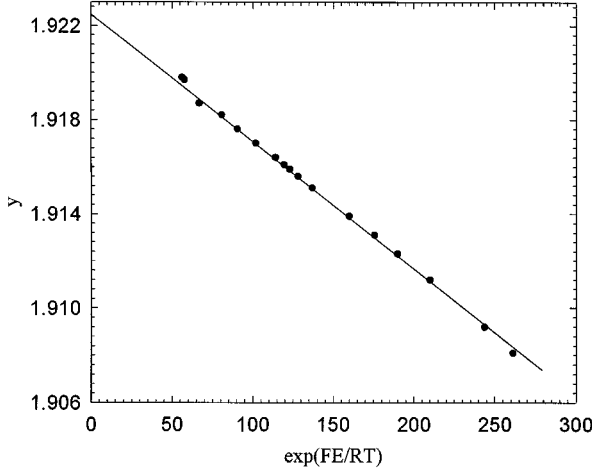
FIG. 8. The parameter y of Ag_yTe plotted versus the function $\exp(FE/RT)$ for the determination of the stoichiometric point of $Ag_{1.92}Te$ at 160°C.
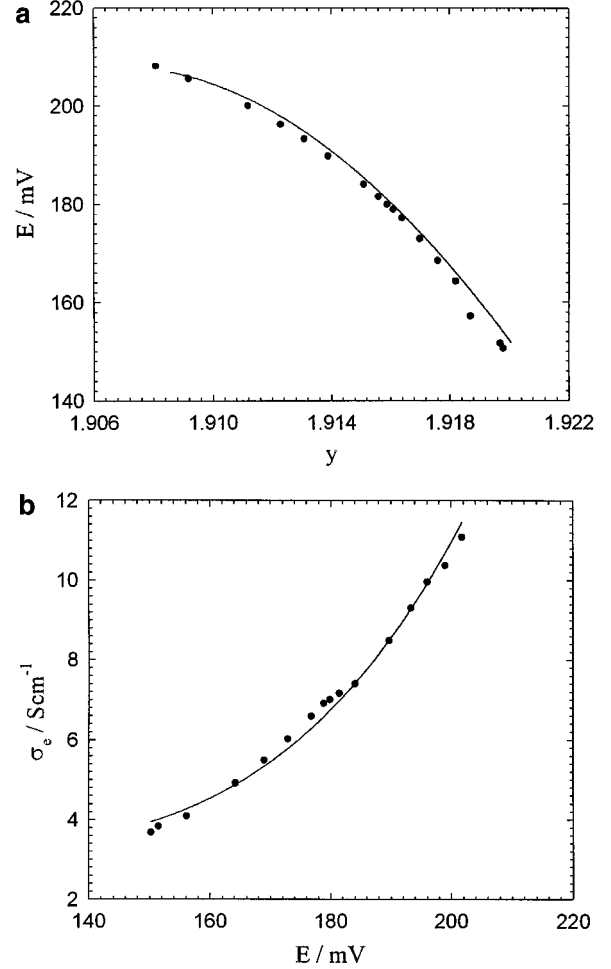
5.33×10^{-5}. Finally, a fit of Eq. [15] to the experimental data of Fig. 6 results in the characteristic parameters given in Table 1. As the stoichiometric point ($y^0 = 1.9225$, $E^0 = 120.13$ mV) obtained from the fitting procedure is far beyond the stability range of $Ag_{1.92}Te$, the condition $E \gg E^0$ noted above is certainly fulfilled. Therefore, one can deduce that the mole fraction of the electrons is much smaller than the mole fraction of the holes. Assuming electrons as well as holes to be nondegenerate, the electronic conductivity can be written as

$$
\sigma_e = \frac{Fx_e^0}{V_m} \left\{ b_e \exp\left[-\frac{F(E - E^0)}{RT} \right] \right.
$$

$$
\left. + b_h \exp\left[\frac{F(E - E^0)}{RT} \right] \right\}, \qquad [16]
$$

where the molar volume V_m of $Ag_{1.92}Te$ amounts to 42.6 cm^3 mol^{-1}. The symbols b_e and b_h denote the mobility of electrons and holes, respectively. The fit of Eq. [16] to the electronic conductivities of Fig. 5 yields the parameters b_e and b_h which are also included in Table 1. The perfect coincidence between the measured data and the calculated curves applying Eqs. [15] and [16] together with the para-

FIG. 9. (a) Comparison between the theoretical coulometric titration curve (solid line) calculated from Eq. [15] and experimental data (filled circles). (b) Experimentally determined electronic conductivities (filled circles) compared to calculated values (solid line) by taking Eq. [16] into account.

meter set given in Table 1, is shown in Fig. 9. Recently, in contrast to the model used here, the composition dependence of the electronic conductivity of α-Ag_2Te at 300°C has been interpreted in terms of degenerate electrons and nondegenerate holes (18). Hence, electrons as well as holes are essential for the description of the electronic transport properties of α-Ag_2Te, whereas in the case of $Ag_{1.92}Te$ the holes are the significant electronic defect type. It must be concluded that the mixed conductor $Ag_{1.92}Te$ can be regarded as a nondegenerate semiconductor at least at a temperature of 160°C.

5. SUMMARY

This work is a first example for the investigation of the composition dependence of the chemical diffusion

TABLE 1
Characteristic Parameters of the Electronic Transport Properties of $Ag_{1.92}Te$ at 160°C

y^0	x_e^0	E^0/mV	b_e/cm^2 V^{-1} s^{-1}	b_h/cm^2 V^{-1} s^{-1}
1.9225	1.33×10^{-3}	120.13	0.837	0.417

coefficient of a mixed conductivity compound with electronic transport numbers deviating considerably from unity. Galvanostatic polarization experiments were performed at $160°C$ using an asymmetric electrochemical cell, with $Ag_{1.92}Te$ located between an ionic and an electronic electrode. With electronic transport numbers obtained from separate measurements of the partial ionic and electronic conductivities recently derived, evaluation formulas allow the determination of the chemical diffusion coefficient of $Ag_{1.92}Te$ within its range of composition. Additionally, the composition dependence of the electronic conductivity and the coulometric titration curve could be interpreted by a simple model taking into account nondegenerate electrons and holes.

ACKNOWLEDGMENT

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