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Kinetic Studies on the Selenization of Silver

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In order to elucidate the kinetics of selenization of silver by liquid selenium, the Ag/Ag_2Se interface reaction rate, the ionic conductivity of Ag^+ in Ag_2Se layer, the $Ag_2Se/Se(l)$ interface reaction rate, and the over-all reaction rate were determined. The Ag/Ag_2Se interface reaction rate was found to be given by

$$v = 1.6\times 10^9\{\exp(-32300/RT)\}(a_{Se}) \quad \text{eqv cm}^{-2}\cdot\text{s}^{-1}$$

The following mechanism was proposed for the interface reaction.

$$2Ag(Ag) + Se(Ag_2Se) \longrightarrow 2Ag^+(Ag_2Se) + Se^{2-}(Ag_2Se)$$

It was found that the driving force of the $Ag_2Se/Se(l)$ interface reaction is very small and Ag_2Se is in equilibrium with Se(l). On an assumption that the over-all reaction is controlled by both the Ag/Ag_2Se interface reaction and the diffusion of Ag^+ in Ag_2Se, the over-all reaction rates were calculated. The results agree with the observed ones.

Tarnishing reaction of metals proceeds in three steps; (i) reaction at the metal/scale interface, (ii) diffusion of electrons and ions through the growing scale and (iii) reaction at the gas (or liquid)/scale interface. Most kinetic studies on dry corrosion are concerned with the measurement and analysis of over-all reaction. If diffusion is rate controlling, the parabolic law holds, and if the interface reactions are rate controlling, the linear law holds. However, neither law holds if the reaction is controlled by both diffusion and interface reactions.

In order to determine the rate-controlling step more precisely, it is desirable to measure the reaction rate of each step separately and to compare the observed over-all reaction rate with the one calculated from the rates of three steps. For example, if step (ii) is rate controlling, the parabolic rate constant is related to the diffusion constant of the slowest diffusion species, as given by Wagner's equation.[1] If step (i) or (iii) is rate controlling, the linear rate constant should be equal to the rate of reaction at either one of two interfaces. Rickert and Tostmann studied the sulfurization of silver by sulfur vapor from this viewpoint.[2] Wagner, Rickert and their co-workers explained the sulfurization of silver and copper by liquid sulfur as controlled by steps (i) and (ii).[3,4] However, no work has been carried out on the reaction controlled by more than one step, with separate measurement of the reaction rate of each step and a comparison of the over-all reaction rate with the calculated one.

The purpose of the present study is to measure the Ag/Ag_2Se interface reaction rate, the ionic conductivity of Ag^+ in Ag_2Se, the $Ag_2Se/Se(l)$ interface reaction rate and the over-all reaction rate of selenization of silver by liquid selenium, and to compare the observed over-all reaction rate with the one calculated from the results of separate measurements.

Tubandt and his co-workers investigated the selenization of silver by solid selenium,[5,6] but that by liquid selenium has not been studied yet. Rickert, in a study on the Ag/Ag_2Se interface reaction,[7] recently found that the reaction rate was proportional to the -1.5—-3.0 power of activity of silver in Ag_2Se. However, we found it to be proportional to the -2 power.[8] This led us to reinvestigate kinetically the Ag/Ag_2Se interface reaction. So far no work on liquid/scale interface reaction seems to have been carried out yet.

Experimental

Materials. Silver (99.9%) and selenium (99.99%) were used. Cylindrical silver selenide was Prepared by the reaction of silver with selenium in a Pyrex tube. The product was sliced into pellets. AgI pellets, 3—7 mm thick, were prepared by pressing AgI powder under a pressure of 7 t/cm². Sometimes, $AgI-Al_2O_3$ pellets, 1 mm thick, were employed as an electrolyte. They were prepared by mixing nearly the same amounts of powdery AgI and Al_2O_3 and pressing the mixture.

Measurement of the Rate of Ag/Ag_2Se Interface Reaction. The coulometric titration method was employed. The apparatus is shown in Fig. 1. A pressure of 4 kg/cm² was applied to the Ag/Ag_2Se interface with a Pyrex tube to secure contact between the pellets. Since Ag_2Se and AgI tend to deform plastically, Ag/Ag_2Se interface often underwent bending in a cell $Ag/Ag_2Se/AgI/Ag$, and the interface reaction did not proceed uniformly. However, an $AgI-Al_2O_3$ pellet

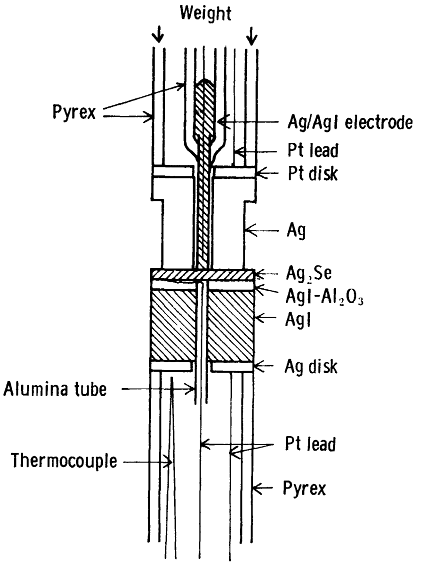

Fig. 1. Apparatus for the coulometric titration method.

unterwent no plastic deformation. Thus a thin AgI-Al_2O_3 pellet was inserted between AgI and Ag_2Se pellets. The detail of this method was described elsewhere.[9,10]

Measurement of the Rate of $Ag_2Se/Se(l)$ Interface Reaction. The apparatus is shown in Fig. 2. Three pellets of Ag, AgI, and $Ag_2Se(I)$, 10 mm in diameter, were assembled in series and pressed with a Pyrex tube, 10 mm in outer and 6 mm in inner diameter. The lower end of the Pyrex tube was finished as flat as possible so that liquid selenium might be kept in the tube without leaking. An Ag/AgI electrode in a small alumina tube, 1.2 mm in outer diameter, was placed in the pyrex tube and the tip was brought to contact with the $Ag_2Se(I)$ pellet.

The reaction rate was measured as an electric current with an ammeter and the potential difference between $Ag_2Se(I)$ pellet and Ag with a potentiometer. The thickness of the $Ag_2Se(II)$ layer formed, Δx, was calculated by integrating the reaction rate with respect to time.

Measurement of the Selenization of Silver by Liquid Selenium. Wagner's pellet method[1,4,9,11] was used. A silver cylinder, 8 mm in diameter, and an $Ag_2Se(I)$ pellet, 10 mm in diameter, were assembled and pressed with a Pyrex tube, 10 mm in outer diameter and 6 mm in inner diameter (Fig. 3). A pressure of 4 kg/cm^2 was applied to the Ag/Ag_2Se interface by means of a spring. The lower end of the Pyrex tube was made flat so that the liquid selenium could be kept in the tube without leaking. It was difficult to observe the position of $Ag_2Se/Se(l)$ interface from outside, so the reaction was followed by observing the length of the silver cylinder y by means of a cathetometer. The increased length of selenide scale, $x-x_0$, was calculated from the decreased length of the silver cylinder, y_0-y, where x_0 and y_0 are the thickness of the silver selenide pellet and the length of the silver cylinder at the beginning of the reaction, respectively. Values of x_0 were 0.153 cm (250 °C), 0.070 cm (300 °C), and 0.114 cm (350 °C), and y_0 was 0.3 to 0.8 cm. After the reaction was completed, the thickness of the formed scale was measured and compared with the calculated thickness.

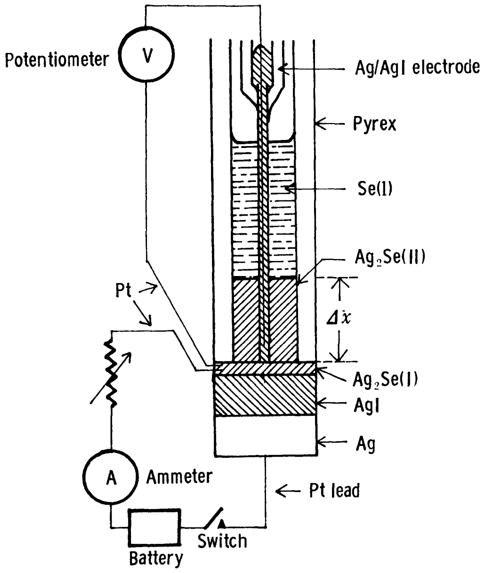

Fig. 2. Apparatus for the measurement of the rate of $Ag_2Se/Se(l)$ interface reaction.

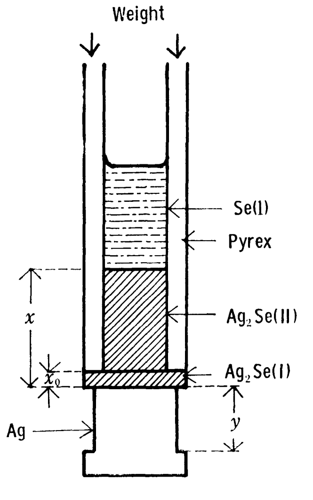

Fig. 3. Apparatus for the measurement of over-all reaction rate.

Results and Discussion

Ag/Ag_2Se Interface Reaction. a_{Ag}'', the silver activity of Ag_2Se at the Ag/Ag_2Se interface is calculated from E'', the potential difference between Ag_2Se and Ag by

$$E'' = -\frac{2.303RT}{F}\log a_{Ag}'' \qquad (1)$$

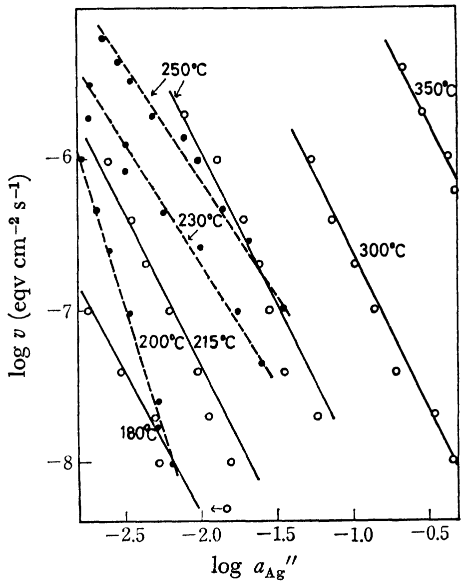

Fig. 4. Plot of log v vs. log a_{Ag}''
○: This work. ●: Rickert.

A plot of the logarithm of reaction rate v(eqv cm^{-2} s^{-1}) against log a_{Ag}'' is given in Fig. 4. Solid lines show our results and broken lines the ones by Rickert.[7] The values of n by Rickert vary from −1.5 to −3.0, while ours are close to −2.0, irrespective of the temperature, being essentially the same as $n=-1.9$ to -2.3

Table 1. Values of n

Temperature (°C)	n
180	-2.0 ± 0.5
215	-2.2 ± 0.6
250	-1.9 ± 0.5
300	-1.9 ± 0.4
350	-1.8 ± 0.4

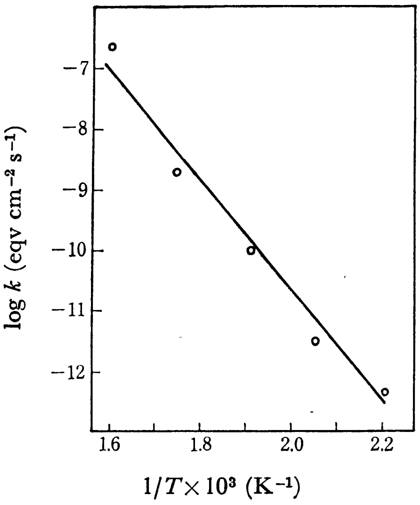

Fig. 5. Arrhenius plot of k.

for the Ag/Ag_2S interface reaction.[9]

The rate constants at $\log a_{Ag}''=0$, k, can be obtained from the intercept of the extrapolated lines with the ordinate. Figure 5 shows the Arrhenius plot of k. We see that linearity holds. Thus, the rate equation is expressed in the forms:

$$v = 4.0\times 10^7\{\exp(-42000/RT)\}(a_{Ag}'')^{-2} \quad \text{eqv cm}^{-2}\cdot\text{s}^{-1} \tag{2}$$

$$v = 4.0\times 10^7\{\exp(-42000/RT)\}(a_{Se}''/a_{Se}^*) \quad \text{eqv cm}^{-2}\cdot\text{s}^{-1} \tag{3}$$

where a_{Se}'' and a_{Se}^* denote the selenium activity in Ag_2Se at the Ag/Ag_2Se interface during the course of reaction and that in equilibrium, respectively. According to Kiukkola and Wagner,[12] $\Delta G°$, the standard free energy of formation of Ag_2Se in a temperature range 167—400 °C is given by

$$\Delta G° = -9.76 - 0.0074T = RT\ln a_{Se}^* \quad \text{kcal}\cdot\text{mol}^{-1} \tag{4}$$

by means of which, Eq. (3) can be rewritten as

$$v = 1.6\times 10^9\{\exp(-32300/RT)\}(a_{Se}'') \quad \text{eqv cm}^{-2}\cdot\text{s}^{-1} \tag{5}$$

Ag_2Se and Ag_2S have the same crystal structure,[13] and the high ionic conductivity of silver ions. Moreover, n is nearly the same. Thus, the same mechanism as in the Ag/Ag_2S interface reaction[9] is proposed for the Ag/Ag_2Se interface reaction:

$$2\text{Ag(Ag)} + \text{Se}(Ag_2Se) \longrightarrow 2\text{Ag}^+(Ag_2Se) + \text{Se}^{2-}(Ag_2Se) \tag{6}$$

where, (Ag) denote the metal phase and (Ag_2Se) the silver selenide phase.

$Ag_2Se/Se(l)$ Interface Reaction and Ionic Conductivity of Ag^+ in Ag_2Se. When the switch is turned off, Ag_2Se(I) is in equilibrium with liquid selenium (Fig. 2) and the potential difference $E°$ between Ag_2Se and Ag is given by

$$E° = -\Delta G°/2F \tag{7}$$

where $\Delta G°$ is the free energy of formation of Ag_2Se. If the silver activity in Ag_2Se in equilibrium with liquid selenium is represented by a_{Ag}^*, we have

$$E° = -\frac{2.303RT}{F}\log a_{Ag}^* \tag{8}$$

When the switch is turned on, Ag^+ ions are transported from Ag to the Ag_2Se(I)/Se(l) interface through AgI and Ag_2Se(I), while electrons flow from Ag to the Ag_2Se(I)/Se(l) interface through the outer circuit and Ag_2Se(I). Ag^+ ions and electrons arriving at the Ag_2Se(I)/Se(l) interface react with liquid selenium to form Ag_2Se(II). As a result, the Ag_2Se(II) layer grows in the pyrex tube and the Ag/AgI electrode is buried in the Ag_2Se(II) layer. When a constant current I_0 is let to flow constantly, the reaction at the Ag_2Se(II)/Se(l) interface proceeds at a rate $I_0/2F$ and the difference in silver activity takes place at the interface between Ag_2Se(II) and Se(l). If silver activities in Ag_2Se(II) at the Ag_2Se(II)/Se(l) interface and in Ag_2Se(I) are a_{Ag}' and $a_{Ag}(\Delta x)$, respectively, and the thickness of Ag_2Se(II) layer is Δx, the following relations are obtained.

$$E' - E(\Delta x) = \frac{I_0\cdot\Delta x}{\sigma_{Ag^+}\cdot S} \tag{9}$$

$$E' = -\frac{2.303RT}{F}\log a_{Ag}' \tag{10}$$

$$E(\Delta x) = -\frac{2.303RT}{F}\log a_{Ag}(\Delta x) \tag{11}$$

where S is the cross-sectional area of Ag_2Se(II) layer, and σ_{Ag^+} is the ionic conductivity of Ag^+ in Ag_2Se. In Eq. (9), σ_{Ag^+} is assumed to be independent of the silver activity in Ag_2Se.[14,15]

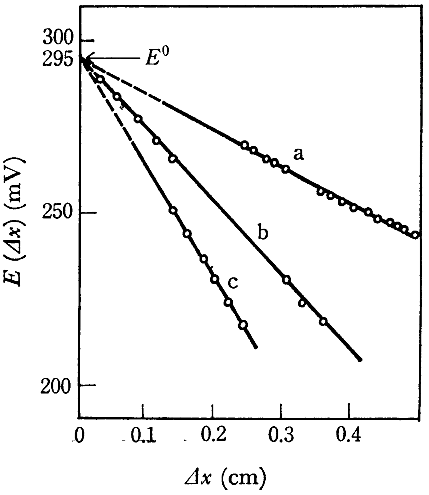

Fig. 6. Plot of $E(\Delta x)$ *vs.* Δx; reaction rate at Ag_2Se/Se(l) interface at 250°C.
a: $I_0\cdot S^{-1}=385$ mA·cm^{-2} b: $I_0\cdot S^{-1}=770$ mA·cm^{-2}
c: $I_0\cdot S^{-1}=1155$ mA·cm^{-2}

Figure 6 shows the plots of $E(\Delta x)$ *vs.* Δx at 250 °C. E' is determined from the intercepts of the extrapolated lines with the ordinate, $\Delta x=0$. $E°$ is shown by an arrow. E' is independent of the current and coincides with $E°$. It is thus concluded that the interface reaction proceeds with very small driving force, Ag_2Se being actually in equilibrium with Se(l). Equation (9) indicates that σ_{Ag^+} can be obtained from the slope of the plots in Fig. 6. The value 3.6 ohm^{-1} cm^{-1} obtained is in good agreement with the result obtained by the four probe conductivity measurement by Okazaki.[16)]

Contribution of Three Steps to the Over-all Reaction. Wagner and Rickert,[3)] and Donner and Rickert[4)] treated the sulfurization of silver and copper by liquid sulfur as controlled by both diffusion and metal/scale interface reaction. Ag_2Se and Se(l) are actually in chemical equilibrium during the reaction. The over-all reaction of selenization is considered to be controlled by both the diffusion in Ag_2Se and the Ag/Ag_2Se interface reaction, and Rickert-Wagner's method can be used for the analysis.

For the diffusion step, we have

$$\frac{dx}{dt}=\frac{\sigma_{Ag^+}\cdot V\cdot RT}{2x}\log\frac{a_{Ag}''}{a_{Ag}^*}$$
$$=\frac{\sigma_{Ag^+}\cdot V}{2F\cdot x}(E^\circ-E'') \tag{12}$$

and for the reaction at Ag/Ag_2Se interface,

$$\frac{dx}{dt}=\frac{V\cdot S_i\cdot k}{2S_l\cdot F}(a_{Ag}'')^{-2}$$
$$=\frac{V\cdot S_i\cdot k}{2S_l\cdot F}\exp\left(\frac{2E''F}{RT}\right) \tag{13}$$

where V is the molar volume of Ag_2Se, x the thickness of Ag_2Se layer, S_i the area of Ag/Ag_2Se interface, and S_l the cross-sectional area of the grown Ag_2Se layer. From Eqs. (12) and (13) we obtain the following expressions for x and t.

$$\log x=\log\frac{\sigma_{Ag^+}\cdot S_l}{k\cdot S_i}+\log(E^\circ-E'')-\frac{2E''F}{2.303RT} \tag{14}$$

$$\log(t+t^0)=\log\frac{S_l^2\cdot\sigma_{Ag^+}\cdot F}{4k^2\cdot S_i^2\cdot V}+\log\left\{\frac{RT}{F}-4(E^\circ-E'')\right\}$$
$$-\frac{4E''F}{2.303RT} \tag{15}$$

where t^0 is a constant determined by the initial condition $x=x_0$ for $t=0$. Eliminating E'' from Eqs. (14) and (15), and inserting the σ_{Ag^+} value and k value we obtained, we obtain x as a function of t. In Fig. 7, solid lines show the calculated values and open circles the observed values. Agreement between the calculated and observed results is good.

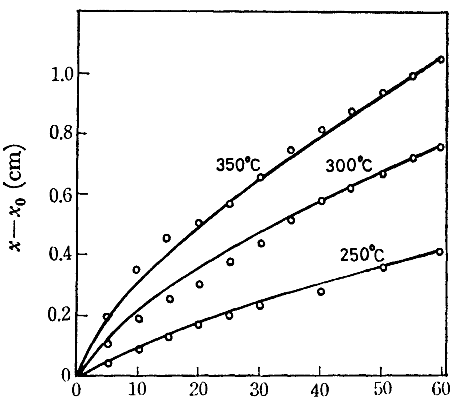

Fig. 7. Plot of $x-x_0$ *vs.* time.
○: observed values ——: calculated values

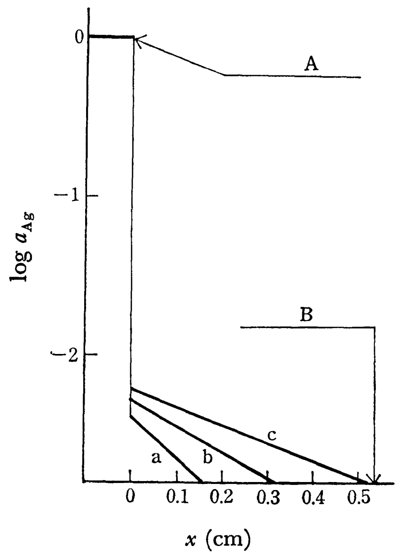

Fig. 8. Distribution of a_{Ag} in Ag_2Se layer under reaction at 250 °C.
a: $t=0$ min b: $t=25$ min c: $t=50$ min
A: Ag_2Se is in equilibrium with metallic silver
B: Ag_2Se is in equilibrium with liquid selenium

The distribution of silver activity during the reaction can be obtained by combining Eqs. (14) and (15). Figure 8 shows the plots of $\log a_{Ag}$ against x. We see that the Ag/Ag_2Se interface reaction is the slowest.

Summary

(1) The Ag/Ag_2Se interface reaction was investigated kinetically. The rate equation is found to be

$$v=1.6\times10^9\{\exp(-32300/RT)\}(a_{Se})\quad \text{eqv cm}^{-2}\cdot\text{s}^{-1}.$$

The following mechanism was proposed.

$$2Ag(Ag)+Se(Ag_2Se)\longrightarrow 2Ag^+(Ag_2Se)+Se^{2-}(Ag_2Se)$$

(2) The rate of Ag_2/Se(l) interface reaction and the ionic conductivity of Ag^+ in Ag_2Se were measured. It was found that Ag_2Se and Se(l) are actually in chemical equilibrium during the course of reaction.

(3) The over-all reaction rate of silver selenization was determined kinetically. Assuming that the selenization is controlled by both the diffusion of Ag^+ ions and the Ag/Ag_2Se interface reaction, the over-all reaction rates were calculated. The calculated values agreed with observed ones.

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