

Corrosion of Silver by Outgassing from Rubber

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Corrosion of silver by outgassed sulfur species from rubber has been investigated by means of quartz crystal microbalance technique (QCM) and cathodic reduction technique. Silver specimens were placed together with a rubber of predefined quantity in an enclosed environment. Corrosion progressed linearly with time and silver sulfide was found as the corrosion product during all the tests. No significant dependence on RH was observed, while the corrosion rate increased as temperature rose. Furthermore the corrosion rate increased logarithmically with the quantity of the rubber placed in the exposure environment. It may be suggested that the corrosion rate of silver is determined by the amount of outgassed sulfur species which is a function of temperature and the quantity of rubber contained in the exposure environment.

Keywords : silver sulfide, rubber, outgassing, quartz crystal microbalance, cathodic reduction, diffusion, electronic devices

1. Introduction

Silver is known to be corroded by sulfur pollutants in air, such as hydrogen sulfide and carbonyl sulfide and forms black sulfide layer. Even a comparatively low corrosion rate observed for silver can significantly influence the reliability of electronic equipment. We have been investigating the parameters affecting the corrosion of silver and have proposed a simple corrosion test for silver.^{1),2)} Rubber materials are frequently used in electronic equipment as sealing and cushion materials. Outgassing from rubber has known to cause corrosion of silver,³⁾ however, little is known about what kind of gases outgassed from rubber are responsible for the corrosion and how they affect the corrosion rate.

The present paper is to find out the important factors which affect the corrosion of silver by outgassing from rubber. Main factors investigated are temperature, relative humidity and quantity of the rubber contained in the exposure environment.

2. Experimental

For corrosion rate measurement, we employed two different methods to measure submicron order corrosion rate

of silver by outgassing from a rubber, quartz crystal microbalance technique (QCM) and cathodic reduction technique. The quartz crystal microbalance (QCM) has been used to follow the corrosion mass loading. Its excellent mass sensitivity allows the determination of small mass gain in the order of ng/cm². The QCM consists of a thin circular quartz crystal cut with an AT orientation of 25 mm diameter, an oscillator and associated electronics. The resonant frequency of the crystal is 6 MHz. They were coated on both sides by vacuum deposition of chromium (thickness 10 nm) and silver (thickness 0.5 μm). On the side that was in contact with sulfur species during corrosion tests, the coated area was 1.33 cm². The frequency can be measured with an accuracy of 0.1 Hz by a universal counter and a PC stored and handled the frequency data. The frequency will change in direct proportion to mass change due to corrosion on the crystal according to the Sauerbrey equation,⁴⁾ leading to a mass change sensitivity of 12.3 ng/cm²/Hz.

$$\Delta f = -C\Delta m/A \quad (1)$$

where Δf is the frequency change, C (Hzcm²g⁻¹), mass sensitivity coefficient that is independent of the coated material, Δm , mass change, A , exposure area. Upon identification of the corrosion product formed as silver sulfide, the mass change was then converted to thickness change by assum-

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Table 1. Testing Conditions

Temperature (°C) ※1	Relative Humidity (%) ※2	Mass of Rubber (g) ※3
31, 48, 60, 71	75	0.61
71	10, 40, 75	0.61
71	75	0.061, 0.61, 6.1, 61

※1 Varied by constant temperature oven

※2 Varied by using different saturated salt solution

※3 Varying the number of pieces of rubber

ing the theoretical density of silver sulfide, 7.32 g/cm^3 .

The cathodic reduction technique was used to determine the corrosion film thickness and identify the corrosion product after exposure of five days. The reduction was performed in a deaerated solution of 0.1 M KCl at a current density of $50 \mu\text{A/cm}^2$. The silver specimen was prepared by vacuum coating chromium (10 nm thick) followed by silver deposition ($0.5 \mu\text{m}$) onto a pyrex glass substrate. Electrical lead was provided by soldering a copper wire to the upper part of the silver specimen surface and insulated by Teflon coating.

In both measurements the silver specimens were suspended from the top of the cylinders and placed at 2 cm above a rubber material which was placed at the bottom of the glass cylinders.

The rubber used was a commercial chloroprene sheet of 1 mm thick, which was cut into a small piece of $10 \times 5 \times 1$ mm in size. The number of the pieces placed into the glass cylinders was determined according to the required mass of the rubber. A saturated salt solution and distilled pure water, each contained in a 10 ml beaker was placed at the bottom of the glass cylinders for RH control. The salts used were lithium bromide and sodium bromide. The RH over the lithium bromide used at 31, 48 and 71°C was approximately 10%, while the RHs over the sodium bromide were 40%, 50% and 60%, respectively.

The glass cylinders were then placed into a constant temperature oven. The tests were carried out for 5 days. The corrosion behavior of silver was measured as a function of temperature ($31\text{--}71^\circ\text{C}$), relative humidity (10–75%RH) and quantity of rubber materials (0.061 g–61 g). Table 1 shows the details of the testing conditions.

3. Results

The exposure test caused silver to be tarnished. The central part of the specimen after exposure at 71°C and 75%RH for 5 days is shown in Fig. 1. An example of the corrosion film thickness increase with time is given in Fig. 2, which was measured as mass loading during

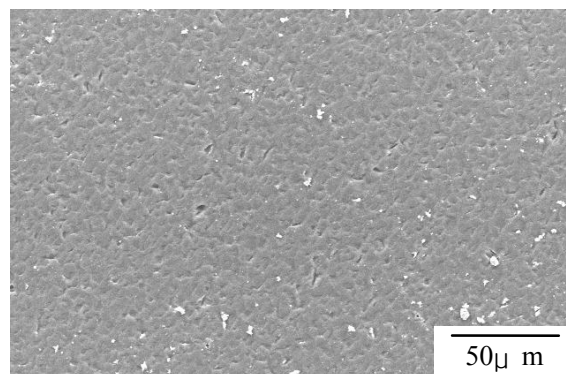


Fig. 1. Scanning electron microscopic observation of the surface after exposure at 71°C and 75% RH for 5 days

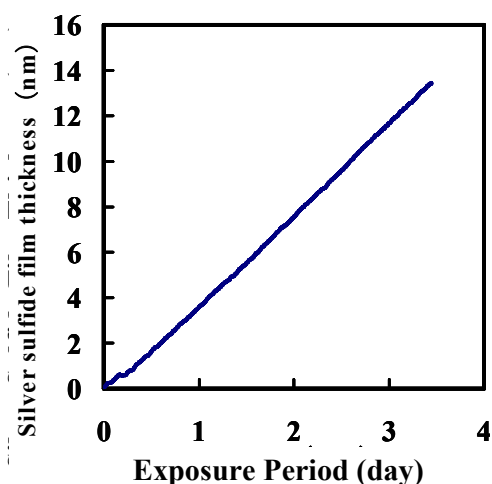


Fig. 2. An example of corrosion film (silver sulfide) growth behavior at 71°C and at 75%RH

corrosion by QCM. The test was carried out at 71°C and 75%RH. Corrosion progresses linearly with time during the time span exposed. On all specimens and in all exposure conditions the principal corrosion product was found to be silver sulfide as determined by XRD and cathodic reduction similar to those found in the tests with solid sulfur.^{1),2),5),6)}

Fig. 3 shows a typical example of the potential-time relationship during cathodic reduction of the corrosion products which were formed after exposure of 5 days at 71°C and 75%RH. A slow decrease in the potential was found in the vicinity of -0.75 V vs. SCE, which is known reduction potential of silver sulfide (Ag_2S)⁶⁾ The thickness of corrosion films is obtained according to the equation

$$T = 10^4 \text{ Mit}/\rho nF \quad (1)$$

where T is the film thickness, M is the molecular weight

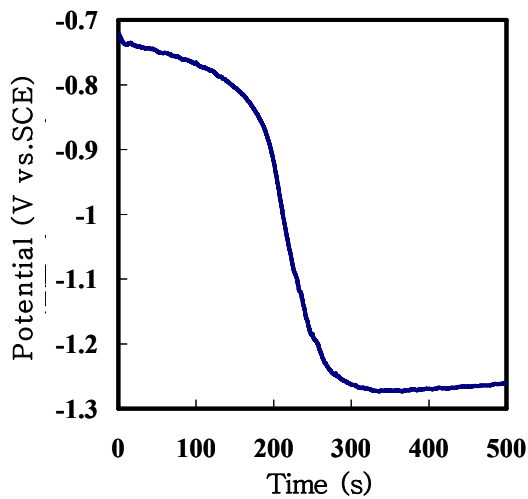


Fig. 3. An example of potential-time relationship during cathodic reduction of the specimen exposed for 5 days at 71 °C and 75%RH

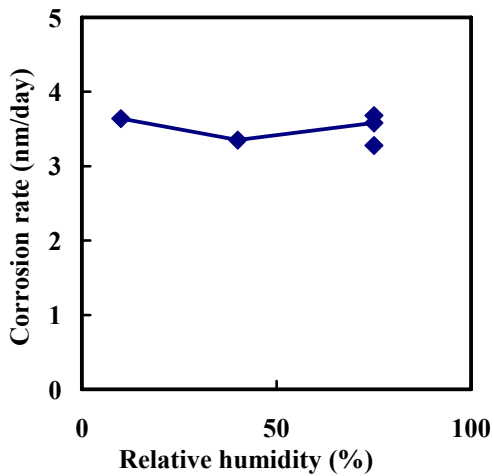


Fig. 4. Corrosion rate of silver as a function of relative humidity at 71 °C with rubber mass of 0.61 g

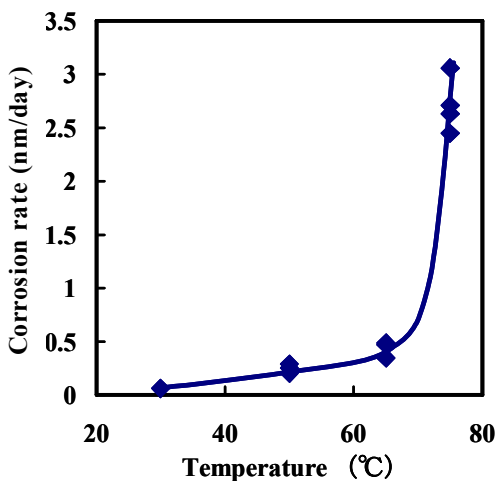


Fig. 5. Corrosion rate of silver as a function of temperature measured at 75%RH with rubber mass of 0.61 g

of Ag_2S 247.8, i is the current density $50 \mu\text{A}/\text{cm}^2$, t is the reduction time (s), ρ is the density of film $7.32 \text{ g}/\text{cm}^3$ and F is Faraday constant.

From this linear relationship between corrosion and time, the average corrosion rates of silver at different temperatures and at different humidity were calculated. The results are summarized in Figs. 4 and 5. No significant dependence on RH was observed as shown in Fig. 4, while the corrosion rate increased as temperature rose as seen in Fig. 5. These behaviors agree with the results obtained by the solid sulfur exposure test.^{1,2)} The role of temperature on corrosion can be explained by the fact that number of sulfur species available in the exposure environment is determined by the outgassing of sulfur species from the rubber. This indicates the significance of availability of sulfur species for corrosion.

The absence of significant effect of relative humidity on corrosion rate may suggest that the reaction mechanism of a direct attack of silver by sulfur species without association of water molecules for tarnishing. Furthermore the corrosion rate increased logarithmically with the quantity of the rubber contained in the exposure environment as shown in Fig. 6. This again indicates that the availability of sulfur species is critical for corrosion.

In order to check whether the outgassing process is determined by the surface process or bulk diffusion process, the effect of surface area of the rubber on corrosion was examined by varying the surface area of the rubber from 13 cm^2 to 30 cm^2 , while keeping the mass of the rubber unchanged as 6.1 g. The corrosion rate measured was 2.1 nm/day with the 13 cm^2 rubber, while 2.0 nm/day with the 30 cm^2 rubber. This indicates that the outgassing process is controlled by the bulk, not by the surface.

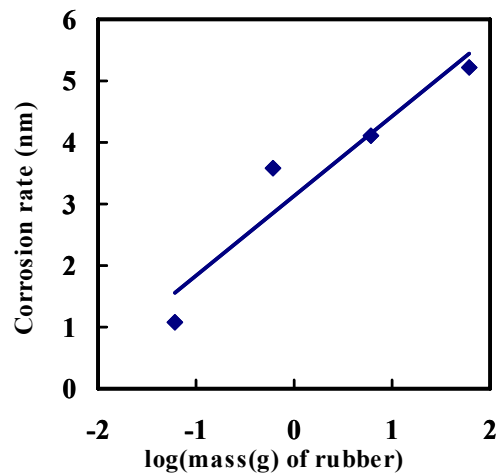


Fig. 6. Corrosion rate of silver as a function of rubber mass measured at 71 °C and 75%RH

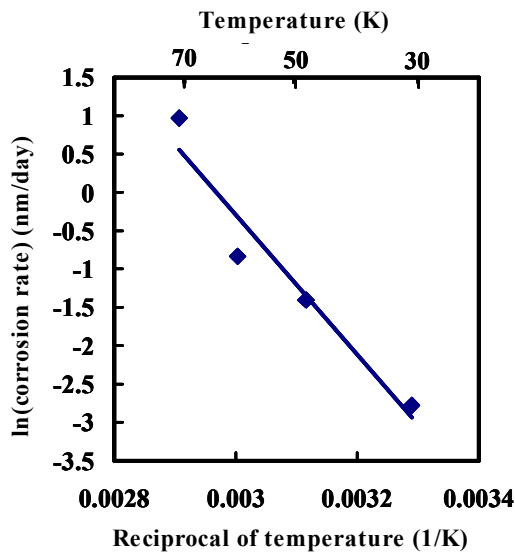


Fig. 7. Arrhenius plot of corrosion rate of silver

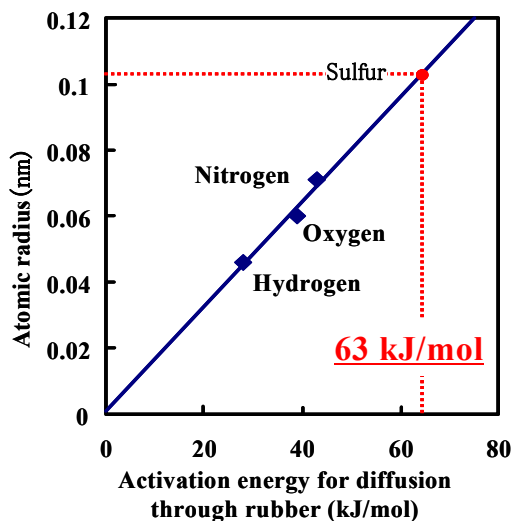


Fig. 8. Relationship between activation energy for diffusion through rubber and atomic radius

4. Discussion

The present result of linear corrosion film growth shows a good agreement with the previous investigations on corrosion of silver in sulfur containing environment. The effect of RHs on corrosion rate was not evident as similar to the test with solid sulfur.¹⁾ The independence of the corrosion rate on relative humidity indicates that free sul-

fur directly reacts with silver and moisture does not play a major role in contrary to most cases of corrosion of electronic materials. On the other hand, the effect of temperature and mass of rubber was very remarkable as seen from Figs. 4 and 5. These and the observed linearity of the corrosion rate at the conditions of the present study suggest that the process of corrosion is controlled by the availability of sulfur species at the silver surface.

Fig. 7 shows a plot of \ln (corrosion rate) against reciprocal of absolute temperature. The linear relationship yields an activation energy of 66 kJ/mol. Since no reference has been found for diffusion of sulfur species in rubber, we estimated the activation energy for diffusion of sulfur from the relationship between the activation energy for diffusion of hydrogen, oxygen and nitrogen, and respective atomic radius as shown in Fig. 8. The value of 63 kJ/mol for estimated activation energy of sulfur atom for diffusion through rubber is close to the measured activation energy. In addition the corrosion rate increases with increasing amount of rubber in the exposure environment. It may be concluded that the corrosion rate of silver is determined by the amount of outgassed sulfur species. Furthermore it may be suggested that free sulfur present in the rubber is released by diffusion as an outgassing sulfur species.

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