Secondary Electron Emission from Conductive, Liquid Polyethylene Glycol 1500

K. Doblhofer, K. P. Charlé, and D. Veltwisch

Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin-Dahlem, Germany

(Z. Naturforsch. **31 a**, 75 – 79 [1976]; received December 6, 1975)

A thorough study of the secondary electron emission (SEE) yield from liquid Polyethylene glycol 1500 (PEG) was made. This liquid (m. p. 45 °C) has a low enough vapor pressure at a working temperature of about 50 °C. In addition, it has the advantage of being a good solvent for salts which dissociate and thus render the solutions conductive. It was found that the presence of the electrolyte salt does not affect the secondary electron yield curves.

A striking result is that the yield curves obtained from the PEG solutions are very well reproducible (ca. ±7%). By fitting the experimental data to a formula given by the elementary theory of SEE it can be clearly seen that this liquid polymer shows quite a different SEE behaviour compared with that reported for chemically similar solid polymer films. The results obtained agree well with the data for polymer silicon oils, suggesting that liquid polymers differ in their SEE behaviour from the corresponding solids.

Finally, it is demonstrated that the reduced yield curves can be fitted to the physically meaningful Bethe loss formula at least as well as using the conventional approach.

Introduction

Secondary electron emission (SEE) has been studied for many years to obtain information of both theoretical and practical interest[1–3]. With special techniques it has also been possible to study the SEE from nonconducting species, such as organic polymers. Thereby it is found that the SEE parameters of liquid polymers (Silicon pump oils[4, 5]) are quite different from the data for solid polymer films[6]. This might be due to differences in the chemical structure, but it is also considered possible that liquid polymers have in general a SEE behaviour different from the solids. To clarify this point a thorough study of the SEE yield from liquid Polyethylene glycole 1500 (PEG), Merck, melting point approx. 45 °C was made. This compound fits, with respect to chemical composition, into the group of organic polymers investigated as solid films. This liquid has a low enough vapor pressure and has the additional advantage of being a good solvent for salts which dissociate and thus render the solutions conductive. Therefore, the experiments could conveniently be conducted essentially as customary for metals. Of course, it had to be established, at first, that the dissolved salts had no effect on the SEE yield curves of PEG.

Experiments

Details of the electron gun are shown in Figure 1. The electrons were, with a pair of Helmholtz coils, deflected by 90° onto the solution, thus the heat radiation from the emission cathode could not reach the solution surface and raise the vapor pressure. This deflection feature was also conveniently used to direct the electron beam onto the solutions for just such short a time as necessary to read the current values from the electrometers. Prolonged elec-

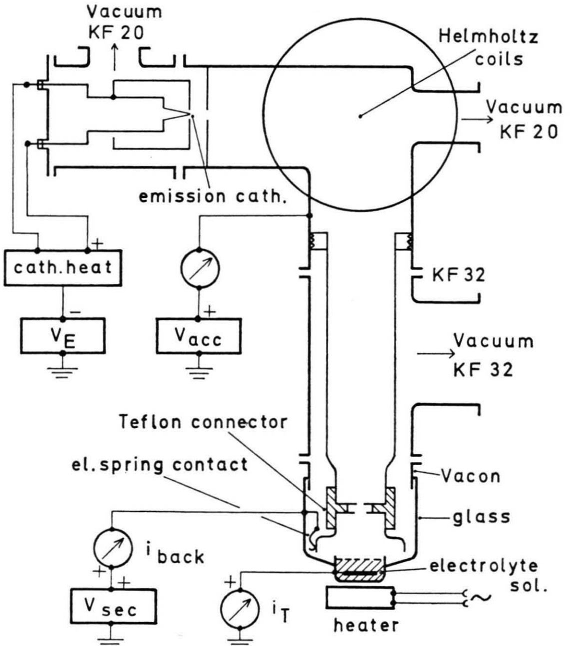

Fig. 1. Electron-gun used to irradiate the PEG solutions with 0 – 1500 eV electrons.

tron bombardment of the solutions gave, particularly at higher electron energies, drifting current values, apparently due to gas from solvent decomposition (the pressure reading on the manometer rose to 2 or 3×10^{-6} torr, see below). Sufficiently high electron currents (ca. 50 nA) reached the solution in this simple arrangement which made focussing of the electron beam unnecessary.

The apparatus was mainly built from stainless steel. The cell for the solutions was made from Pyrex Glass which was connected with the steel via Vacon collars. The connections shown in Fig. 1 as KF are Leybold "Kleinflansche" with the dimensions being the inner diameters of the tubes in millimeters. Via a piece of glass tubing (el. insulation) and a trap cooled with liquid air the cell was connected with the Leybold 200 l/sec oil diffusion pump stand.

The electrical connections and measurements were made in a standard manner[1–3] with the exception of an auxiliary acceleration voltage, V_{acc}, applied to the electron gun to make easy the deflection of the electrons with the Helmholtz coils. The primary electron energy, E_{p}, was varied by floating the heating power supply for the emission cathode to the value V_{E}. With increasing V_{E} the acceleration voltage V_{acc} was reduced such that $V_{\text{E}} + V_{\text{acc}} =$ 2000 volts which made readjustment of the deflection coil currents unnecessary. When V_{sec} was varied between $+50$ and -50 volts with respect to V_{acc} a variation of the apparent yield, σ, as shown in Fig. 6 of Ref. 7 was observed, thus V_{sec} was kept on a potential equal to V_{acc} or $(V_{\text{acc}} - 10)$ volts. σ was calculated from $\sigma = i_{\text{back}}/i_{\text{p}}$, where $i_{\text{p}} = i_{\text{back}} - i_{\text{T}}$ (Figure 1).

The solvent used for the measurements was polyethyleneglycol (PEG) 1500 (Merck-Schuchardt), melting point 45°. One liter dissolved, at 50 °C, at least 0.1 mole of the following salts: $LiClO_4$, CsI, KI, $Tb(NO_3)_3$, $Ba(ClO_4)_2$, and $CuCl_2 \cdot 2\,H_2O$. With such solutions, after degassing, the pressure in the system, with the vacuum pump on, could be kept at less than 1×10^{-6} torr (measured with a Leybold IM6 ionisation manometer in a distance of approximately 30 cm from the cell). Neither a temperature rise of the solution by 20 °C nor freezing the solution to liquid nitrogen temperature changed this pressure reading. This was taken as indication that the vapor pressure of this solvent at 50 °C was below 10^{-6} torr.

The actual measurements were made by at first degassing the solution in the cell on a separate pump stand (10^{-6} torr) for an hour or so. Then the solution was cooled to room temperature, whereby it solidified. Under dry nitrogen the cell containing the solution was quickly transferred to the experimental apparatus and pumped to 10^{-6} torr. Then it was warmed again whereby it melted without splashing. With a short iron bar in the cell, which could be rotated by a rotating magnet the solution was stirred thoroughly from time to time to ensure homogeneity of the solution.

Theory

Within the framework of the elementary theory of SEE the true secondary yield is given by the formula

$$\delta = K \frac{E_{\text{p}}}{R(E_{\text{p}})} \left[1 - \exp\left(- \frac{R(E_{\text{p}})}{\lambda_{\text{esc}}} \right) \right] \tag{1}$$

deduced by Lye and Dekker[8] which accounts roughly for straggling of the primaries. K is a constant *, λ_{esc} is the (energy independent) escape length of the secondaries and $R(E_{\text{p}})$ is the maximum effective range or penetration depth of the primaries incident with energy E_{p}.

For the calculation of $R(E_{\text{p}})$ from the energy loss per path length $\mathrm{d}E/\mathrm{d}x$ the simple loss formula[8]

$$-\mathrm{d}E/\mathrm{d}x = A/E^n \tag{2 a}$$

(A is a constant *, the exponent n has to be determined by fitting) as well as Bethe's loss formula (see e. g. Ref. 3)

$$-\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{A'}{E} \ln \frac{E}{\bar{I}} \tag{2 b}$$

(A' is a constant * and $\bar{I}$ has the meaning of a mean ionisation energy) were used since the former lacks physical justification if it is not regarded as an approximation to the latter[3, 9], valid only in a certain energy range.

A comparison of the reduced yield curves (see below) obtained with (2 a) and (2 b) shows that the energy range where the simple loss formula can be regarded as a good approximation to Bethe's loss formula becomes smaller with decreasing n or

---

* The constants K, A, and A' do not enter the reduced quantities used in the elemetnary theory.

increasing $\bar{I}$**. Hence, since the computational effort is not much increased if one uses (2 b) instead of (2 a), Bethe's loss formula should be preferred. From (1) the reduced yield curve

$$\delta_{\mathrm{red}}(\varepsilon_{\mathrm{p}}) = \delta(E_{\mathrm{p}})/\delta(E_{\mathrm{p,max}}) \tag{3}$$

is obtained where

$$\varepsilon_{\mathrm{p}} = E_{\mathrm{p}}/E_{\mathrm{p,max}} \tag{4}$$

is reduced primary energy with respect to the primary energy $E_{\mathrm{p,\,max}}$, where the yield δ has its maximum. Since to the author's knowledge the reduction procedure has been demonstrated only for the simple loss formula (2 a) [8] it will be shortly explained how one gets reduced yield curves for an arbitrary $R(E_{\mathrm{p}})$: If one introduces the reduced range

$$\varrho(\varepsilon_{\mathrm{p}}) = R(E_{\mathrm{p}})/R(E_{\mathrm{p,max}}) \tag{5}$$

so that $\varrho(1) = 1$, and the ratio of the range at $E_{\mathrm{p,\,max}}$ to the escape length λ_{esc}

$$\gamma_{\mathrm{m}} = R(E_{\mathrm{p,max}})/\lambda_{\mathrm{esc}} \tag{6}$$

one obtains from (1) and (3)

$$\delta_{\mathrm{red}}(\varepsilon_{\mathrm{p}}) = (1 - e^{-\gamma_{\mathrm{m}}})^{-1} \frac{\varepsilon_{\mathrm{p}}}{\varrho(\varepsilon_{\mathrm{p}})} (1 - e^{-\gamma_{\mathrm{m}}\varepsilon_{\mathrm{p}}}) \,. \tag{7}$$

Since $\delta_{\mathrm{red}}(1) = \delta_{\mathrm{red,\,max}}$, the condition

$$\left.\frac{\mathrm{d}\delta_{\mathrm{red}}}{\mathrm{d}\varepsilon_{\mathrm{p}}}\right|_{\varepsilon_p=1} = 0$$

yields the equation $\left(\varrho'(1) = \left.\frac{\mathrm{d}\varrho}{\mathrm{d}\varepsilon_{\mathrm{p}}}\right|_{\varepsilon_p=1}\right)$

$$\varrho'(1)/[\varrho'(1) - 1] = (e^{\gamma_{\mathrm{m}}} - 1)/\gamma_{\mathrm{m}}$$

which is readily solved numerically for γ_{m} with sufficient accuracy. The only quantity remaining is the exponent n in (2 a) or the reduced mean ionisation energy $i = \bar{I}/E_{\mathrm{p,\,max}}$ in (2 b). Hence either n or i are the parameters which are used for fitting the reduced theoretical yield (7) to the experimental one.

Results

A striking result was that the yield curves obtained from the PEG solutions were very well reproducible (ca. ±7%), indicating a very stable equilibrium of the interfacial structure. The yield curves were identical (within the exp. error) when the final pressure value in the system had not quite been reached (7×10^{-6} torr on the manometer), or when the solution temperature was raised to 70 °C, or after 3 days of pumping, with repeated stirring, freezing, and thawing. This was in contrast to results with polished metal surfaces which were initially used to test the instrument [7, 10]. They gave the well-known poorly reproducible results (a heat treat-

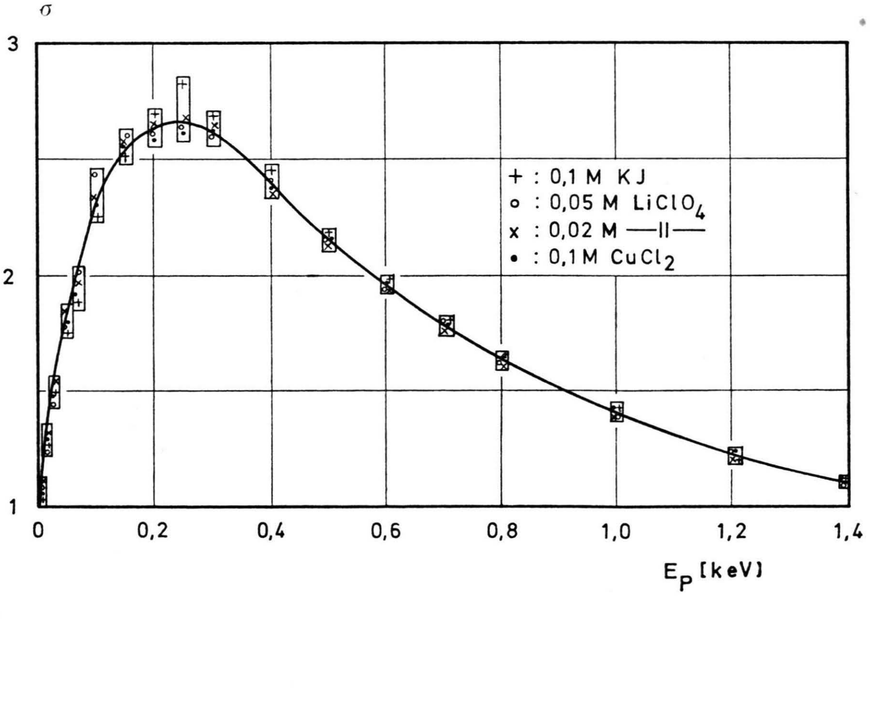

Fig. 2. Apparent secondary electron yield curve for liquid solutions of selected inorganic salts in polyethylene glycol 1500, at 50 °C.

** E. g.: $n = 1/2$ in (2 a) is a good approximation in the energy range $E_{\mathrm{p,max}} \leqq 4\,E_{\mathrm{p,max}}$ if $\bar{I} \sim 0.165\ E_{\mathrm{p,max}}$ in (2 b); $n = 2/3$ works well at least up to $E_{\mathrm{p}} \approx 6\,E_{\mathrm{p,\,max}}$ if $\bar{I} \sim 0.07\ E_{\mathrm{p,max}}$ (see Figure 3).

ment of the metals was not possible in the glass cell). Within the experimental error the yield curves were the same for 0.1 M solutions of $LiClO_4$, CsJ, KJ, $Tb(NO_3)_3$, $Ba(ClO_4)_2$, and $CuCl_2 \cdot 2\,H_2O$ (Figure 2). A variation of the $LiClO_4$ concentration between 0.02 and 0.5 M had no effect either. Hence the effect of the added salt is negligible and the measured yield is that of PEG.

The true secondary yield δ is obtained from the measured yield σ by subtracting the fraction of the rediffused primaries, i. e.

$$\delta = \sigma - \eta\,. \tag{8}$$

Since it is well known that for elements with small atomic number ($Z \lesssim 30$) η is nearly independent of the primary energy and tends to decrease with decreasing Z [2, 3, 11], one expects this also to be so for compounds of elements with small Z. Indeed, measurements on some diffusion pump oils [4, 5] and some aromatic hydrocarbons [12] confirm that η is nearly constant in the energy range of interest ($E_p = 150$ to 2000 eV) and small ($\approx 0.12 - 0.16$ for the various materials). Hence

$$\eta = 0.15$$

is used as a reasonable estimate for PEG to calculate the true secondary yield from (8).

For comparison with the elementary theory the experimental results have to be reduced. According to (3) and (4) the parameters needed for this reduction are

$$\delta_{max} = 2.50 \quad \text{and} \quad E_{p,max} = 250\ \text{eV}\,.$$

Figure 3 shows that a good fit to formula (7) is obtained in the energy range $E_{p,max} \leqq E_p \lesssim 6\,E_{p,max}$ with either $n = 2/3$ if the simple loss formula (2 a) is used, or with $i \approx 0.075$ (exactly $\ln i = -2.6$) corresponding to $\bar{I} \approx 19$ eV, if Bethe's loss formula (2 b) is used. The corresponding ratios of $R(E_{p,max})$ to λ_{esc} are

$$\gamma_m(n = 2/3) = 1.62 \quad \text{and} \quad \gamma_m(\ln i = -2.6) = 1.91\,.$$

Discussion

Since the ratio γ_m of the maximum range $R(E_{p,max})$ of the primaries to the escape length λ_{esc} of the secondaries is known from the fitting procedure, one could calculate or at least estimate λ_{esc} if $R(E_p)$ would be known. $R(E_p)$ was measured for one of the diffusion pump oils [5] by the method of the mirror substrate [11, 13]. Unfortunately, the measured maximum range varies roughly like E_p^2, whereas the measured energy dependence of the secondary yield [4, 5] would require $R \sim E_p^{5/3}$ within the framework of the elementary theory. This discrepancy might be due either to a failure of the elementary theory or to the method of measurement.

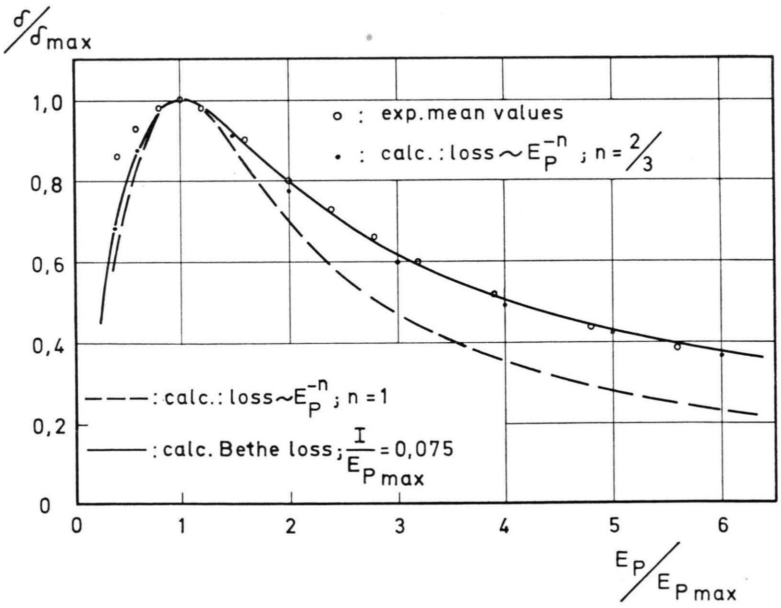

Fig. 3. Reduced true secondary electron yield fitted to the theory [cf. Eqs. (2 a), (2 b) and (7)]. The calculated curve with $n=1$ is included for comparison. The experimental mean values are taken from the curve in Figure 2.

Whatever the reason might be, it makes a reasonable estimate of λ_{esc} for PEG impossible, since reliable information on $R(E_{\text{p}})$ in polymers is lacking at present.

The comparison with independently measured reduced SEE curves of some diffusion pump oils (extracted from Ref. 4, 5) shows that these are quite similar to that of PEG with exponents n in the range $1/2 \lesssim n \leqq 2/3$ or i in the range $0.075 \lesssim i \lesssim 0.2$, though the fit is not as good as that for PEG obtained in this work. It should be noted that the similarity between these substances is not confined to the general shape of the reduced yield curves since all the energies $E_{\text{p, max}}$ lie in the narrow range $175-250$ eV and the maximum yields are of the same order of magnitude ($\delta_{\max} \approx 2.0-2.5$). This indicates that differences in the chemical composition of the liquid polymer are of no consequence for the SEE behaviour.

On the other hand, recently reported measurements of the secondary yield of thin organic polymer foils [6] indicate that they, with the exception of the perfluoro polymer, form another group of materials with a different behaviour of the secondary yield. While the $E_{\text{p, max}}$ values are in the same energy range the maximum yield is higher $(3-4)$. The main difference to the group of liquid polymers is the high value of about 1 for the exponent n. It should be noted that the difference between the n values corresponds to significantly different reduced yield curves (cf. Figure 3).

Thus, it may be concluded that the SEE behaviour of solid polymers differs from liquids. However, since SEE is mainly a surface effect (the escape length is approximately 30 Å, as directly measured for one of the diffusion pump oils [5]), the difference may be due to the properties of the surface of the investigated commercial polymer foil only [6]. This view is supported by the fact that the energy dependence of the reduced yield of clean solid polyaromatic compounds, such as pyrene [12] is also described by an exponent n not exceeding $2/3$; i. e. their SEE behaviour is like that of the liquid polymers in this respect. Further, the surfaces of the polymer foils were pretreated by rinsing with alcohol only [6]. When compared with metals, where surface treatments such as strong heating over extended periods of time are needed to obtain reproducible results (which is, of course, not feasible with polymers) one may suspect that the measured parameters are not necessarily characteristic for the solid polymers themselves. The SEE yield curves obtained for liquid polymers may, therefore, be a better representation for polymer SEE in general, because of their superior surface properties.

Acknowledgement

The assistance of Dr. W. Engel (Institut für Elektronenmikroskopie am Fritz-Haber-Institut der Max-Planck-Gesellschaft) in designing the electron gun as well as of Ing. R. de Boer and Mr. H. J. Maier in carrying out some of the experiments is gratefully acknowledged.

[1] R. Kollath, Encyclopedia of Physics, Vol. 21, p. 232, ed. S. Flügge, Springer-Verlag, Berlin 1956.

[2] A. J. Dekker, Solid State Physics, Vol. 6, p. 251, eds. F. Seitz and D. Turnbull, Academic Press, New York 1958.

[3] W. Brauer and O. Hachenberg, Advances in Electronics and Electron Physics, Vol. 11, p. 413, ed. L. Maston, Academic Press, New York 1959.

[4] K. Goto and K. Ishikawa, Jap. J. Appl. Physics **6**, 1329 [1967].

[5] K. Goto and K. Ishikawa, Jap. J. Appl. Physics **7**, 227 [1968].

[6] R. F. Willis and D. K. Skinner, Solid State Commun. **13**, 685 [1973].

[7] H. Gobrecht and F. Speer, Z. Physik **135**, 685 [1973].

[8] R. G. Lye and A. J. Dekker, Phys. Rev. **107**, 977 [1957].

[9] J. R. Young, Phys. Rev. **103**, 292 [1956].

[10] N. Campbell, Philos. Mag. **29**, 369 [1915].

[11] I. M. Bronstein and R. B. Segal, Sov. Phys. Solid State **1**, 1365 [1960].

[12] L. Ya. Bubnov and E. L. Frankevich, Phys. Status Solidi b **62**, 281 [1974].

[13] I. M. Bronstein and R. B. Segal, Sov. Phys. Dokl. Acad. Nauk. **3**, 1184 [1958].