

Electron Injection into Dielectric Liquids by Field Emission

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(Z. Naturforsch. 26 a, 169—170 [1971]; received 2 December 1970)

For the generation of excess electrons in dielectric liquids in most experiments ionization by high energy radiation was used.

We would like to report here on the injection of electrons into organic liquids (tetramethylsilane, neohexane, n-hexane, cyclopentane, benzene) by field emission using line emitters (razor blades, Schick Safety Razor Co.) and applying voltages up to 10 kV. The blade (36 mm length) was mounted 1.5 mm opposite of a stainless steel plane electrode in a pyrex glass tube.

Qualitative experiments with controlled emission have been carried out by several authors¹⁻⁶. In most of the cases liquefied gases (H₂, N₂, Ar, He, O₂) and only exceptionally not specially purified hydrocarbons have been investigated.

The emission of electrons from a line emitter into ultra high vacuum can be described by the Fowler-Nordheim equation⁷:

$$\ln \frac{i}{V^2} = \ln \left\{ A \cdot \frac{\beta^2 K}{\varphi} \right\} - B \varphi^{3/2} \frac{1}{\beta V}, \quad (1)$$

(*i* current, *V* applied voltage, *A* emitting area, φ work function, $F = \beta V$ field strength at the emitter, *K*, *B* parameters slightly depending on φ and *F*).

This equation should hold also for emission in liquids with a modified φ .

According to HALPERN and GOMER^{5,6}, Fowler-Nordheim (FN) behavior has been found only in the case of liquid H₂ at low electric fields with a transition to space charge limited currents (SCLC) at higher fields. In all other liquids only SCLC have been observed, which are characterized by

$$\sqrt{i} \sim V. \quad (2)$$

The field strength interval at which transition from field emission controlled to SCL-current occurs is determined by the mobility of the electrons in the liquid. The greater the mobility, the higher the value of the field strength up to which FN behavior should be observable.

Recently SCHMIDT and ALLEN⁸ measured mobilities of electrons in carefully purified hydrocarbons which are several orders of magnitude greater than the values reported for negative charge carriers in less purified liquids. It seemed therefore of interest to study field

emission in such purified hydrocarbons since with the given electrode separation FN-behavior could be expected for a large interval of applied voltages.

The liquids used were chemically pure (99% or better). They were purified by conventional chemical procedure, fractionated from drying agents, introduced into vacuum and stored over CaH₂. The cell was evacuated to 10⁻⁵ Torr and the liquid condensed through a frit (pore diameter $\approx 20 \mu\text{m}$) into an auxiliary vessel attached via another frit (pore diameter $\approx 1.5 \mu\text{m}$) to the injection cell. The radii of curvature of the blades were not measured. Values reported range from 200 Å⁹ to 1250 Å³.

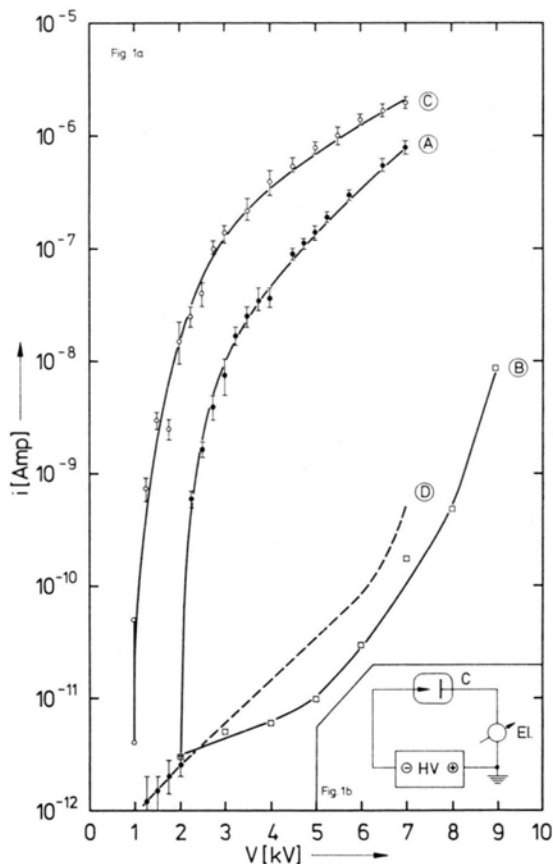


Fig. 1 a. Current as a function of applied voltage (at 20 °C). A: Tetramethylsilane; B: Tetramethylsilane, O₂-saturated, 1 atm; C: Benzene; D: Tetramethylsilane, blade positive; the curve shows the general dependence, the currents were not reproducible and decreased with time.

Fig. 1 b. Scheme of the circuit; EL: Keithley-Electrometer Mod. 602; HV: regulated power supply; C: Injection cell.

¹ E. W. MÜLLER, Erg. Exakt. Naturw. 27, 313 [1953].

² G. V. JORGENSEN and E. WILL, Rev. Sci. Instrum. 33, 55 [1962].

³ G. COE, J. F. HUGHES, and P. E. SECKER, Brit. J. Appl. Phys. 17, 885 [1966].

⁴ R. COELHO, C. R. Acad. Sci. Paris 262 B, 992 [1966].

⁵ B. HALPERN and R. GOMER, J. Chem. Phys. 43, 1069 [1965].

⁶ B. HALPERN and R. GOMER, J. Chem. Phys. 51, 1031 [1969].

⁷ R. H. FOWLER and L. NORDHEIM, Proc. Roy. Soc. London A 119, 173 [1928].

⁸ W. F. SCHMIDT and A. O. ALLEN, J. Chem. Phys. 52, 4788 [1970].

⁹ Privat communication, American Safety Razor Co.

Typical results obtained are shown in Fig. 1, where also the electric circuit is inserted. Figure 2 shows a semilogarithmic plot of i/V^2 vs. $1/V$ for tetramethylsilane and benzene. The straight line indicates that the

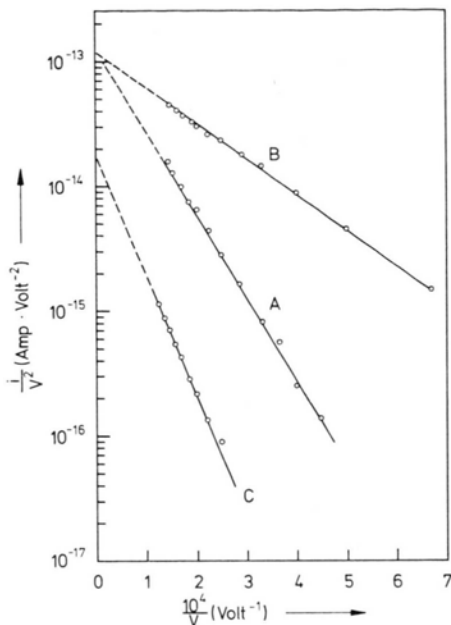


Fig. 2. Fowler-Nordheim plot for tetramethylsilane (A, C) and benzene (B).

current was emission controlled according to Eq. (1). This behavior was observed for all liquids listed above.

The data presented in Figs. 1 and 2 were taken with the same blade. Curve A of Fig. 2 shows the FN plot for the data obtained in tetramethylsilane with a fresh razor blade. The FN plot for benzene, curve B of Fig. 2, has a smaller slope which indicates that the work function is lower. After a series of experiments with different liquids the cell was filled with tetramethylsilane again. Curve C of Fig. 2 was obtained now. According to Eq. (1) the slope of the curve is determined by φ and β . The change in slope of curve A and C of Fig. 2 can only be attributed to a change in β . This conclusion is supported by the lower intercept of curve C for $1/V=0$. A change in β probably results from a change of the radius of curvature of the blade caused by blunting.

Some experiments were carried out with solutions of electron scavengers (O_2 , SF_6 , CH_3Br). The presence of an electron scavenger had a pronounced influence on the $i=f(V)$ dependence at lower voltages as can be seen from curve B of Fig. 1. Over a limited range of voltages the current seems to be space charge limited. At higher voltages the current increases more rapidly and becomes emission controlled.

When a positive voltage was applied to the blade in the case of saturated hydrocarbons the current did not change dramatically but gradually increased with the applied voltage (curve D, Fig. 1). The ratio of i_-/i_+ was of the order of 10^3 .

In benzene i_+ increased sharply with the applied voltage indicating field ionisation.