

MEYER-NELDEL RULE (COMPENSATION EFFECT) IN SEMICONDUCTIVE OLIGOHYDROQUINONE

B.Sh. BARKHALOV¹, F.Sh. MAMEDOV²

¹ *Institute of Physics of the Azerbaijan National Academy of Sciences
named by academician G.M. Abdullayev*

H. Cavid pr., 33, Baku, Az 1143

² *Azerbaijan Architectural-Engineering University, Department of Physics,
Ayna Sultanova str., 5, Baku, Az 1073*

Üzvi yarımqeçirici oliqohidrokinonda Meyer-Neldel qaydasının (kompensasiya effektinin) öyrənilməsinin nəticələri təqdim olunmuşdur. Göstərilmişdir ki, termooksidləşdirici destruksiyanın səviyyəsindən asılı olaraq oliqohidrokinonun elektrikeçiriciliyi və onun aktivləşmə enerjisi qeyri-monoton dəyişir və kifayət qədər geniş temperatur intervalında bu dəyişmələr Meyer-Neldel qaydasına uyğun olaraq baş verir.

Представлены результаты исследования правила Мейера-Нелделя (эффекта компенсации) в органическом полупроводнике олигогидрохиноне. Показано, что в зависимости от степени термоокислительной деструкции электропроводность олигогидрохинона и его энергия активации немонотонно изменяется и в довольно широком интервале температур эти изменения происходят в согласии с правилом Мейера-Нелделя.

The results of the study Meyer-Neldel rule (compensation effect) in organic semiconductor oligohydroquinone have been presented. It has been shown that depending on the depth of thermo-oxidative destruction the electric conductivity of oligohydroquinone and its activation energy vary non-monotonically and over a rather wide temperature range the variations are taking place in accordance with the Meyer-Neldel rule.

1. INTRODUCTION

The Meyer-Neldel rule [1] is observed in many processes in nature. The two main stream fields that are most affected by it are diffusion processes where it is also known as the compensation effect [2] and semiconductor conduction. Areas of semiconductors where the Meyer-Neldel rule is detected include: porous and amorphous silicon [3, 4], microcrystalline silicon films [5], glassy materials [6] and organic materials [7, 8] in various devices such as charge-coupled devices [9] and thin-film transistors [4]. The Meyer-Neldel rule for conduction processes states that the activation energy for conduction can depend on various parameters ranging from the (partial) pressure [10] to bias as well as technological factors.

In general, for a semiconducting material, DC conductivity increases exponentially with temperature indicating that the conductivity is a thermally activated process. Mathematically it can be expressed as:

$$\sigma = \sigma_0 \exp(-\Delta E / kT) \quad (1)$$

where ΔE is called the activation energy and σ_0 is called the pre-exponential factor.

The above equation is termed as Arrhenius law and is used to determine the activation energy for electrical conduction. Defects or doping in semiconductors can lead to lower effective activation energy and to spread in the values for ΔE for the same property in one material.

In most of the semiconducting materials, σ_0 does not depend on ΔE . However, in many organic and amorphous materials, σ_0 is found to increase exponentially with ΔE [1, 3-8]. It was found empirically, for the first time, by Meyer and Neldel in 1937 [1] that σ_0 satisfies a relation:

$$\sigma_0 = \sigma_{00} \exp(\Delta E / kT_0) \quad (2)$$

where σ_{00} and kT_0 are positive constants within a class of related materials. This expression is termed as Meyer – Neldel rule for DC conductivity.

In this report we present results of study of observation Meyer-Neldel rule in organic semiconductor oligohydroquinone. In general, in experiments changing composition of the material changes the activation energy. In the present work we have changed ΔE by changing a depth of thermo-oxidative destruction of the organic semiconductor oligohydroquinone.

It has been established earlier that when an organic oligohydroquinone semiconductor is heated in air it is subjected to thermo-oxidative destruction [11]. As this takes place, irreversible variations occur in its composition, structure, and hence, in its properties (fusibility, solubility, reactivity, electrical exchange capacity, paramagnetism, etc.) depending on the temperature and duration of the treatment. In this connection it is of interest to clarify how the semiconductor properties of oligohydroquinone vary depending on the level of its thermo-oxidative destruction. Determination of the «thermal destruction-electric conductivity» relation would allow one to change purposefully the electrophysical parameters of oligohydroquinone.

2. EXPERIMENTAL

Oligohydroquinone ($M_n=530$, $M_w=670$, and the hydroxyl group content 28.9%) was obtained by anionic polymerization of *n*-benzoquinone in an alcohol-alkaline medium and separated and cleaned by the method described elsewhere [12]. Its thermo-oxidative destruction was carried out under isothermal conditions by holding powder-like specimens in air for 1.5 hours at a specified temperature in the range from 423 to 673 K, the rate of change being 25°.

DC and AC electrical measurements were performed on pellets pressed from a powder under a pressure of 2.5×10^3 kg/cm² (the pellets were 0.1 to 0.3 cm thick and each of them had an area of 1.0 cm²). The electrodes were applied by thermal sublimation of silver in vacuum. The possible effects of edge currents on the results were controlled by measurements with the use of a guard ring. IR-spectra were taken on pellets made of KBr substrate and the oligohydroquinone specimen under study with the use of UR-20-spectrometer. The concentration of paramagnetic centres in the specimens was determined from EPR-spectra taken for powders with the use of an RE-1306-spectrometer (standard: 2,2; 6,6-tetramethyl 1-4-oxypiperidine-1-oxy1).

3. RESULTS AND DISCUSSIONS

Fig. 1 gives the current-voltage characteristics (CVC) of oligohydroquinone specimens at 293 K. The dependences of I on U are non-linear in the region of low voltages, which is likely to be associated with the prevalent contribution of hopping conductivity [13]. Besides, a non-monotonic dependence of the conductivity of oligohydroquinone specimens on the destruction temperature is observed.

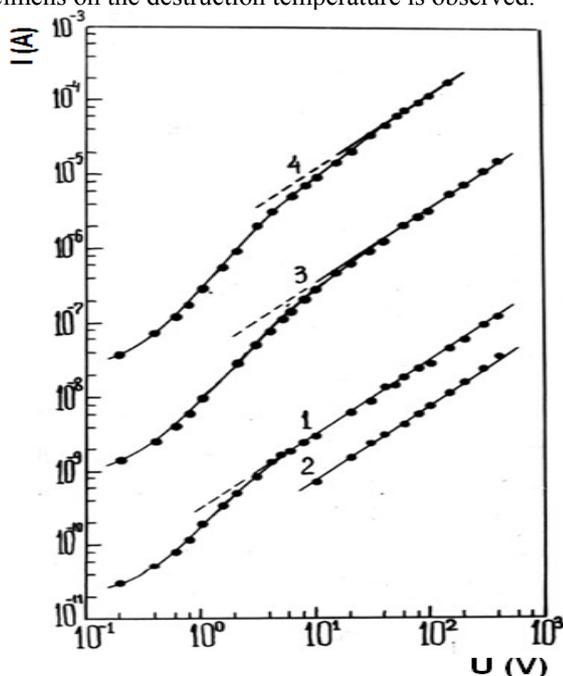


Fig. 1. Current-voltage characteristics at $T=293\text{K}$ for oligohydroquinone specimens obtained at 423 (1), 473 (2), 573 (3), and 673 K (4) (Pellet thickness = 0.18 cm).

The frequency dependences of the electric conductivity of oligohydroquinone specimens are shown in Fig. 2. It is seen that the conductivity (σ) of specimens treated at relatively low temperatures increases as $\sigma \sim f^s$ (where $s \approx 1.0$) with growing of the frequency f . The conductivity of specimens held at relatively high temperatures varies somewhat and a linear dependence of σ on f is observed only in the high-frequency region. The insert in Fig. 2 gives the dependence of the electric conductivity of oligohydroquinone specimens at a frequency of 10^6 Hz on the isothermal-destruction temperature. It is seen that both the value and the sign of the conductivity variation are a complex function of the

sothermal oxidative destruction temperature of the oligohydroquinone. It should be noted that a relatively high conductivity of oligohydroquinone at AC is the result of the prevalent contribution of hopping conductivity [14].

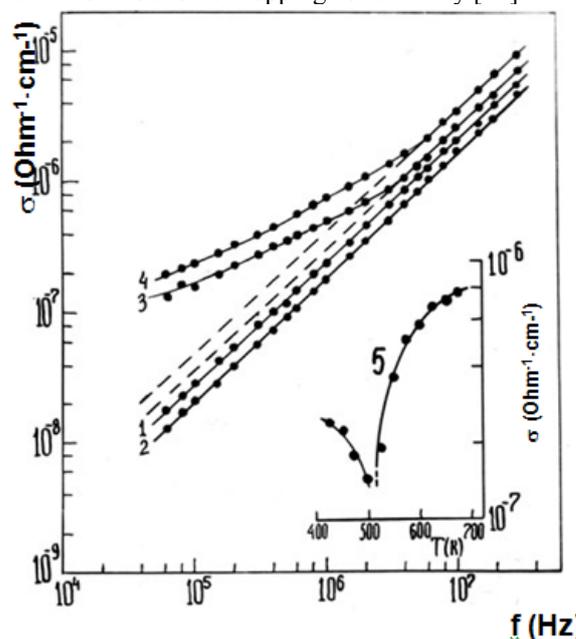


Fig. 2. Frequency dependences of the electric conductivity of oligohydroquinone specimens obtained at 423 (1), 473 (2), 573 (3), and 673 K (4). The insert gives the dependence of σ for specimens at a frequency of 10^6 Hz and at $T = 293$ K on the oligohydroquinone destruction temperature.

The variations observed in the electrical properties of the specimens are in good agreement with the data obtained as a result of studying the compositions and structures of the oligohydroquinone destruction products. Thermo-oxidative destruction of oligohydroquinone at $T < 498$ K fails to bring about substantial variations in the elementary composition, whereas the IR-spectra of the specimens show an increase of the relative intensity of the absorption band of quinone C=O groups in the 1650 cm^{-1} region. In this case a partial oxidation of hydroquinone and quinone bonds and a recombination of the radical semiquinone-type centres are likely to take place. At $T > 523$ K an intensive oxidation, dehydration, dehydroxylation and dehydrogenation of hydroquinone links begin, which leads to the structurization of oligohydroquinone. In elementary analyses of the products an increase of the carbon content and a decrease of the hydrogen content are observed whereas IR-spectra show a decrease of the relative intensity of the absorption bands of hydroxyl (in the 3400 to 3600 and 1200 cm^{-1} regions) and aromatic CH- groups (in the 830 and 870 cm^{-1} regions). As this takes place, the solubility and fusibility of these specimens deteriorate, as compared to the initial oligomer. The products of thermo-oxidative destruction of oligohydroquinone are infusible and insoluble at $T > 623$ K. Their high carbon content and the diffuse nature of their IR-spectra also bear witness to the formation of joined and carbonized products.

As known [14] the paramagnetic centers in polymers with a developed system of conjugation are decisive factors in charge-transfer processes in electric fields. The

concentration of paramagnetic centers, measured by us in oligohydroquinone specimens is in good agreement with the structural and chemical variations taking place in oligohydroquinone in the course of thermo-oxidative destruction (Fig. 3). The observed nature of variations in the concentration of paramagnetic centers corresponds to the non-monotonic variation of the electrical properties of the specimens both with DC (Fig. 3) and AC (insert in Fig. 2).

The non-monotonic nature of the dependence of the electric conductivity of the oligohydroquinone specimens on the level of their thermo-oxidative destruction is also preserved while studying the temperature dependence of the electric conductivity of specimens at DC (Fig. 4).

A region of an exponential dependence of σ on T is revealed over a wide temperature range. As the oligohydroquinone destruction temperature grows, the value of σ varies substantially. At the same time, a non-monotonic variation of the activation energy E also occurs. However, as this takes place, the compensation effect known as the Meyer-Neldel rule is met:

$$\log \sigma_0 = \alpha + \beta E \quad (3)$$

where α and β are constant coefficients.

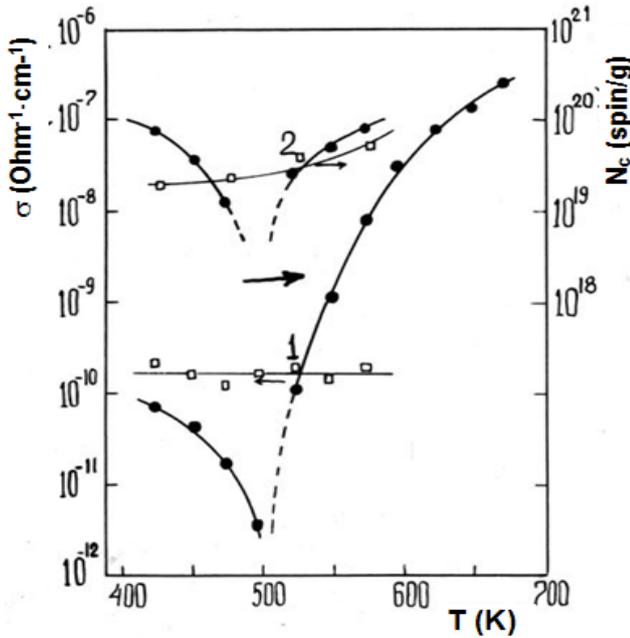


Fig.3. Temperature dependences of the electric conductivity on DC at $U=100$ V and $T=293$ K (1) and concentration of paramagnetic centers (2) of oxidative destruction of oligohydroquinone.

Measurements have shown that when the linear sections of the dependence of $\log \sigma$ on $10^3/T$ are extrapolated to $10^3/T = 0$, they intersect at one point with the coordinates $\sigma'_0 = 8 \times 10^{-5} \Omega^{-1} \text{cm}^{-1}$ and $10^3/T = 2.14 \text{ K}^{-1}$. Earlier, while analyzing the electrical properties of some polymers with a conjugation system [15, 16] it was suggested to characterize their semiconductive properties not by two parameters (σ_0 and K) but by three parameters (σ'_0 , T_0 , and E) in the following expressions:

$$\sigma = \sigma'_0 \exp\left(\frac{E}{kT_0}\right) \exp\left(-\frac{E}{kT}\right) \quad (4)$$

where σ'_0 is a factor independent of E .

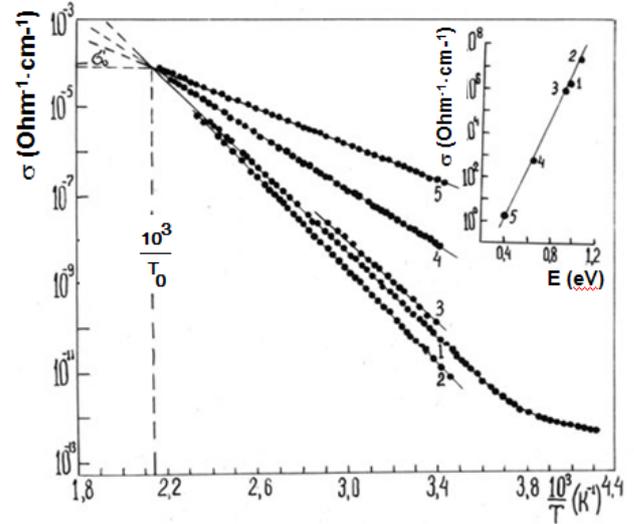


Fig.4. Temperature dependences of the electric conductivity at DC for oligohydroquinone specimens subjected to thermo-oxidative destruction at temperatures 423 (1), 473 (2), 523 (3), 573 (4) and 673 K (5). The insert is the dependence of σ_0 on E .

Upon taking the logarithm of the temperature-independent pre-exponent we obtain:

$$\log \sigma_0 = \log \sigma'_0 + \frac{0.43}{kT_0} E$$

Expression (5) coincides with the Meyer-Neldel rule (1) at constant $\alpha = \log \sigma'_0$ and $\beta = \frac{0.43}{kT_0}$. The values of α and β

calculated from the experimentally established values of σ'_0 and T_0 are in a good agreement with those found from expression (1) on the basis of the slope of the dependence of $\log \sigma_0$ on E (Table).

Table
Meyer-Neldel rule parameters for oligohydroquinone

Method of determination	Parameters			
	α	β, eV^{-1}	$\sigma'_0, \Omega^{-1} \text{cm}^{-1}$	T_0, K
$\log \sigma_0 \sim E$	-4.2	11.20	7×10^{-5}	458
$\log \sigma \sim T^{-1}$	-4.1	10.75	8×10^{-5}	467

Thus, depending on the of thermo-oxidative destruction the electric conductivity of oligohydroquinone and its activation energy vary non-monotonically and over a rather wide range, the variations are taking place in accordance with the Meyer-Neldel rule.

- [1]. *W. Meyer and H. Neldel. Z. Tech.*, 1937, 18, 588.
- [2]. *D. J. Fisher. Defect and Diff. Forum* 192-193.
- [3]. *Y. Lubianiker and T. Balberg. J. Non-Crystalline Solids*, 1998, 227-230, 180.
- [4]. *M. Kondo, Y. Chida, A. Matsuda. J. Non-Crystalline Solids*, 1996, 198-200, 178.
- [5]. *S. K. Ram, S. Kumar, R. Vanderhaghen, et al. J. Non-Crystal. Solids*, 2002, 299-302, 411.
- [6]. *K. Shimakawa, P. Abdel-Wahab. Appl. Phys. Lett.*, 1997, 70, 652.
- [7]. *N. Mehta, K. Singh, S. Kumar. Philosophical Magazine*, 89, No. 9, 2009, 797-806.
- [8]. *E. J. Meijer, M. Matters, P. T. Herwig et al. Appl. Phys. Lett.* 2000, 76, 3433.
- [9]. *R. Widenhorn, L. Mundermann, A. Rest, E. Bodegom. J. Appl Phys.*, 2001, 89, 8179.
- [10]. *D.M. Goldie. J. Mat. Science*, 2002, 37, 3323.
- [11]. *A.V. Ragimov, B.A. Mamedov, A.I. Kuzayev et al. DAN Azerb. SSR*, 1980, No.10, 54.
- [12]. *A.V. Ragimov, B.A. Mamedov, B.I. Lyogonky. Vysokomolek. Soyed.*, 1977, A19, No. 11, 2538.
- [13]. *B.I. Shklovsky. Fiz. i Tekhn. Poluprovodnikov*, 1972, 6, No. 12, p. 2325.
- [14]. *Yu.A. Vidadi, A.V. Ragimov, B.A. Mamedov et al. Phys. Stat. Sol. (a)*, 1983, 79, No. 2, 645.
- [15]. *Yu. A.Vidadi. Phys. Stat. Sol. (a)*, 1980, 61, No.1, 59
- [16]. *Yu.A. Vidadi. Zh. Fiz. Khim.*, 1980, 55, No.9, 2483.