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Ferroelectric-like behaviour of melanin: Humidity effect on current-voltage characteristics

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ABSTRACT

The influence of low vacuum on quasistatic current-voltage (I–V) dependences and the impact of wet air pulse on dynamic bipolar I-V-loops and unipolar I-V-curves of fungal melanin thin layers have been studied for the first time.

The threshold hysteresis voltages of I–V dependences are near to the standard electrode potentials of anodic water decomposition.

Short wet air pulse impact leads to sharp increase of the current and appearance of “hump”-like and “knee”-like features of I-V-loops and I-V-curves, respectively.

By treatment of I-V-loop allowing for I-V-curve shape the maxima of displacement current are revealed. The peculiarities of I-V-characteristics were modelled by series-parallel RC-circuit with Zener diodes as nonlinear elements.

As a reason of appearance of temporal polar media with reversible ferroelectric-like polarization and ionic space charge transfer is considered the water-assisted dissociation of some ionic groups of melanin monomers that significantly influences electrophysical parameters of melanin nanostructures.

1. Introduction

Melanins belong to the class of polyfunctional biospherical nanostructural macromolecules [1,2]. Being hydrated under environment conditions melanin can be considered as natural organic material or synthetic disordered polymer with hybridized mixed electronic-ionic conductivity and can be classified as one of bio-electronic materials [3–9].

Natural melanins are formed due to enzymatic metabolism in the course of melanogenesis process [1,2] resulting in the mixture of 5,6-dihydroxyindole (DHI) and 5,6-dihydroxyindole-2-carboxylic acid (DHICA) as precursors of main monomeric units, including their various oxidized forms, in particular, 5,6-indolequinone (IQ) and 5,6-indolequinone carboxylic acid (IQCA), and also proteins, lipids and some metal ions.

Synthetic melanins and eumelanins [3–10] can be formed from the same DHI and DHICA basic units taken in definite percentage. DHI and DHICA monomer units can exist in various oxidation states and linked randomly with each other forming quasi-planar oligomers and nanostructures.

The interest for melanin extracted from fungi, plants, animal and human pigments, synthetic melanin and melanin-like materials [9] is connected with their promising applications in photo- and other types of protection [11,12], neuro-functionality [1,13], free radical scavenging (in particular, biosensing) [1], and solution of melanoma problem [2]. Melanins including fungal one are widely discussed in terms of prospects for photovoltaic applications [14–17], including development of donor-acceptor compositions of melanin with other compounds [18]. During the decades of research history of melanin (from 1960s [19,20]) a multitude of intense studies in the areas of biology [1,2,12,13,19], chemistry [19,21,22] and physics [5–9,15–18,20–30] was performed.

Almost 40 years ago melanin was considered as natural amorphous organic semiconductor [28,29] and lately was proposed as electronic-ionic hybrid conductor for molecular bioelectronics [8,9]. Later heteropolymer model [1] and nano-scaled aggregate model [24,25] of eumelanin were proposed and decisive role of chemical disorder was established [22]. Recently, in the issue of current-voltage *dc* and infra-low frequency *ac* characterization, eumelanin was considered as promising for space charge

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storage based memory devices [26], protonic devices and other bio-electronic applications [27].

Being always partially hydrated, depending on surrounding humidity level melanins possess water molecules influenced physical properties, in particular bistable electrical switching phenomena [28,29], electrical charge storage effect [3,4], hopping conductivity and polarization [5–7], hysteretic current-voltage characteristics [26,27].

Current-voltage characteristics of metal/melanin/metal systems have been investigated in quasistatic mode [26–28]. These results give the information about electrical charge transport and trapping/release processes on their final quasi-stationary stage. In order to obtain more information about the initial stage of charge transfer processes, the study of current-voltage characteristics in dynamic mode is necessary, and so the step from static to dynamic operation mode in melanin conductivity investigations is required.

Earlier we reported [31–37] about the considerable and fast reaction on the humidity impact for a number of nonorganic porous systems, namely zeolite-like Na-Y and mesoporous MCM-41 systems [31], porous Si [33–35] complex metal-oxide ceramics [32,35] and $LiNbO_3$-films [36,37]. These studies proved the efficiency for examining the changes of parameters of bipolar and unipolar dynamic current-voltage characteristics connected with the pulse change of humidity in dynamic operational mode. Therefore, in this paper we present a comparison of the results for static humidity influence on quasistatic current-voltage characteristics and pulse humidity impact on dynamic current-voltage characteristics of natural melanin. By discussing the obtained results, we aim to provide scientific insights into the mechanisms of electrical transfer supported by equivalent scheme modeling.

2. Experimental

2.1. Sample preparation

The powder of studied fungal melanin was extracted from basidial fungi and purified by Prof. L.F. Gorovyi (Institute of Cell Biology and Genetic Engineering, National Academy of Sciences of Ukraine) [38,15]. The absorbance, luminescence and photovoltaic properties of the fungal melanin were characterized elsewhere [15]. The melanin powder was dissolved in distilled water at the concentration of 10 mg/ml (1 w/w%), and thin films were obtained by drop casting of water solution on the substrates with In:Sn oxide, ITO, electrodes. The substrates had two strips of ITO electrodes placed in parallel close to each other forming channel that length and width were 100 μm and 4 mm, respectively. The film layer of melanin and ITO electrodes formed planar structure of ITO/melanin/ITO (PSM). The films of melanin were very inhomogeneous by thickness forming dendrite fibers. Average film thickness measured by rod micrometer was about 10 μm.

2.2. Measurements

The basic method applied for examining the influence of static and pulse humidity changes on electrical parameters of PSM was current-voltage characterization. Static humidity influence was studied by its effect on quasistatic current-voltage characteristics. Pulse humidity influence was studied by its impact on dynamic current-voltage characteristics as in our previous studies of porous and mesoporous systems [31–37]. Taking into consideration different levels of photosensitivity depending on various kinds of melanin, different surrounding conditions, material state and type of used sample structure (see e.g. Ref. [9,21,26]) all the measurements were performed for the samples screened by opaque casing.

Quasistatic current-voltage characteristics (I-V-dependences) were obtained in air atmosphere of relative humidity about 70% under the normal pressure and under low vacuum 50 Pa (0.38 Torr). The measurements were performed in uni-cycle mode of applied *dc* voltage in the range of (0 to ±100) V with 3 approximately equal logarithmical steps per decade. Current values were registered with a Keithley 6514 electrometer as current achieves of its quasistatic value after 2–5 min of relaxation.

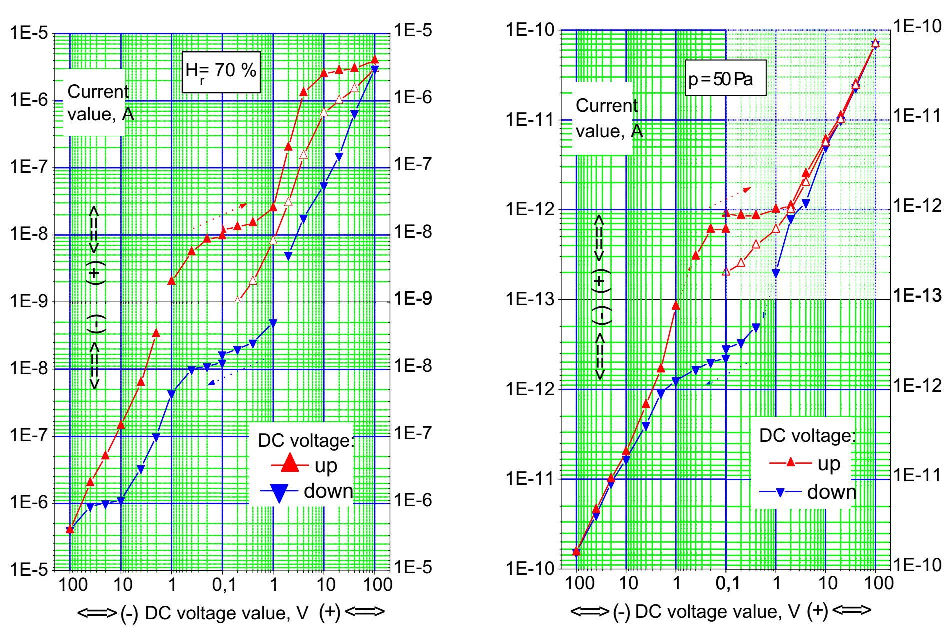

Fig. 1. Quasistatic unipolar current-voltage dependences of ITO/Melanine/ITO planar structure at atmosphere air pressure (left) and at low vacuum (right). Positive and negative runs marked by (+) and (−) respectively. Poling run marked by open symbols.