

Electrochemical impedance spectroscopy of organic polyiodides with different anion composition and proton disorder

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Organic polyiodides are perspective materials for solid-state dye-sensitized solar cells. Therefore, investigation of dielectric properties and conductance mechanisms is critically important for their further applications. As it was demonstrated, the electrochemical impedance spectroscopy (EIS) is appropriate experimental technique for characterization of polyiodide behavior [1].

In the framework of this report, the impedance spectra (IS) of polyiodide crystals with different anions: symmetric I_5^- anion in case of tetramethylammonium pentaiodide (**1**) and symmetric I_3^- anion in diiodobutenyl-bis-thioquinolinium triiodide (**2**) were investigated in frequency range 0.1 Hz - 1 MHz at temperatures 123 K - 298 K. To identify the dielectric relaxation processes and parameters of electric conductivity, different representation such as complex dielectric, electric modulus and conductivity spectra of IS were employed.

Independently on temperature, the exact values of direct current conductivity (σ_{DC}) could not be derived from real part of electric conductivity spectra (σ'). However, one can estimate the upper limits of the DC conductivity for samples **1** and **2** as 5×10^{-12} S/cm and 10^{-12} S/cm, respectively. As follows from the analysis of the imaginary part of the complex conductivities of both samples, they have both drift and hopping mechanisms of electric conductivity.

Dielectric spectra of samples have rather complicated nature and contain information about relaxation processes. As most of these processes are in the low frequency range, it is more convenient to observe and identify them using electric modulus representation. At high temperatures (at $T=333$ K for **2** and at $T=298$ K for **1**), one can clearly observe (fig. 1) three relaxation modes. The first one can be observed at the lowest frequency ($f = \sigma_{DC} / \epsilon_{\infty} \epsilon_0$) and can be assigned to the electric conductivity. The second one is probably originated due to the relaxation of Maxwell Wagner polarization because of the heterogeneous structure of the samples. The third mode was found in the middle part of the frequency range and was preliminary attributed to the rotation of molecules owing to the coupling of their dipole moments with probing voltage. Relatively slow relaxation frequency of this mode was explained by their significantly high moment of inertia.

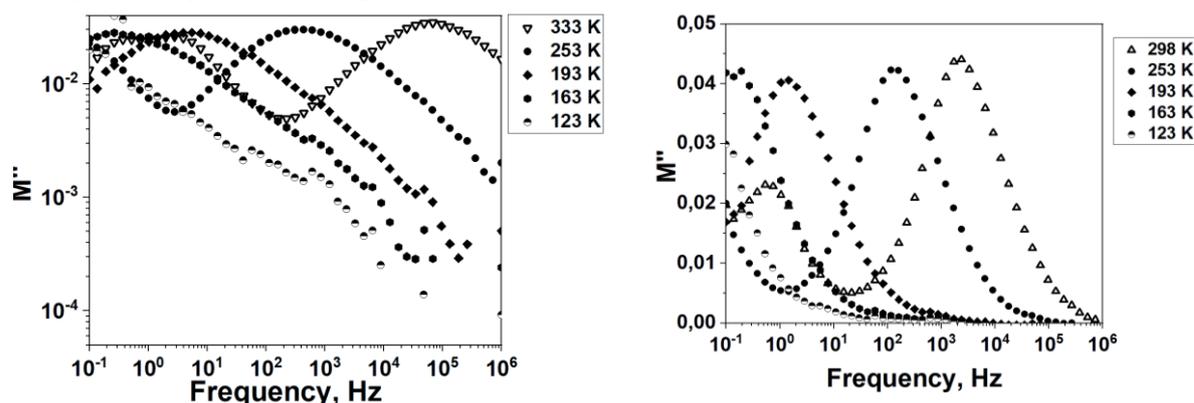


Figure 1. Dependence of the imaginary part of the electric modulus on frequency for tetramethylammonium pentaiodide **1**(right) and diiodobutenyl-bis-thioquinolinium triiodide **2** (left).

Further development of the research on the way towards understanding the nature of undergoing processes and their role in material design may be connected with the study of the influence of illumination effect by the light irradiation of different wavelength as it happens in dye-sensitized solar cells.

Funding for this research was provided by the Ministry of Education and Science 4.1157.2017/4.6.

1. H. Yu, L. Yan, Y. He, H. Meng, W. Huang, *Chem. Commun.*, **53**, 432 (2017).