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Hyper capacity of MCM-41<nematic> supramoleculer structure in the radio-frequency range

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Properties

ABSTRACT

Purpose: of this paper was: 1) to synthesize supramolecular MCM-41<nematic> structure (p-cyanogen phenyl ether of n-heptyl benzoic acid - 40%)>> with inserted guested nematic and 2) to study its dielectric properties.
Design/methodology/approach: Supramolecular MCM-41<nematic> structure has been synthesized by vacuum encapsulated method at room temperature. Dielectric properties have been studied by impedance spectroscopy method in the frequency range 10^{-3}-10^{6} Hz by "AUTOLAB" complex of "ECO CHEMIE" (Holland), supported by computer programs FRA-2 and GPES.
Findings: We have found a tremendous increase of the permittivity and a low value of the tangent of angle of electric losses, as well as the appearance of low frequency inductive response.
Practical implications: Super high capacitors of radio range and time-delay lines allow to use them in a direct incorporation into nanoelectronics devices as a new class of super high capacitors and nanostructured time-delay lines.
Originality/value: First time we have received: 1) supramolecular structure of the configuration of molecular-lattice nonorganic matrix with a non nematic substrate, 2) significant inductive response in such structures.
Keywords: Molecular-lattice structures; Intercalation; Supramolecular compounds; Impedance spectroscopy

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1. Introduction

Recent rapid development of nanotechnology demands effective work of autonomous nanodevices which are based on the integration of the energy blocks into the nanostructure architecture. However the problem of the development of devices for energy generation, transformation and storage in nanodevices as well as for the important nanoelectronic components such as delay line, or varycaps only now has been announced.

The purpose of this paper is to find out possible ways of the solution of the above mentioned problems.

2. Idea and the technique of experiment

It is obvious, that a significant increase of energy-conversion efficiency of the matter unit of mass and volume can not be reached only by extensive expansion of the frame of new cathode materials nowadays without fundamentally altering the conceptual positions. In this context, the principally new regularities of the interface charge transport, as well as the capacity and Faraday energy storage of high efficiency, can be achieved by using the third type of matter organization - clathrate or supramoleculer in the electroenergy generation processes. Clathrates [1] are of the special type of matter structural organization. They can be formed as compounds of insertion molecules of one type (called "guest") into the "guest positions" of crystal structures consisted from the molecules of another type. Inserted "guests" do not form any strong chemical bond with the crystal lattice called "host".

The determined supramolecular structures can be valuable not only for Faraday current creation, but also for capacitive accumulation of charge and energy. The first results, received in the past few years, showed anomalous behaviour of dielectric permittivity of segnetoelectrics, encapsulated into the nano structures like honeycomb [2]. These results became the base for the arrangement of this idea to the significant increase of energy capacitance of the capacitors out of segnetoelectric state, which often makes narrow temperature conditions and thus narrows the directions of their application. In another words, the problem of the behaviour of the easily polarized molecules, particaliarly nematics molecules, inserted into the clathrates created cage has arisen.

To reach this goal we used a molecular-lattice mesoporous regular structure on the SiO_2 - MCM-41 [3] base as the host-matrix. This structure is of hexagonal structure type like honeycomb with walls thickness of 0.6…0.8 nm and calibrated pore sizes. According to the electron microscopy data the pore sizes are ~3.7 nm.

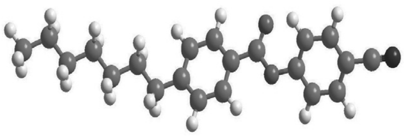

Fig. 1. Structure of nematic molecule (CPhEHBA) - 40%

Synthesis of hierarchic doublet matrix MCM-41< nematic> structure has been carried out in the following way: after thermal vacuum desorption, carried out at 140°C temperature during 2 hours at residual pressure 1.33 Pa keeping the pressure stable this structure was cooled to 80°C temperature and then penetrated by the liqiud-crystall nematic (p-cyanogen phenyl ester of 40% n-heptyl benzoic acid), molecular structure of which is shown in Fig. 1. After washing off the surface of the adsorbed organic precursor and drying at 130°C temperature, the obtained hybrid material was pressed in tablets of m = 88 mg, diameter d = 8.35 mm, and height l =1.43 mm. Indium contacts have been deposited on both sides of the tablets by thermal vacuum deposition.

Kinetics of the current creation intercalation was studied by impedance spectroscopy in the frequency range 10^{-3}-10^{6} Hz by "AUTOLAB" complex of "ECO CHEMIE" (Holland), supported by computer programs FRA-2 and GPES.

3. Results and discussion

Frequency dependencies of specific resistance of molecular-lattice structure before and after nematic insertion are given in Fig. 2. As one can see, the insertion of liquid crystal molecules into the molecular-lattice silicate structure leads to the increase of specific resistance and frequency dispersion.

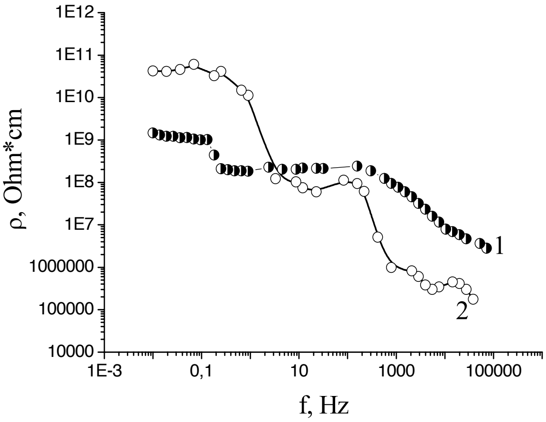

Fig. 2. Frequency dependences of specific resistance of molecular-lattice structure before (1) and after nematic insertion (2)

It is easy to see that generally $\rho(\omega)$ functions have ordinary frequency dependence: they consist of steady low frequency branch (it is different for different materials). At higher frequency this branch begins to decrease. However the middle frequency independent branch, which significantly converges after nematic insertion is non-trivial.

For electroconductivity (σ) such behaviour is described by the equation

$$\sigma = \sigma_{dc} + A\omega^{n} , \qquad (1)$$

where σ_{dc} is measured in direct current specific electroconductivity, caused by free current carriers, A and n are parameters dependent on temperature and composition.

The second term in (4) represents polarization component of total electroconductivity, which particularly leads to the charge carrier hopping over localized states in the vicinity of Fermi level, or excitation processes of electron capture into the band tails or bands of non-localized states. Such mechanism predicts the appearance of the capacitive response of localized states and frequency dependent impedance, which was confirmed by the existence of high frequency arc from the construction of total impedance in implicit plane with coordinate axes of its real and implicit components ReZ - ImZ (see Fig. 3a). In this case the low frequency branch corresponds to the charge transport through intergrain margins. Linear branch placed between mentioned above arches most probably corresponds to the impedance of inhomogeneous layer of a certain thickness. Its elementary volume possesses by implicit conductivity is characterized by a fixed phase i.e., reflects particles of mezo porous silicate matrix.

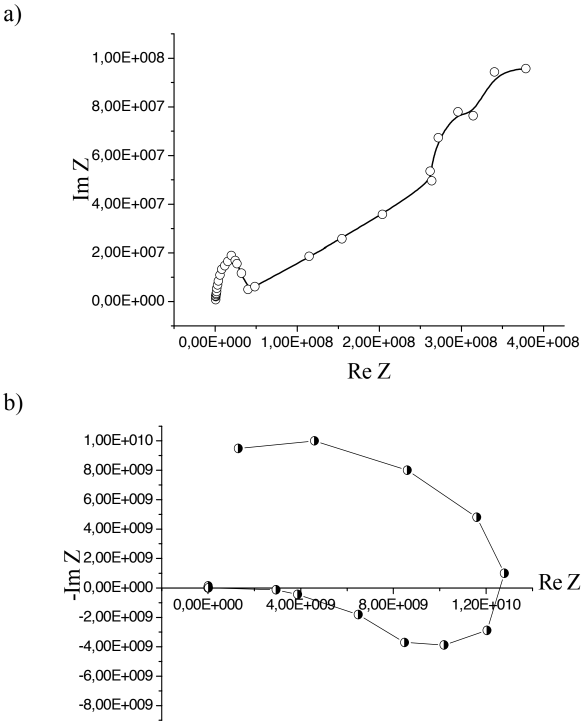

Fig. 3. Nyquist diagrams for molecular-lattice structure before (a) and after (b) nematic insertion

Frequency dependences of implicit impedance Z have been analyzed by tabular-analytical method using program package ZView 2.3 (Scribner Associates). Approximation error did not exceed 4%. As a result the analog circuit that modulates corresponding impedance locus which contains two parallel RC sections $C_V||R_V$ and $C_B||R_B$. They are concatenated by phase element (NUP), as it is shown in Fig. 4.

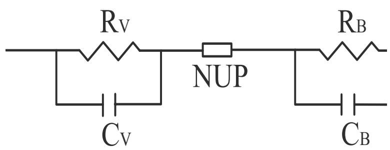

Fig. 4. Equivalent circuit for ceramics received from meso porous MCM-41Element NUP is determined in implicit plane as follows [4]

$$X_i(j\omega)=\left\{\left[Z_{i,CPE}(j\omega)-r_0\right]^{-1}-\left[Z_{i,CPE}(j\omega)+r_0\right]^{-1}\right\}^{-1}, \qquad (2)$$

where $Z_{i,CPE}(j\omega)=A_i^{-1}(j\omega)^{-n_i}$.

Testing the proposed model of experimental data showed good results. Kramers-Kroning factor did not exceed $3\cdot10^{-5}$.

Nematic insertion into molecular-lattice structure moving into inductive quadrant of implicit plane mostly transforms low frequency of impedance locus (see Fig. 3b). Such phenomenon of "negative" capacity is well known, however its mechanism has not yet been clarified and probably its nature is not unified. Mostly it is explained by capture of injected carriers and their holding by trapping centers during the time commensurable with half period of sine-shaped signal [5,6]. According to another a more general mechanism, inductive behaviour appears even if sizes of the layers where charge is inserted are small or supersmall, i.e., several nano-meters range [7].

It should be emphasized that interest to the phenomenon of negative capacitance is not only scientific one: structures with negative capacitance allow the effective solution of the problem of hold-up circuits in nanodevices, nanolimited geometry of which excludes 'a-priori' coil usage.

From the point of view of practical usage of such capacitor structures concerning their quality, the studied frequency range was chosen such that tangent of loss angle should not exceed unit. This frequency range corresponded to mentioned above demands was chosen for the analysis of the dielectric permittivity behaviour. As it follows from Fig. 5 such region covers frequency range (studied in extreme case) $0.01\text{-}10^5$ Hz. Here dielectric permittivity sharply increasing after molecules insertion (Fig. 6) possesses by anomalous dispersion, the nature of which can be caused also by jumping charge transport. However mechanism of such anomalous behaviour is probably more complicated in these structures.

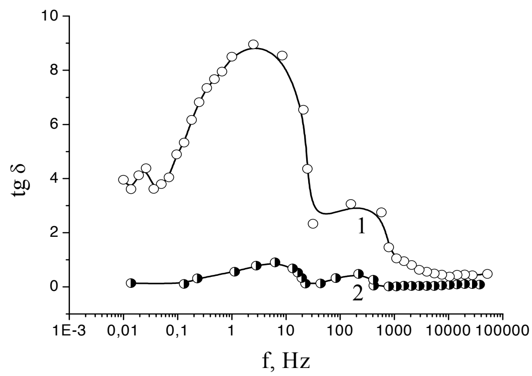

Fig. 5. Frequency dependences of tangent of loss angle of molecular lattice structure before (1) and after nematic insertion (2)

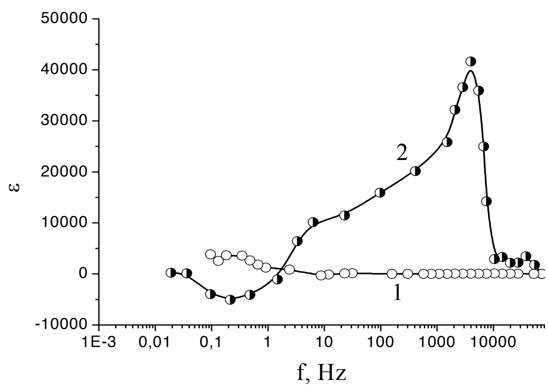

Fig. 6. Frequency dependences of permittivity of molecular lattice structure before (1) and after nematic insertion (2)

Table 1.
Comparative characteristics of low voltage capacitors

Capacitors	Voltage, V	Specific capacitance of active system, mF/cm^3	tg δ (100 Hz)
Oxide-semiconductor polar K 53-16	1.6	~ 0.6	> 0.12
Oxide-semiconductor tantalum K 53-20	1.6	~ 0.14	< 0.12
Oxide - aluminium K 53-30	3	~ 0.72	< 1.2
Tantalum-oxide volumetric-poroud K 52-1	3	~ 0.38	0.15
Proposed capacitor (1 micrometer thickness)	>3.5	~340	0.08

Described above behaviour of dielectric permittivity shows a forthcoming of multiformity of Col-Cola diagrams, confirmed experimentally.

Practically usage of such structures is obvious. First of all it is a new class of super high capacitors (Table 1) and nanostructured time-delay lines, which can be directly incorporated into nanoelectronics devices.

4. Conclusions

1. Supramolecular structure with inserted guest nematic provides huge rise of dielectric permittivity and low value of the tangent of loss angle as well as appearance of low frequency inductive response.
2. Its usage for the technology of r-frequency capacitors will increase specific capacitance by a factor of 500 and simultaneously decrease the electric losses.
3. The ability of MCM-41<nematic> supramoleculer structure to cause the inductive response opens new opportunities for the formation of nanostructural delay lines for nanoelectronics devices.

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