

# Quantum accumulation of electric energy in inorganic/organic clathrates

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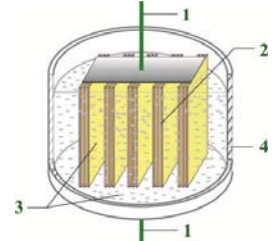
The device fabrication technology for generating and accumulating electric energy is based on the idea of application of materials with developed internal surface and distinctly anisotropic nature of chemical bond. The substances of described above nature are required to possess large values of permittivity (over 10<sup>5</sup>) and loss tangent less than 1, especially for frequencies under 10<sup>-2</sup> Hz. The possibility for injection of electrons into nanoheterophases's interface was anticipated theoretically [1, 2] under listed above conditions and such structures demonstrate the phenomenon of quantum accumulation of energy.

This work deals with synthesis and electric properties investigation of GaSe-based samples intercalated with thiourea SC(NH<sub>2</sub>)<sub>2</sub> and <SC(NH<sub>2</sub>)<sub>2</sub>><SmCl<sub>3</sub>>> and mesoporous silica matrix MCM-41 intercalated with thermo-expanded graphite TEG by means of impedance spectrometry method.

The character of impedance frequency dispersion, loss tangent and permittivity for synthesized samples was determined.

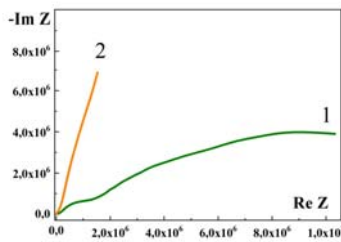
### Experimental methods and techniques:

- Intercalation/deintercalation technique
- Impedance spectroscopy of investigated samples

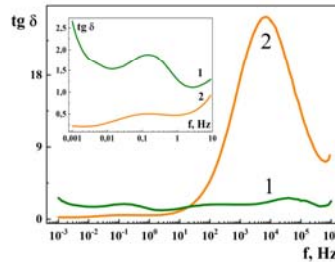


**Scheme 1.** The device prototype for quantum accumulation of energy:  
 1-shunts, 2-working electrode, 3-electrolyte, 4-counter electrode

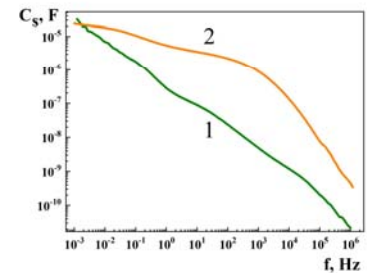
### Impedance spectrometry for GaSe-based samples



**Figure 1.** Nyquist plots for quantum accumulator with initial GaSe-electrode (1) and expanded GaSe matrix (2).



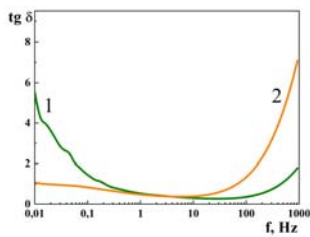
**Figure 2.** Frequency  $f$  dependence of loss tangent  $tg \delta$  for quantum accumulator with initial GaSe-electrode (1) and expanded GaSe matrix (2).  
 Inset - loss tangent in 10<sup>-2</sup>-10 Hz range.



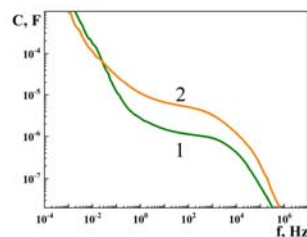
**Figure 3.** Frequency  $f$  dependence of capacitance  $C$  for quantum accumulator with initial GaSe-electrode (1) and expanded GaSe matrix (2).

### Impedance spectrometry for GaSe<CS(NH<sub>2</sub>)<sub>2</sub>> and GaSe<CS(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>>

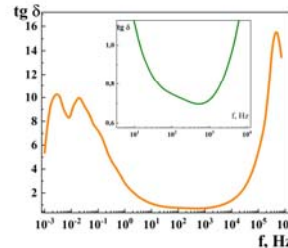
### Impedance spectrometry for MCM-41<SmCl<sub>3</sub>>



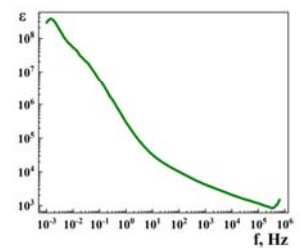
**Figure 4.** Frequency  $f$  dependence of loss tangent  $tg \delta$  for quantum accumulator with GaSe<CS(NH<sub>2</sub>)<sub>2</sub>> (1) and GaSe<CS(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>> (2).



**Figure 5.** Frequency  $f$  dependence of capacitance  $C$  for quantum accumulator with GaSe<CS(NH<sub>2</sub>)<sub>2</sub>> (1) and GaSe<CS(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>> (2).



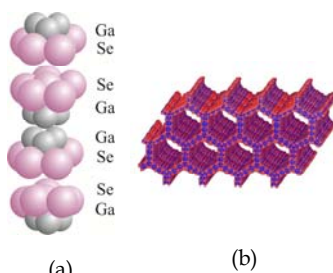
**Figure 6.** Frequency  $f$  dependence of loss tangent  $tg \delta$  for quantum accumulator with MCM41<TEG> electrode.  
 Inset - loss tangent in 10<sup>-1</sup>-10<sup>4</sup> Hz range.



**Figure 7.** Frequency  $f$  dependence of permittivity  $\epsilon$  for quantum accumulator with MCM41<TEG> electrode.

### CONCLUSIONS

- The phenomenon of quantum accumulation of energy was demonstrated in electrochemical cells with working electrodes with developed intrinsic surface and distinctly anisotropic nature of chemical bonds. The scheme of the cell for quantum accumulation of energy is working electrode/  $\gamma$ -BL+N-MP:MA:TMA / Al.
- GaSe, GaSe<SC(NH<sub>2</sub>)<sub>2</sub>>, GaSe<SC(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>> or MCM41<TEG> were used as working electrodes; The mixture of  $\gamma$ -Butyrolactone  $\gamma$ -BL and N-Methyl-2-pyrrolidone N-MP in 70%:30% (weight) ratio respectively were used for electrolyte preparation in combination with Maleic acid MA and Trimethylamine TMA of final ratio  $\gamma$ -BL+N-MP:MA:TMA=80%:10%:10% (weight). Aluminium plate was used as counter electrode.
- The working electrode with fourfold expanded matrix of GaSe demonstrates faradaic energy accumulation. Loss tangent  $tg \delta$  is less than 1 in infra-low frequency region and specific capacitance is 10 F/g at frequency 10<sup>-3</sup> Hz.
- The working electrode based on the MCM41<TEG> composite material with well developed surface demonstrates maximum value of permittivity  $\epsilon \cdot 10^8$  at frequency 10<sup>-3</sup> Hz in combination with loss tangent  $tg \delta$  less than 1.
- The quantum accumulator with GaSe<CS(NH<sub>2</sub>)<sub>2</sub>> or GaSe<CS(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>> working electrodes performs pseudocapacitive charge accumulation. The loss tangent  $tg \delta$  is less than 1 in 2\*10<sup>-1</sup>+5\*10<sup>2</sup> Hz frequency range with maximum capacitance 6.55\*10<sup>6</sup> F for GaSe<CS(NH<sub>2</sub>)<sub>2</sub>> and  $tg \delta$  is less than 1 in 2\*10<sup>2</sup>+6\*10<sup>1</sup> Hz frequency range with maximum capacitance 7.55\*10<sup>-5</sup> F for GaSe<CS(NH<sub>2</sub>)<sub>2</sub><SmCl<sub>3</sub>>> electrode.



**Scheme 2.** Initial matrix of GaSe (a) and MCM-41 (b)