FEATURES OF PROTON TRANSFER AND PHASE TRANSFERS IN SYSTEM C_{60}-$CsHSO_4$

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Introduction

The interest to the investigation of composite materials consisting of ionconducting and dielectric (or semi-conducting) phases has grown strongly in recent years. It’s because of those unusual mechanical and conducting properties and great prospects of those industrial applications including protonconducting membranes for fuel cells.

Composite materials containing ionic crystals dispersed in oxide matrix are the most investigated of such systems. Composite materials containing cationconducting solid electrolytes are investigated much lower. The oxide - $CsHSO_4$ systems are the most investigated of cation-condusting systems. Strong lowering of temperature of superionic transfer was shown in this systems but ionic conductivity of this materials is lower then $CsHSO_4$ conductivity. This phenomenon was explained in [1] by high conducting phase stabilization on oxides surface. On the other hand no strong superionic transfer temperature lowering was shown in $CsHSO_4$ – SnO_2 system, but electronic and ionic conductivity parts were much higher then for initial composites [2]. According to [3] calculations these results were explained by protons injection from electrolyte volume on SnO_2 surface.

The aim of this work was conductivity and phase transfers features investigation in $CsHSO_4$-C_{60} composite materials.

Results and discussion

Composite materials were prepared from initial components abrasive wearing and those pressing in pellets and vacuumization for 12 hours. The pressing was carried out directly in measuring cell with Pt foil electrodes for electrochemical measurements.

Electronic conductivity was determined by measurements at DC current and was lower then 10^{-8} Ohm/cm. Ionic conductivity was determined by impedancemetry method (Elins, Z350M). Typical impedance hodographs are represented on fig 1.

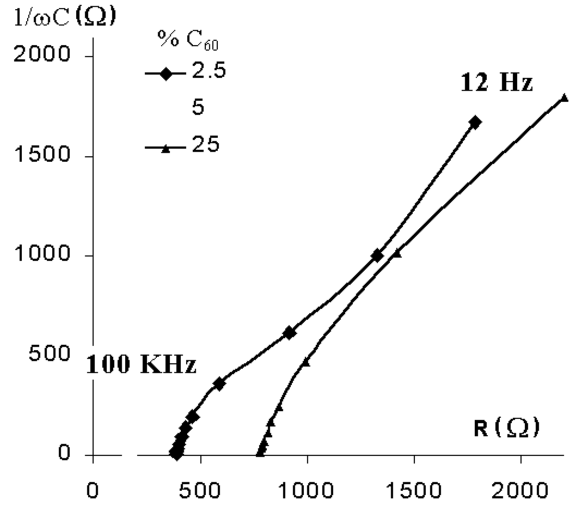


Fig 1. Typical impedance hodographs of C_{60}-$CsHSO_4$ system for different fullerene contents at 180^0 C.

An analysis of full equivalent schematic was not carried out; the value of ionic conductivity was determined as real part high frequency intercept with real axis.

The conductivity concentration dependences of composite material are represented on fig 2. It looks like a curve with two extremums – at 6 and 35% of fullerene contents at all temperatures. The positions of extremums do not depend on a way of fullerene preparation and cleaning but this intensity depends. DSC investigations were carried out to clarify these effects and for investigation of obtained composite materials.

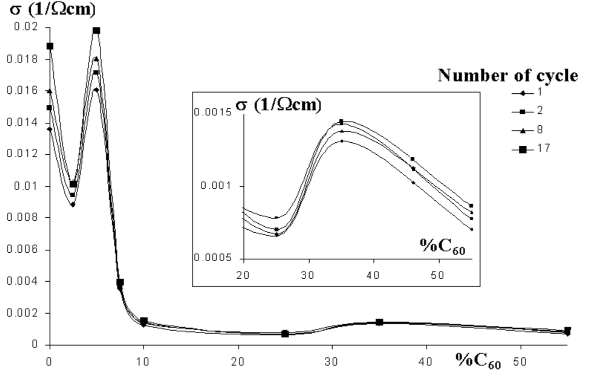
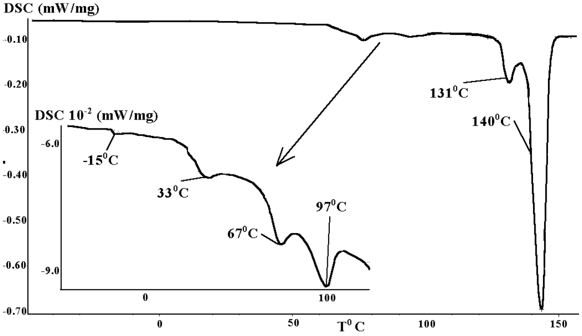


Fig 2. Conductivity concentration dependences for different cycles of heating-cooling at 180^0 C.

Endothermic effects are observed on DSC curves of investigated composite materials at –15±1^{0}C and 140±0.5^{0}C (DSC 204– Netzsch) independently on composition of material and a way of fullerene preparation. These effects correspond to orientation phase transfer of fullerene and superionic transfer of $CsHSO_4$ (fig 3). The heats of these transfers monotonically decrease with decrease of amount of phase corresponding the transfer and do not depend on composition of material (fig 4).



Puc 3. DSC curves of composite material after first cycle of heating-cooling.

But there are two other effects observed on DSC curves, which do not correspond to any component of composite materials. These values nonmonotonically change with change of composition of material (fig 5). The process of fullerene dispergation into $CsHSO_4$ matrix is observed on microphotographs at different cycles of heating-cooling. It can be explained by that the $CsHSO_4$ crystalls are quite mechanically strong before temperature of phase transfer, but they become plastic and fluid phase after it.

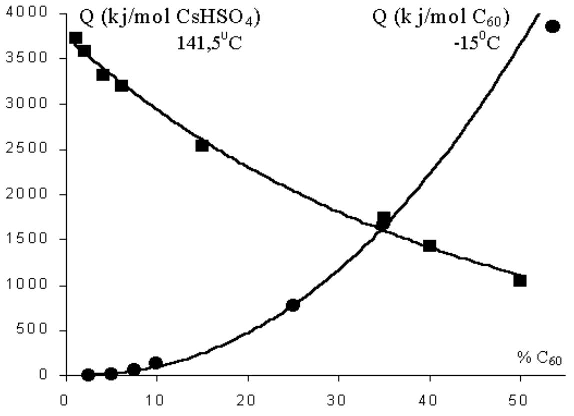


Fig 4. Thermal effects concentration dependences calculated for mol of component

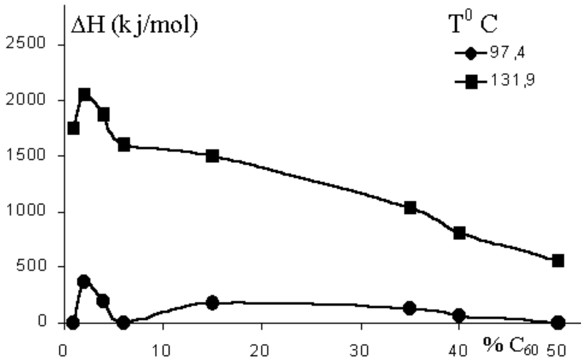


Fig 5. Heats of transfers concentration dependences.

The dependence of thermo and electrical properties of composite material vs. it's composition can be explained by $CsHSO_4$ intercalation in to fullerite matrix. $CsHSO_4$ do not forms separate crystal phase under intercalation and it's clasters obtain new proton conducting properties.

References

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