

# High conductive hybrid polymer CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>-Butvar compounds

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**Abstract.** Hybrid polymer compounds (1-x)CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>-xButvar (x=0–0.3), synthesized with different solvents (ethanol and isopropanol) were first synthesized and investigated. Fundamental possibility of creating new highly conductive thin polymer electrolytes based on CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> was shown. An optimal synthesis method was determined. The crystal structure of CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> (P2<sub>1</sub>/c) remains unchanged in the polymer system. The thickness of the electrolyte is no more than 50-100 μm. Proton conductivity increases by 2 orders of magnitude and depends on the composition. The highest conductivity was 10<sup>-1</sup> S/cm at 135 °C. Changes in conductivity are caused by dispersion of the salt, as well as by the presence of insignificant amounts of residual water under the synthesis conditions.

## Introduction

Acid salts with the general formula M<sub>n</sub>H<sub>m</sub>(AO<sub>4</sub>)<sub>p</sub> – (di)hydrogen phosphates, sulfates, selenates of alkali metals (n, m, p - integers) have high proton conductivity at 100-250 °C due to the existence of superionic phases with disordered hydrogen bond network. High conductivity is associated with the transfer of structural protons. The acid salts of MHSO<sub>4</sub>, MH<sub>2</sub>PO<sub>4</sub> and MH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> are most suitable for use as membranes in electrochemical devices. The first data on fuel cells (FCs) with membranes with acid salts appeared in 2004-2005 [1-3]. These FCs have a number of several advantages over the ones with Nafion membrane [4]. The possible candidate for the membrane is CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> - cesium pentahydrogen diphosphate [5-8]. CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub> has a monoclinic structure P2<sub>1</sub>/c with unit cell parameters a = 10.879 Å, b = 7.768 Å, c = 9.526 Å, β = 96.60°, Z = 4 [5,8]. Despite the high content of protons, the conductivity of single crystals is low, 10<sup>-4</sup> S/cm at temperatures up to 145 °C, and falls below 10<sup>-8</sup> S/cm at T <90 °C. Low conductivity with high activation energy, E<sub>a</sub> ≈ 2 eV, is associated with a strong hydrogen bond network, which impedes proton transfer. The conductivity of polycrystals exceeds single crystals by three orders of magnitude due to the formation of a pseudo-liquid layer at the crystallite boundary with high mobility of protons [6,7]. A number of high conductive nanocomposites with dispersed silica and tin pyrophosphate have been obtained [9-13]. Recently CsH<sub>5</sub>(PO<sub>4</sub>)<sub>2</sub>-Cr-MIL-101 composites showed high proton conductivity 10<sup>-2</sup>-10<sup>-3</sup> S/cm at 80–140°C due to salt amorphization in

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pore space matrix [14]. Flexible hydrophobic thin-film membranes with high conductivity at intermediate temperatures are of significant interest for electrochemical devices.

This work is devoted to the synthesis of new polymer  $(1-x)\text{CsH}_5(\text{PO}_4)_2$ -xButvar composite ( $x=0-0.3$ ,  $x$  - mass fraction) and investigation of structural and electrotransport properties. Polymer compounds were synthesized by tape casting using different solvents and methods of salt introduction into the polymer matrix. Butvar® B98 with thermal stability and extremely low water absorption, successfully used for the synthesis of highly conductive electrolytes, was chosen as a polymer heterogeneous matrix [15-18]. The presence of three different functional groups ensures high adhesion to various types of surfaces.

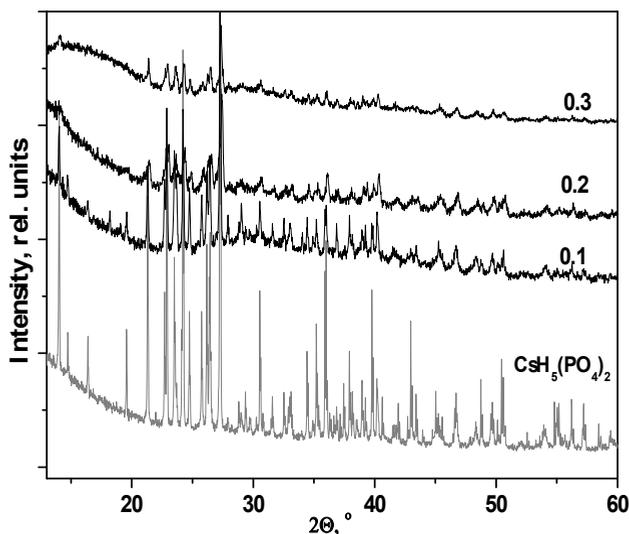
## Experimental

$\text{CsH}_5(\text{PO}_4)_2$  was synthesized by slow evaporation from an aqueous solution containing  $\text{Cs}_2\text{CO}_3$  (pure grade) and  $\text{H}_3\text{PO}_4$  (chemically pure grade) in a required stoichiometric ratio and was kept at  $100^\circ\text{C}$  to remove excess moisture. Ethyl (E) and isopropyl (I) alcohols with the boiling points  $78.37^\circ\text{C}$  and  $82.4^\circ\text{C}$  were used as solvents. Hybrid systems were synthesized by methods, differed by the manner of salt addition and used solvents. According to the first one a pre-synthesized  $\text{CsH}_5(\text{PO}_4)_2$  was added to an alcohol solution of Butvar. In the other way, the salt was synthesized by dissolving the starting components ( $\text{Cs}_2\text{CO}_3$  and  $\text{H}_3\text{PO}_4$ ) in ethanol. The solvent was removed by heating and intensive mechanical stirring and applied by tape casting using a TOB film deposition device. The conductivity was measured on films or tablets pressed from films with silver electrodes in cooling mode from  $135^\circ\text{C}$  at a rate of  $1^\circ\text{C}/\text{min}$  in the air with a relative humidity, RH~10-25% using an Instek LCR - 821 and E7-20 impedance meters. A Hitachi TM 1000 scanning electron microscope was used to evaluate the particle and film size. The phase composition was determined using a Bruker D8 Advance diffractometer ( $\lambda\text{CuK}\alpha_1=1.5406\text{ \AA}$ ) with a one-dimensional Lynx-Eye detector and a  $\text{K}\beta$  filter. Differential thermal analysis was performed on STA 449 F/1/1 JUPITER thermal analyzer (5 K/min in argon and oxygen atmosphere).

## Results and discussion

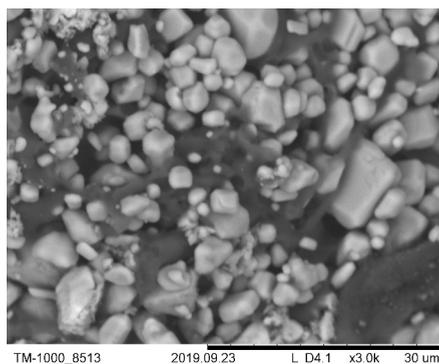
The results showed the ineffectiveness of introducing pre-synthesized  $\text{CsH}_5(\text{PO}_4)_2$  into the polymer, due to the formation of larger aggregates, as well as their coagulation (up to 5-7  $\mu\text{m}$ ) upon heating and stirring. It was shown that conductivity values for  $(1-x)\text{CsH}_5(\text{PO}_4)_2$ -xButvar (E) significantly exceed those for the system synthesized in isopropanol, which were close to the initial  $\text{CsH}_5(\text{PO}_4)_2$ . Therefore the main attention will be paid to  $(1-x)\text{CsH}_5(\text{PO}_4)_2$ -xButvar (E) obtained by dissolving the starting components.

The reflections of the synthesized  $\text{CsH}_5(\text{PO}_4)_2$  fully correspond to [5, 8] (Fig. 1). According to XRD patterns, no chemical interaction between the components was observed



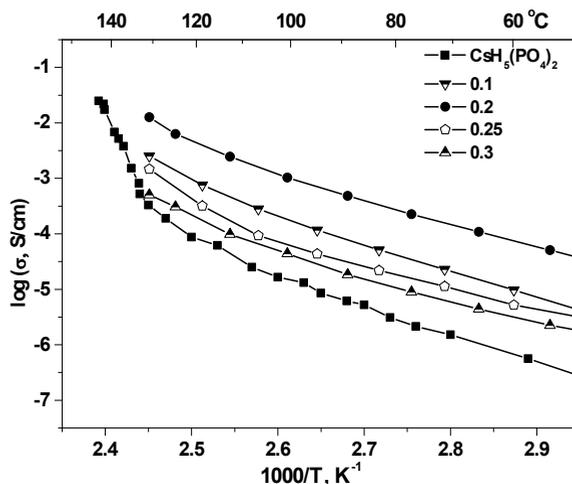
**Fig. 1.** XRD patterns of  $\text{CsH}_5(\text{PO}_4)_2$  and  $(1-x)\text{CsH}_5(\text{PO}_4)_2-x\text{Butvar (E)}$  with different polymer content in hybrid systems.

The crystal structure of the salt ( $\text{P}2_1/c$ ) remains unchanged. With  $x$  increase the intensity of salt reflections decreases significantly more than the salt mass fraction in the sample. There is some broadening of the peaks, indicating the salt dispersion. DSC data show a more significant decrease in the enthalpy of melting in comparison with the initial salt, which is also associated with the salt dispersion. The enthalpy of  $\text{CsH}_5(\text{PO}_4)_2$  melting varies from  $-92.3 \text{ J/g}$  to  $-57.2 \text{ J/g}$  for  $x = 0.2$ , which is greater than the ratio of mass fractions. An increase in the fraction of the polymer up to  $x = 0.15$  and  $x = 0.2$  results in the formation of a thin film with a thickness of  $50\text{-}100 \mu\text{m}$  with a fairly uniform distribution of salt particles (Fig. 2), which provides membrane flexibility and increased hydrolytic stability. The average salt particle size in the polymer matrix is  $3\text{-}4 \mu\text{m}$ .



**Fig. 2.** Electron microscopic images of  $\text{CsH}_5(\text{PO}_4)_2\text{-}0.2\text{Butvar (E)}$ .

The conductivity was calculated from the resistance values with the minimum capacitive component. With increasing temperature the proton conductivity increases due to the rise of the number of current carriers and their mobility. The character of the temperature dependence of the conductivity of polymer systems is similar to that for  $\text{CsH}_5(\text{PO}_4)_2$ , which shows that the conductivity mechanism remains unchanged (Fig. 3).



**Fig. 3.** Temperature dependence of conductivity of  $(1-x)\text{CsH}_5(\text{PO}_4)_2-x\text{Butvar}$  (E) with different contents of Butvar

For  $(1-x)\text{CsH}_5(\text{PO}_4)_2-x\text{Butvar}$  (E), the highest proton conductivity is observed, where the difference with  $\text{CsH}_5(\text{PO}_4)_2$  is two orders of magnitude. The conductivity reaches  $10^{-2}$  S/cm at  $135^\circ\text{C}$  under  $\text{RH}=25\%$ . The activation energy of conductivity decreases with  $x$  to  $0.96$  eV ( $x = 0.1$ ) and  $0.83$  eV ( $x = 0.2$ ) in comparison with  $\text{CsH}_5(\text{PO}_4)_2$  ( $1.05$  eV for polycrystals). The conductivity is highly dependent on the composition. With  $x$  increase the proton conductivity increases, reaches a maximum at  $x = 0.2$ , and then decreases up to 1–1.5 orders of magnitude due to the percolation threshold "conductor-insulator" type. The conductivity increase deals most likely with salt dispersion and the presence of insignificant amounts of residual adsorbed water at salt particles and salt-polymer interface formed under synthesis, which ensures efficient proton transfer. Indeed the thermogravimetric data showed that the polymer compound has a weak endothermic effect associated with the removal of water with the weight loss of  $\sim 0.1\%$ , in comparison with pure  $\text{CsH}_5(\text{PO}_4)_2$ .

## Conclusion

The possibility of creating new highly conductive thin polymer electrolytes based on  $\text{CsH}_5(\text{PO}_4)_2$  and Butvar has been shown. For the first time, the hybrid  $(1-x)\text{CsH}_5(\text{PO}_4)_2-x\text{Butvar}$  polymers were synthesized and electrotransport and structural properties were studied. The synthesis of polymer film electrolytes was carried out in a medium of various solvents such as ethanol and isopropanol. The salt synthesis by dissolving the starting components in ethanol is more preferable for the formation of thin polymer  $(1-x)\text{CsH}_5(\text{PO}_4)_2-x\text{Butvar}$  (E) compositions with  $\sim 50\text{--}100$   $\mu\text{m}$  thick and the higher proton conductivity ( $10^{-2}$  S/cm at  $135^\circ\text{C}$ ). The chemical interaction between the components was not observed. A significant increase in the conductivity is associated with dispersion, as well as the presence of insignificant amounts of adsorbed water at the salt - polymer interface under the synthesis that provides effective proton transfer. Polymer systems have demonstrated high chemical and thermal stability at temperatures up to  $135^\circ\text{C}$ , which makes them promising for further researches and using in electrochemical devices and medium-temperature fuel cells.

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