



Article Novel Highly Dispersed Additive for Proton-Conducting Composites

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Abstract: The proton conductivity and structural properties of $(1-x)CsH_2PO_4-xZnSnO_3$ composites with compositions of x = 0.2-0.8 were studied. Zinc stannate ZnSnO₃ was prepared by the thermal decomposition of zinc hydroxostannate ZnSn(OH)6, which was synthesized by hydrolytic codeposition. To optimize the microstructure of ZnSnO₃, thermal decomposition products of ZnSn(OH)₆ were characterized by thermal analysis and X-ray diffraction, Fourier transform infrared spectroscopy, low-temperature nitrogen adsorption, and electron microscopy. The study reveals that the thermolysis of ZnSn(OH)₆ at temperatures of 300–520 °C formed an X-ray amorphous zinc stannate with a high surface area of $85 \text{ m}^2/\text{g}$ possessing increased water retention, which was used as a matrix for the formation of the composite electrolytes CsH₂PO₄–ZnSnO₃. The CsH₂PO₄ crystal structure remained in the composite systems, but dispersion and partial salt amorphization were observed due to the interface interaction with the $ZnSnO_3$ matrix. It was shown that the proton conductivity of composites in the low-temperature region increased up to 2.5 orders of magnitude, went through a smooth maximum at x = 0.2, and then decreased due to the percolation effect. The measurement of the proton conductivity of the $ZnSnO_3$ – CsH_2PO_4 composites revealed that zinc stannate can be used as a heterogeneous additive in other composite solid electrolytes. Therefore, such materials can be applied in hydrogen production membrane reactors.

Keywords: thermolysis of ZnSn(OH)₆; zinc stannate; composites; composite solid electrolytes; cesium dihydrogen phosphate

1. Introduction

Materials based on the oxide systems Zn–Sn–O possess numerous functional properties and are thus of growing interest to researchers. For instance, zinc stannate has recently been utilized as anode material for sodium-ion and lithium-ion batteries [1–3]. Additionally, several works [4–6] have highlighted the potential for stannates as materials for supercapacitors and solar cell electrodes. Because of its chemical reactivity, excellent electronic properties, and perovskite structure, ZnSnO₃ is widely used for gas and organic compound sensors [7–20]. Zinc stannates also have numerous applications in electronics, catalysis, and photocatalysis [21–27].

In the Zn–Sn–O system, zinc metastannate ZnSnO₃ and zinc orthostannate Zn₂SnO₄ are present. Zinc metastannate ZnSnO₃ has an orthorhombic elementary lattice with a perovskite-like crystal structure, while zinc orthostannate Zn₂SnO₄ has a cubic lattice with a spinel-type structure. Various methods are used to obtain these compounds, including low-temperature ion exchange, sol–gel technology, and coprecipitation followed by thermal treatment [4,28–32]. Among them, the sol–gel method is the most commonly used approach



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). due to its ease of control, low-temperature, and high efficiency for obtaining various homogeneous nanostructures. However, for practical applications, coprecipitation is typically used as it is a more readily available and easy-to-implement method. Previously, it was demonstrated that hydroxostannates $MSn(OH)_6$ of alkali-earth metals $MSnO_3$ and M_2SnO_4 (M = Mg, Ca, Sr, Ba) can be obtained by thermal decomposition [33–36]. Notably, the stannates obtained by thermolysis possess a relatively high specific surface area (10–100 m²/g) and can be utilized as functional additives to obtain composite solid electrolytes [34]. According to the literature data [5,37–39], zinc stannates are mostly synthesized through the thermal decomposition of the hydroxostannate ZnSn(OH)₆. This process results in the formation of highly dispersed products, which can be utilized to obtain the composite materials. However, zinc stannates are characterized by higher chemical resistance to acids compared with alkaline earth metal stannates.

This makes them a promising heterogeneous additive for creating composite proton solid electrolytes with acidic alkali metal salts, such as CsH₂PO₄, which have a high conductivity up to 6×10^{-2} S/cm at 230 °C [40–42]. Cesium dihydrogen phosphate undergoes a superprotonic phase transition at 230 °C, which results in a significant increase in its conductivity to 6×10^{-2} S/cm. At low temperatures (20–230 °C), the conductivity dependence has an Arrhenius form with an activation energy of 0.9 eV, while at high temperatures (230–260 °C), the superionic conductivity activation energy is 0.42 eV. An abrupt increase in conductivity during the superionic phase transition is observed, from 10^{-7} S/cm to 6×10^{-2} S/cm (at T > 230 °C). To suppress the dehydration and increase the stability range of the high-temperature phase, the formation of an increased partial pressure of water vapor is necessary [43]. CsH₂PO₄ is a promising proton membrane for medium-temperature fuel cells [44,45]. Currently, investigations are focused on creating highly conductive composite and polymer electrolytes with modified salts in a larger temperature range, as well as searching for electrochemically active electrode compositions for medium temperature fuel cells based on cesium dihydrogen phosphate [46–58].

Earlier, it was demonstrated that the modification of CsH_2PO_4 with such highly dispersed complex oxides, such as $SrZrO_3$ [48] or NdPO_4 [52], resulted in the formation of composite solid electrolytes with a high proton conductivity. Similarly, highly dispersed zinc stannate, $ZnSnO_3$, may also be regarded as a promising additive to create proton-conducting composite electrolytes. The present study is focused on studying the decomposition products of the zinc hexahydroxostannate precursor, which are suitable for use as a matrix for the creation of CsH_2PO_4 – $ZnSnO_3$ composite proton solid electrolytes, as well as investigating their transport properties. The synthesis of nanosized particles of $ZnSnO_3$ was carried out by the thermal decomposition of the zinc hexahydroxostannate precursor $ZnSn(OH)_6$. The obtained highly dispersed $ZnSnO_3$ was used as a disperse additive for the preparation of the CsH_2PO_4 – $ZnSnO_3$ composites, and the transport properties of these proton solid electrolytes were investigated as a function of composition and temperature.

2. Materials and Methods

2.1. Materials

The starting reagents used included zinc powder (98% pure, MGP Metall, Russia), sodium stannate trihydrate (97% pure, Profsnab LLC, Moscow, Russia), hydrochloric acid (37% water solution, 99% pure, Khimprom LLC, Perm region, Russia). Solutions of HCl, NaOH, and ZnCl₂ were prepared in double distilled water obtained using a laboratory BE-2 purification system. All of the chemicals were used as received, without further purification. The crystals of CsH₂PO₄ were grown through isothermal evaporation from an aqueous solution of cesium carbonate (99% pure, Rare Metals Plant, Novosibirsk, Russia) and phosphoric acid (98% pure, Vekton LLC, Saint-Petersburg, Russia) in the stoichiometric ratio.

2.2. Synthesis of the Precursor $ZnSn(OH)_6$

Zinc hydroxostannate ZnSn(OH)₆ was synthesized by hydrolytic co-precipitation as follows: First, 0.0375 mol of metallic zinc Zn was dissolved in 25 mL of a 4 M hydrochloric acid solution. In this solution, 10 g (0.0375 mol) of Na₂SnO₃ × 3H₂O was dissolved to achieve an atomic ratio of Zn:Sn = 1:1. Then, 100 mL of 1 M NaOH solution was gradually added to the resulting solution, while maintaining the acidity of the medium within a pH = 8–9. The pH value was monitored using an HI 2221 Laboratory pH Meter. The mixture was continuously stirred for 24 h to provide complete quantitative co-precipitation of zinc and tin (IV). The resulting white precipitate was filtered off from the mother liquor, washed with distilled water until a negative qualitative reaction to the presence of Cl⁻ ions in the solution was achieved, and dried in an oven at 105–110 °C for 4 h (Figure 1).



Figure 1. Synthesis scheme of the precursor.

2.3. Characterization

The microstructure and phase composition of the samples were determined by X-ray diffraction (XRD). X-ray diffraction patterns were recorded at room temperature using a Bruker D8 Advance diffractometer with CuK α radiation in the 2 θ range from 10 to 70°. The phases formed in the system were identified using the Crystallographica Search-Match, Version 2.1 program and the PDF4 database. The average crystallite size was estimated from diffraction line broadening in X-ray diffraction patterns using the Scherer formula

C

$$l = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where *d* is the average crystallite size, λ is the X-ray wavelength (1.54051 Å), β is the full width at half maximum of the diffraction peak, θ is the diffraction angle, and k = 0.9. Thermal analysis (TA) of the dried powders was performed on a NETZSCH Jupiter 449C STA synchronous thermal analyzer coupled to QMS 403C Aëolos (TG-QMS) mass spectrometer in an argon flow at temperatures in the range of 20-700 °C at a heating rate of 10 °C/min. The microstructure of the samples was studied by field emission scanning electron microscopy (SEM) using Hitachi SU8000 electron microscope (Tokyo, Japan). The images were taken in the secondary electron recording mode at an accelerating voltage of 2–30 kV and a working distance of 8–10 mm. The sample's X-ray energy dispersive spectra (EDS) were measured with the use of an Oxford Instruments add-on for electron microscope. Analytical measurements of the EDS were optimized using a previously established method, as outlined in the references [52,59]. Prior to the measurements, the samples were affixed to an aluminum mount with a 25 mm diameter and secured firmly with conductive graphite adhesive tape. Additionally, the morphology of the unmodified samples was studied to preclude any surface effects due to the application of the conductive layer, as noted in [60]. The specific surface area was determined by analyzing the BET isotherms

of low-temperature nitrogen adsorption at 77 K using a Quantachrome Nova 1000e static instrument. The pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) method. The proton conductivity of the composites in the $(1-x)CsH_2PO_4-xZnSnO_3$ (x = 0.2, 0.4, 0.6, 0.8) system was measured using a two-electrode circuit on alternating current with an Instek LCR-821 impedance meter (12–200 kHz frequency range) and an IPU-1RLC-1/2008 precision electrochemical meter (1 Hz–3.3 MHz frequency range). The composites of the specific compositions were synthesized by thoroughly mixing the components in an agate mortar and heating the pelletized samples at 230–240 °C. Pellets of 6 mm in diameter and 1–1.5 mm thick were pressed from the samples to measure the electrical conductivity, using a pressure of 30–50 MPa. The electrical conductivity of the samples with deposited silver electrodes was measured under cooling conditions at a rate of 1–2 °C/min in an atmosphere with a high water vapor content (10%, 20%, and 30% molar ratio) in the temperature range of 170–250 °C, followed by cooling in air with a relative humidity of 40% [48,52].

3. Results and Discussion

The results from the atomic emission spectrometry analysis showed the minimal residual content of zinc (less $0.1 \ \mu g/mL$) and tin (less than $0.2 \ \mu g/mL$) in the mother solution. This indicates that the reaction (2) went to completion, yielding a precipitate with a stoichiometric ratio of Zn:Sn = 1:1. XRD data revealed that the chemical co-precipitation resulted in the formation of zinc hexahydroxostannate ZnSn(OH)₆, which possesses a vismirnovite structure with a cubic unit cell and symmetry, space group Pn3m, similar to schoenfliesite [61,62]. The diffraction pattern of the sample is shown in Figure 2 (curve 1).



Figure 2. X-ray diffraction patterns of initial $ZnSn(OH)_6$ (1) and thermolysis products obtained at temperatures of 300–520 °C (2), 600 °C (3), and 700 °C (4).

The value of the lattice parameter, determined using the Rietveld method with Powder Cell 2.4 software, was a = 0.77647 ± 0.00084 nm, and was in good agreement with literature data (a = 0.78 nm [39,62], PDF4, card no. 73-2384). The following reaction results in the formation of ZnSn(OH)₆:

$$ZnCl_2 + Na_2Sn(OH)_6 \rightarrow ZnSn(OH)_6 + 2 NaCl$$
(2)

According to scanning electron microscopy data (Figure 3a), the freshly deposited $ZnSn(OH)_6$ samples were cubic well-grained single crystals of 150–250 nm in size. According to the results of the chemical microanalysis carried out by the EDS method, the



Zn:Sn:O atomic ratio fell within the range of (10 ± 1) : (10 ± 1) : (63 ± 3) , which was close to the stoichiometric ratio for ZnSn(OH)₆.

Figure 3. SEM images of freshly deposited $ZnSn(OH)_6$ (**a**) and after its calcination at 520 °C (**b**) and 700 °C (**c**).

According to the thermal analysis data (Figure 4), when $ZnSn(OH)_6$ is heated, successive processes occur, accompanied by changes in the mass, structure, and phase composition, which are consistent with the XRD results. A weight loss of about 18.7% was observed when the sample was heated to a temperature between 50–520 °C, which quantitatively agreed with the calculated value (18.87%) for the reaction:

$$ZnSn(OH)_6 \rightarrow ZnSnO_3 + 3 H_2O \tag{3}$$



Figure 4. Synchronous thermal analysis curves obtained during the thermal decomposition of a ZnSn(OH)₆ sample: mass change (TG), thermal effects (DSC), and the ionic current of the mass spectrometer measured for the atomic mass number m/z of 18 amu corresponding to water molecules evolving from the sample.

The reaction was accompanied by an endothermic effect with a maximum at $T_{max} = 268 \ ^{\circ}C$.

According to XRD data, heating $ZnSn(OH)_6$ at 300–520 °C for 4 h produced X-ray amorphous zinc stannate (Figure 2, curve 2). Scanning electron microscopy showed that the dehydrated product was a pseudomorphosis made of nanoparticles of the amorphous phase, retaining the shape and size of the original particles (Figure 3b). At 540–600 °C, an exothermic effect was observed, likely indicating the formation of a weakly crystallized ZnSnO₃ phase with a perovskite structure (card 28–1486, PDF4), with the particle size estimated at being 15–20 nm using the Scherrer equation (Figure 2, curve 3). Zinc metastannate is metastable, and the transition to the stable phase Zn_2SnO_4 with a spinel structure occurred at temperatures above 700 °C, in accordance with the reaction:

$$2 ZnSnO_3 \rightarrow Zn_2SnO_4 + SnO_2 \tag{4}$$

The annealing at 700 °C resulted in the decomposition of the ZnSnO₃ phase into a mixture of the nanocrystalline SnO₂ phase with the cassiterite structure (card 71-652, PDF4) and the Zn₂SnO₄ phase with the spinel structure (card 74–2184, PDF4) (Figure 2, curve 4). Using the Scherrer equation, the estimated size of the nanocomposite particles was less than 60–70 nm for zinc stannate Zn₂SnO₄ and 20–40 nm for tin dioxide. Scanning electron microscopy showed that the pseudomorphosis of the nanoparticle aggregate was preserved (Figure 3c). However, the large cubic aggregates consisted of the weakly aggregated Zn₂SnO₄ nanoparticles surrounded by the smaller particles of tin dioxide visible on the surface of the cubic aggregates.

The FTIR spectra analysis of $ZnSn(OH)_6$ and its synthesized compounds showed the structural features and composition, with the characteristic bands assigned based on published data [63,64]. The FTIR spectra of the obtained zinc hydroxtannate $ZnSn(OH)_6$ and zinc stannate $ZnSnO_3$ samples (Figure 5a) matched previous studies [29,49,65].



Figure 5. (a) FTIR spectra of $ZnSn(OH)_6$ (1) and $ZnSnO_3$ obtained by the thermolysis of $ZnSn(OH)_6$ (2) and kept in air for some time (3). (b) Dependence of mass change (TG) of a $ZnSnO_3$ sample after storage in an air atmosphere of a desiccator.

In the spectra, a wide band of v(OH) stretching vibrations in the 3100–3300 cm⁻¹ region indicated the presence of hydroxyl groups in the precursor and a system of hydrogen bonds in the compound structure. The absorption band at 1180 cm⁻¹ was due to bending vibrations of the Sn–OH bonds, and the moisture deformation vibrations were recorded above 1630 cm⁻¹. These bands decreased with the sample's dehydration during the heat treatment at 600 °C, which was consistent with the weight loss according to the TG results. In the region of the metal–oxygen bonds (900–400 cm⁻¹) of ZnSnO₃, the FTIR spectra showed a strong band at 615 cm⁻¹, corresponding to the symmetric stretching vibrations of the Sn–O bonds (Figure 4a). After holding ZnSnO₃ in the air, a broad diffuse absorption band between 3250–3650 cm⁻¹, corresponding to hydrogen bonds and associated with the stretching vibrations $v(H_2O)$, confirmed the sorption of water vapor. The data of the thermal analysis (Figure 5b) for the sample after storage suggested the absorption of water, approximately up to 0.2 mole of H₂O, per mole of zinc stannate. The results indicate the reversible sorption of ZnSnO₃ water vapor in air and its desorption at elevated

temperatures. Similar to $ZnSn(OH)_6$, $ZnSnO_3$ was characterized by the presence of strongly bound adsorbed water molecules.

Table 1 presents the textural properties, specific surface area, and mean pore size of the initial samples and samples calcined at different temperatures for 4 h. High specific surface area values and the presence of mesopores with sizes around 6 nm were characteristics of the samples created during the thermolysis of $ZnSn(OH)_6$. As the heating temperature increased, the specific surface area values monotonically decreased while the pore sizes increased.

Table 1. Results from the textural study of the initial $ZnSn(OH)_6$ and the products of its thermal decomposition obtained at different temperatures.

Heating Temperature, $^{\circ}C$	110	300	520	600	700
Phase composition	ZnSn(OH) ₆	amorphous		ZnSnO ₃	Zn_2SnO_4 -SnO_2
Specific surface area, $m^2 \cdot g^{-1}$	18	80	85	36	15
Pore size, nm	~1	3	6	4	10

As seen from Table 1, the amorphous zinc stannate, obtained by heating at 520 °C, had a higher specific surface area. This high-surface-area zinc stannate, with increased water retention, was used as a heterogeneous additive for CsH_2PO_4 . The proton conductivity and structural properties of the $(1-x)CsH_2PO_4-xZnSnO_3$ composite system were studied across a range of compositions (x = 0.2-0.8). The XRD patterns indicated no chemical interaction between the components, and the crystalline structure of CsH_2PO_4 was preserved. The intensity of the reflections corresponding to the LT phase of CsH_2PO_4 (P2/1m) decreased significantly more than the salt content in the composite (Figure 6a), resulting in a disordered state of CsH_2PO_4 .



Figure 6. (a) X-ray diffraction patterns of $(1-x)CsH_2PO_4-xZnSnO_3$ composites of various compositions in the comparison with the starting compounds: CsH_2PO_4 (1); x = 0.2 (2); 0.4 (3); 0.8 (4); ZnSnO_3 (5). (b) Electrochemical impedance spectra for $0.8CsH_2PO_4-0.2ZnSnO_3$ sample obtained at 230 °C (black symbols) and 190 °C (empty symbols). Points are experimental data; lines are theoretical curves obtained for the equivalent circuit, with the parameters listed in Table 2. The parameters of the equivalent scheme are described in detail the texts and Equations (5)–(7).

As the molar percentage of $ZnSnO_3$ increased, an amorphous halo characteristic of zinc stannate appeared in the composite (such as at x = 0.8), and the salt was mostly in an amorphous state.

Figure 6b shows the impedance plots of the composites at different temperatures. The impedance hodograph included an arc that represented the electrode processes in the lower frequency region, and a single semicircle that was due to the electrolyte transfer in the higher frequency region. The proton conductivity was calculated from the resistance values with the minimum capacitive component. As the temperature increased, the radius of the single semicircles significantly decreased, indicating greater proton conductivity due to an increase in the number and mobility of the current carriers. For interpretation of the experimental impedance data, the equivalent circuit presented in Figure 6b was used. The circuit includes three impedances, Z_1 , Z_2 , and Z_3 , connected in series. The first impedance includes the active resistance R_1 connected in parallel to the constant phase element (CPE) Q_1 . The second and third impedances are related to the electrode: R_2 and Q_2 are charge transfer resistance and CPE taking into account the electrode polarization effects, respectively, and Q_3 is the diffusion impedance contribution. As a result, the total impedance of the sample is equal to $Z = Z_1 + Z_2 + Z_3$, where

$$Z_1 = \left[R_1^{-1} + Y_1 (i\omega)^{n_1} \right]^{-1}$$
(5)

$$Z_2 = \left[R_2^{-1} + Y_2 (i\omega)^{n_2} \right]^{-1}$$
(6)

$$Z_3 = Y_3^{-1} (i\omega)^{-n_3} \tag{7}$$

As seen from Figure 6b, the theoretical curves obtained for this equivalent circuit fairly fit the experimental data. Results of the fitting are presented in Table 2.

Table 2. Parameters of the equivalent circuit, R_1 , Y_1^0 , n_1 , R_2 , Y_2^0 , n_2 , Y_3 , and n_3 , determined by fitting the impedance data.

Parameter	190 °C	230 °C	
R_1 , k Ω	1.97 ± 0.09	0.176 ± 0.004	
Y_1, S^{1-n_1}	$7.0\times 10^{-10}\pm 0.8\times 10^{-10}$	-	
<i>n</i> ₁	0.882 ± 0.013	-	
R_2 , k Ω	0.96 ± 0.02	0.360 ± 0.005	
Y_2, S^{1-n_2}	$4.0 \times 10^{-4} \pm 0.6 \times 10^{-4}$	$1.6 \times 10^{-4} \pm 0.1 \times 10^{-4}$	
<i>n</i> ₂	0.335 ± 0.008	0.669 ± 0.012	
Y_3, S^{1-n_3}	$4.2 \times 10^{-4} \pm 0.9 \times 10^{-4}$	$5.11 \times 10^{-4} \pm 0.07 \times 10^{-4}$	
<i>n</i> ₃	0.546 ± 0.011	0.594 ± 0.005	

Figure 7 shows a comparison of the proton conductivity of the samples with the initial salts. The ZnSnO₃ matrix initially exhibited a low proton conductivity, not exceeding 2×10^{-8} S/cm in the temperature range below 250 °C. This conductivity was consistent with literature data [40–42]. The temperature dependence of the conductivity revealed two regions related to the superprotonic and low temperature phases of CsH₂PO₄.

The proton conductivity of the low temperature phase follows the Arrhenius law, with an activation energy of ~0.9 eV, and does not exceed 3×10^{-7} S/cm at T < 200 °C due to the strong hydrogen bond network that impedes the proton transfer due to the high energy of defect formation. In the CsH₂PO₄–ZnSnO₃ composites, the conductivity can also be distinguished into two temperature ranges. The introduction of small amounts of additives significantly increased the conductivity of the composites in the low-temperature region, with specific conductivity values depending on composition. At *x* = 0.2, the low-

temperature conductivity reached a maximum, increasing by 2.5 orders of magnitude. Consequently, the conductivity jump during the superionic phase transition decreased significantly at x = 0.2. The increase in the conductivity was due to the disordering and partial amorphization of the salt at the interface between the two phases, which occurred as the fraction of additive increased. However, as x further increased to 0.4, the conductivity began to decrease (Figure 8a), despite the volume fraction of the heterogeneous component not exceeding 30%. In the case of x = 0.6, the conductivity in the low-temperature region sharply decreased to values lower than the initial salt due to the percolation effect. The high-temperature region conductivity decreased almost linearly with an increase in the proportion of additive compared with pure CsH₂PO₄, due to the "conductor–insulator" percolation effect (Figure 8a,b).



Figure 7. Temperature dependence of conductivity for composite systems $(1-x)CsH_2PO_4-xZnSnO_3$ (x = 0.2-0.8) in comparison with CsH_2PO_4 and $ZnSnO_3$. The conductivity measurement was carried out on two to three pellets with the same composition, but the different size. The relative error in the determining the conductivity is 2–5%.



Figure 8. Isotherms of the proton conductivity for the composite systems $(1-x)CsH_2PO_4-xZnSnO_3$ at different temperatures: 138 °C (**a**) and 227 °C (**b**).

Nevertheless, with the addition of small amounts of ZnSnO₃, the proton conductivity at high temperatures remained close to the values of the initial salt. In addition, the intro-

duction of a non-conducting matrix led to an increase in the low-temperature conductivity within a specific range of compositions, but reduced the superprotonic conductivity. The composite effects observed in this system were comparable to the conductivity values seen in the CsH_2PO_4 -SrZrO₃ and CsH_2PO_4 -NdPO₄ systems [48,52], but somewhat lower than for a number of the studied composite systems based on CsH_2PO_4 [50,51,55,58]. This may be due to an insufficiently high specific surface area and the adhesion energy that determine the interface interaction. Nonetheless, for the samples with the highest proton conductivity values at x = 0.2, the stability of high conductivity values in the superionic region was maintained even with long-term, isothermal exposure at lower partial pressures of water vapor (10% and 20%) due to the higher water retention of the $ZnSnO_3$ matrix. Figure 9 shows the stable conductivity values during the long-term isothermal exposure at the partial water vapor concentration of 10% and 20%, which were lower than those used, in accordance with the phase diagram [43]. The proton conductivity retained unchanged values of 8×10^{-3} S/cm at significantly lower partial pressures of water vapor during 150 min at 230 °C (Figure 9). This was likely due to the presence of adsorbed water in the ZnSnO₃ matrix, which was removed at elevated temperatures and prevented dehydration of the CsH₂PO₄ salt within the composite.



Figure 9. Dependence of conductivity of $(1-x)CsH_2PO_4-xZnSnO_3$ (x = 0.2) system on the time of long-term storage at 230 °C (water vapor content was 20 mol%).

4. Conclusions

In this work, the synthesis and the thermal decomposition of zinc hydroxostannate were studied in detail. $ZnSn(OH)_6$ with the cubic crystals of 150–250 nm in size was synthesized by hydrolytic precipitation from the solutions of $ZnCl_2$ and Na_2SnO_3 . Zinc stannate with a high specific surface area ($85 \text{ m}^2/g$) was formed through the thermolysis of $ZnSn(OH)_6$ in the temperature range of 300–520 °C. A weakly crystallized $ZnSnO_3$ phase with a particle size of 15–20 nm was formed at 540–600 °C, while at an annealing temperature of 700 °C, a mixture of nanocrystalline SnO_2 with the cassiterite structure (20–40 nm) and Zn_2SnO_4 (less than 60–70 nm) with the spinel structure was formed. As a result of the thermolysis study, optimal conditions for the formation of highly-dispersed zinc stannate were found, and the obtained materials were further used for the creation of the composite solid electrolytes.

The proton conductivity of the composite systems with the compositions of $(1-x)CsH_2PO_4-xZnSnO_3$ (x = 0.2-0.8) was studied. The CsH_2PO_4 crystal structure remained in the composite systems, but dispersion and partial salt amorphization were observed due to the interface interaction with the ZnSnO₃ matrix. As a result, the conductivity in the low-temperature region increased up to 2.5 orders of magnitude, went through a smooth maximum at x = 0.2, and then decreased due to the percolation "conductor–isolator" effect. The samples with the highest proton conductivity at x = 0.2 demonstrated stable high conductivity values (8 × 10⁻³ S/cm) under long-term isothermal exposure (150 min at 230 °C) at lower partial pressures of water vapor. This will allow this material

to be used in electrochemical applications. Thus, it has been demonstrated that X-ray amorphous zinc stannate $ZnSnO_3$ is a suitable heterogeneous additive in other composite solid electrolytes. The composite solid electrolytes CsH_2PO_4 – $ZnSnO_3$ may be used as solid electrolyte membrane materials in intermediate temperature electrochemical resistors for hydrogen production. Such an approach might be competitive compared with alternative hydrogen production techniques [66–70].

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