Proton-conducting membranes based on CsH$_2$PO$_4$ and copolymer of tetrafluoroethylene with vinylidene fluoride

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Abstract

In this work, proton conductivity, morphology and mechanical properties of (1-x)CsH$_2$PO$_4$–xPF-42 (x=0.05–0.3, weight ratio) membranes were investigated for the first time. Thin flexible membranes for x=0.15 with the uniform distribution of the components were obtained by a tape casting method. Mechanical properties of the membranes were measured by Vickers microhardness tests for a low polymer content (x<0.15), also the tensile strength for membranes with high polymer content x=0.2–0.3 were evaluated. Proton conductivity of the (1-x)CsH$_2$PO$_4$–xF-42 composite polymer electrolytes decreases monotonically with increasing x due to the effect of a «conductor-insulator» percolation. The combination of conductivity, mechanical strength and hydrophobic properties of (1-x)CsH$_2$PO$_4$–xF-42 makes certain compositions of proton-conducting membranes (x=0.2–0.25) promising for their use in intermediate-temperature fuel cells, despite decreased conductivity.

Keywords

- proton conductivity
- cesium dihydrogen phosphate
- fluoropolymer
- p(VDF/TFE)
- tape casting

1. Introduction

Solid Acid Fuel Cell (SAFC) is a promising new type of fuel cells with a CsH$_2$PO$_4$ acid salt as a membrane [1, 2]. Interest in solid acid compounds, such as alkali metal dihydrogenphosphates and dihydrogensulfates, is constantly growing, a number of salts of this family is increasing; as a result, new compounds with Cs$_6$(H$_2$PO$_4$)$_3$, [3–5] and Cs$_4$(H$_2$PO$_4$)$_2$(H$_2$PO$_4$)$_n$ [6] compositions have been recently discovered. However, CsH$_2$PO$_4$ remains the salt with the highest value of proton conductivity. The CsH$_2$PO$_4$ phase at room temperature is characterized by a low conductivity, while at 230 °C there exists its sharp increase by several orders of magnitude due to the phase transition to a Pm-3m superionic phase, which is characterized by a high degree of structural disorder and high proton conductivity, 6·10$^{-2}$ S/cm [7]. To achieve a more efficient and stable operation of H$_2$/O$_2$ FCs based on CsH$_2$PO$_4$ in a wider temperature range, it is necessary to maintain humidity level of pH$_2$O ~0.3 atm. to prevent salt dehydration [8, 9]. The disadvantages of the CsH$_2$PO$_4$ membranes (such as a narrow temperature range of the existence of a highly conductive state, time-dependent plasticity of acid salt in superionic phase, solubility in water, low mechanical strength) can be significantly improved by methods of homogeneous and heterogeneous doping. The search for polymer additives for the synthesis of thin membranes, which combine the flexibility and hydrophobicity of a polymer additive with a high proton conductivity of the acid salt, is being intensively developed. A number of composite membranes based on CsH$_2$PO$_4$ and different polymers such as PVDF, SPEEK, epoxy resin, UPTFE, Butvar B98, p(VDF/HFP) have been investigated [10–16]. At a high concentration of polymer in such systems, the mechanical properties of the membranes are improved, while the high content of the non-conductive component results in a decrease in conductivity due to the effect of the «conductor-insulator» percolation. The «CsH$_2$PO$_4$ – polymer» composites can combine the required mechanical, conductive, and hydrophobic properties. In addition, the solubility of polymer additives in various solvents makes it possible to switch from the solid-phase methods of membrane’s synthesis to the production of thin and flexible films by tape casting technique.

Fluoropolymers are considered as a chemically inert, thermally stable, effective additive to the acid salt CsH$_2$PO$_4$. The previous studies have included PVDF [10], ultrafine PTFE [14], and a VDF/HFP copolymer [15]. Fluoroplast 42 (F-42, similar to Kynar 7200) copolymer of vinylidene fluoride (VDF) with tetrafluoroethylene (TFE)
is a promising polymer matrix for CsH₂PO₄. TFE and VDF can be polymerized in any ratio giving rise to a broad variety of copolymers. A composition of F-42 corresponds to the approximate TFE:VDF component ratio of 29:71. The polymer has a high hydrophobicity due to the high content of fluorine atoms (65.8 wt.%). F-42 is a robust polymer with a high tensile strength (~14.6 MPa), high specific surface resistance (~10¹⁰ Ohm/m). It is chemically resistant to acidic and basic media, and soluble in esters, ketones and N,N-dimethylformamide (DMF) [17–19]. F-42 polymer has high thermal stability with decomposition temperatures above 360 °C. Melting of F-42 at temperatures of 150–160 °C corresponds to the crystallites, but the polymer does not pass into a viscous state. In present work, morphology, mechanical characteristics, transport and structural properties of (1-x)CsH₂PO₄-xF42 polymer composite electrolytes have been studied.

2. Materials and Methods

The CsH₂PO₄ salt was obtained by a slow solvent evaporation of an aqueous solution of Cs₂CO₃ and H₃PO₄ in a ratio of 1:2. Composite electrolytes with a polymer weight ratio of x=0.05–0.15 were synthesized by a thorough homogenization of a suspension of CsH₂PO₄ particles in a solution of p(VDF/TFE) in DMF with a mortar and a pestle with a further drying and uniaxial pressing of formed powder at 300 MPa. For the x=0.2–0.3, a viscous suspension of CsH₂PO₄ particles in polymer solution was spread on a fluoroplastic substrate using a TOB-VFC-150 tape casting machine and dried to form the film.

Proton conductivity measurements were carried out on the thin films ~150 μm for x=0.2 or pellet (x=0.05–0.15) with silver or platinum paste or pressed electrodes. Membranes were subjected to repetitive heating-cooling cycles in the temperature range from 50 to 245 °C. Humid conditions (pH₂O ~0.3 atm) were used at temperatures higher 180 °C to prevent the CsH₂PO₄ dehydration. The conductivity was measured by electrochemical impedance spectroscopy using an P-5X impedance meter (frequency range of 1 mHz to 0.5 MHz) and Instek (12 Hz-200 kHz) in a cooling regime.

Scanning electron microscopy (SEM) images of composites were obtained on the gold sputter-coated membranes using a Hitachi TM 1000 microscope. X-ray diffraction (XRD) analysis was performed on a Bruker D8 Advance diffractometer (λCu Kα = 1.5406 Å) with a one-dimensional Lynx-Eye detector and Kα filter.

Vickers hardness for (1-x)CsH₂PO₄-xF42 (x≤0.15) was determined using a DuraScan 50 microhardness tester EMCO-TEST with an application time of load (0.5 kgf (4.9 N)) for 10 seconds. The measurements were repeated at least ten times for each sample. Dense tablets (5 mm in diameter and 1 mm in thick) were obtained by uniaxial pressing at 300 MPa.

The tensile strength of thin-film polymer composite electrolytes with x >0.15 was measured using an Instron 5944 mechanical testing machine. For the preparation of samples, a punching die of certain sizes was used to obtain the samples with a form of a double blade with a 5 mm wide and 20 mm high working area. The thin-film membrane was stretched at a constant rate of 5 mm/min under atmospheric conditions and the applied load and elongation was recorded. For each x at least six measurements were made, and average value was calculated.

3. Results and Discussion

For the synthesis of composites, the x<0.38 composition range was chosen, since the proton conductivity drops sharply with an increase in the ratio of the polymer additive due to the predominance of the nonconductive component in the membrane volume. Composites with a low content of F-42 x=0.05–0.15 were obtained in the form of pellets. For higher polymer content (x>0.15) it was possible to produce thin flexible films with a thickness ~150 μm by tape casting method. The search for optimal conditions for tape casting process such as solvent used, application speed, the height of the gap, number of layers and the temperature regime of drying has been carried out. DMF was used as a solvent with a high boiling point (T=153 °C) that provides high quality of films obtained.

According to X-ray diffraction data, a monoclinic CsH₂PO₄ (P2₁/m) phase is retained in composite electrolytes over the entire range of compositions.

![Figure 1 XRD data for the (1-x)CSH₂PO₄-xF42 membranes of various composition.](image-url)
With an increase in the weight ratio of a polymer additive, the intensity of the CsH₂PO₄ reflexes decreases in accordance with the change in the mass fraction of the salt (Figure 1). The F-42 fluoropolymer has a sufficiently high degree of crystallinity; the XRD pattern has reflections in a region of 2θ ~ 19° and 40°. The structure of the β-phase of PVDF is realized in the F-42 polymer [20]. For composite electrolytes with x≥0.1, the most intense F-42 reflex appears in vicinity of 19°.

The distribution of components in the volume significantly affects the proton conductivity and mechanical properties of membranes. CsH₂PO₄ is practically insoluble in most known organic solvents, and composite membranes present a polymer matrix with salt particles dispersed in its volume. The study of membrane morphology and determination of the size of salt particles in the polymer matrix was performed using SEM. The resulting membranes exhibit a uniform distribution of components with the salt particles size less than 5 μm (Figure 2).

The nature of the temperature dependences of the composites is close to that of pure salt. The conductivity of the high-temperature phase decreases by less than an order of magnitude for compositions with x≤0.15 (Figure 3). Compared to the initial salt of CsH₂PO₄, the proton conductivity of the composites decreases even at a low volume fraction of the polymer (7.87 vol.% for x=0.05) due to its dielectric nature. A further increase in the polymer content (x>0.2) results in a close-to-linear decrease of conductivity.

To assess the mechanical properties of the membranes, the Vickers microhardness was determined for the acid salt CsH₂PO₄ and hybrid polymer compounds with F-42.

The Vickers microhardness test evaluates the mechanical properties of composite polymer electrolytes in the form of tablets with a low polymer content (x≤0.15) in comparison with initial CsH₂PO₄ salt. The relative density of the obtained tablets “CsH₂PO₄-polymer” was close to 95%. Vickers hardness (HV) was determined by division of the load by the area of the sloping surface of the indentation. With an increase in the content of the polymer additive, the diagonals of the indentation from the diamond pyramid increase (Figure 4). Thus, the Vickers numbers, HV, for the initial salt had the values HV~34, which corresponds to 333.4 MPa, for hybrid membranes containing...
F-42 polymer $x=0.15$, the microhardness decreases by more than two times reaching value ~13 HV. For hybrid compounds, it was shown that with an increase in the mass fraction of the polymer, the ability to resist plastic deformation and, as a result, the mechanical strength increases.

For thin-film membranes with $x>0.15$, the tensile strength was measured as the load at which the sample failed, referred to the initial cross-sectional area of the sample. Films with $x=0.2$–0.3 and thickness of ~150 μm were obtained by applying a two layer of suspension and drying until the solvent evaporation. The magnitude of the breaking stress increased with the increase in the mass fraction of F-42. The maximum value of the breaking stress of a thin-film polymer-composite membrane with $x=0.3$ was 0.7 MPa.

4. Conclusions

The synthesis method of the (1–$x$)CsH$_4$PO$_4$–xF-42 composite electrolytes by tape casting technique was developed. A study of the proton conductivity, structural properties, mechanical characteristics, and morphology of the system was carried out for the first time. According to XRD, F-42 is the chemically inert polymer matrix for CsH$_4$PO$_4$. Composite electrolytes in the form of thin flexible films with the thickness 100–150 μm can be obtained for high polymer content. The (1–$x$)CsH$_4$PO$_4$–xF-42 composites are characterized by a decrease in superionic conductivity in comparison with the initial salt within 1 order of magnitude for $x=0.15$. A further increase in the polymer content ($x>0.2$) results in a conductivity decrease close to linear. Polymer content $x=0.15$ results in the low HV values corresponding to the high robustness of the membranes to plastic deformation. The improvement of mechanical properties and hydrolytic stability makes the investigated composite polymer electrolytes promising for use as proton-conducting membranes in the medium-temperature range fuel cells.

Supplementary materials

No supplementary materials are available.

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Conflict of interest

The authors declare no conflict of interest.

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