Preparation, Characterization, and Stability of the (1-x) CsH₂PO₄ + xTiO₂ Composite Electrolytes for Fuel Cells

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Research Article

Keywords: Cesium dihydrogen Phosphate, Composite Electrolytes, Conductivity, Fuel Cell, FTIR

Posted Date: February 15th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-187102/v1>

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Abstract

Composite Electrolytes $(1-x)\text{CsH}_2\text{PO}_4/x\text{TiO}_2$ ($0 \leq x \leq 0.4$) were prepared and analyzed the structural, thermal, and transport properties. We have investigated the ionic conductivity of the composites electrolyte highly pressurized pellets and found that the conductivity of pure CsH_2PO_4 (CDP) increased three orders of magnitude at the transition temperature. The conductivity value of the composites is greater than pure CDP after 250°C . Arrhenius plots have confirmed the conductive nature of ionic conduction. The dehydration behavior and thermal stability of the materials were observed in terms of differential scanning calorimetry, thermogravimetric analysis and differential thermal analysis, and found that the minimum weight loss for the composite $0.6\text{CDP}/0.4\text{TiO}_2$. The electrodes were prepared with the technique of vapor deposition.

1. Introduction

Today, the consumption of oil in the world is increasing day by day, which is limited. We need to focus on technologies that reduce oil consumption. Fuel cell vehicles are considered a good way to reduce oil consumption. The purpose of the fuel cell is to eliminate air pollution and further greenhouse gases. A fuel cell converts chemical potential energy directly into electrical energy without creating any noise. The fundamental parts of a fuel cell are electrolytes, gas transport processes, anode, and cathode [1, 2]. We will discuss the intermediate temperature fuel cell electrolyte, which is an important part of the fuel cell. CDP is considered as one of the highly conductive materials [3–5] in the family of acid salts $\text{M}_\alpha\text{H}_\beta(\text{NO}_4)_\gamma$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$): $\text{N} = \text{P}, \text{S}, \text{As}, \text{Se}$, and α, β, γ , are integers for fuel cell electrolytes [6–9]. CsH_2PO_4 has proton conductivity 1.8×10^{-6} at a temperature of 150°C [10] and showed high conductivity $2.2 \times 10^{-2} \text{ S cm}^{-1}$ at the temperature of 240°C [11]. Botez et al. [3] reported $1.5 \times 10^{-2} \text{ S cm}^{-1}$ high conductivity of CDP at the temperature of 260°C . CDP achieved high proton conductivity of $2.0 \times 10^{-2} \text{ S cm}^{-1}$ up to 260°C for 50 hours under high atmospheric pressure and high humidity when the container is confined in a small container [12]. It is a good conductive electrolyte but shows some disadvantages such as poor mechanical properties, water solubility, and availability of high conductivity in a short range of temperature 230 to 250°C . CDP decomposes into $\text{Cs}_2\text{H}_2\text{P}_2\text{O}_7$ over 250°C , which reduces conductivity [1, 13]. To overcome this problem, we introduce heterogeneous doping of highly inert oxides such as (SiO_2 , ZrO_2 , TiO_2 , Al_2O_3 , rare earth phosphates, and solid acid) for long-term durability as well as thermal and mechanical stability [14–17]. Hermetically confinement of a pellet in a container is one of the methods to improve the stability and increase the conductivity of superprotonic CDP and its composites. Heterogeneous doping of $\text{Ba}(\text{H}_2\text{PO}_4)_2$ in CDP has shown a good increment in conductivity $\sim 10^{-2} \text{ S cm}^{-1}$ at ~ 200 – 210°C [18]. CDP/ NdPO_4 was reported the high conductivity $0.9 \times 10^{-2} \text{ S cm}^{-1}$ at the temperature 150°C [10], SiP_2O_7 doped with CDP shows high conductivity 44 mS cm^{-1} at 266°C [19].

Now in this present work, we doped TiO_2 with CDP to increase the stability of the material. There is mainly three-phase of a bulk TiO_2 ; rutile, anatase, and brookite. Among them, rutile is a well known high-

temperature stable phase [20, 21]. We synthesized composites electrolyte 0.9CDP-0.1TiO₂, 0.8CDP-0.2TiO₂, 0.7CDP-0.3TiO₂, and 0.6CDP-0.4TiO₂ in weight ratio and observed the transport, thermal properties, ionic conductivity at different temperatures.

2. Experimental

2.1 Sample Preparation

Cesium dihydrogen phosphate (CDP) was prepared from a precursor solution used 25 gm Cs₂CO₃ (Alfa Aesar, 99%) and 15 ml of aqueous phosphoric acid (H₃PO₄-Alfa Aesar, 85%) were dissolved in deionized water (DI). The solution was stirred for 24 hours. After that, the obtained solution was heated in an oven until it turns into a hard-solid amorphous bottom layer. The solid layer was introduced with methanol and the resultant material was then filtered from the mother solution. The precipitate of CDP was dried at 150 °C for 6 hours to get it in solid form, remove residual water, and grinded to produce the powder of CDP [13, 22, 23]. TiO₂ powder was purchased (Alfa Aesar, 99.99%), and added to dry CDP powder, which was produced by the above method. The constituents of composites (1-x) CDP-xTiO₂ where x= (0.0-0.4) were mixed by an agate mortar for 4 hours and a homogeneous powder mixture was prepared. The powder was pressed at a pressure of 7 tonnes (metric)/cm² (0.68646 GPa) for 10 minutes to make the pellets by a hydraulic pellet pressing machine. The diameter and thickness of the pellet were 12 mm and 3 mm, respectively. The pellets were calcined at 100 °C for 2 hours. Silver wires were used for making the electrodes on the surface of pellets by vacuum coating unit (Hind High Vacuum-12A4D). The prepared pellets were used for measuring ionic conductivity.

2.2 Characterization

The XRD was recorded in the range of 2θ from 20° to 60° with Proto AXRD Benchtop (Kα_{1,2} or Kβ wavelength, the energy resolution of 200 eV FWHM, 640 channel high-speed detector). EDX and FESEM data were recorded by FESEM-Quanta 200 FEG. The conductivity was measured by LC Impedance Meter (Hikoki 3532-50) in the frequency range of 50 Hz to 4 MHz at the temperature range from room temperature to 320 °C. The ionic conductivity value was calculated by the resistance value (R). Temperature and time-dependent conductivity plotted by the Arrhenius plots by the following equation

$$\sigma \text{ (S/cm)} = L(\text{cm})/A(\text{cm}^2)R(\Omega)$$

where R is the resistance, L is the thickness of the pellet and A is the area of the pellet.

Fourier Transform Infrared Spectroscopy (FTIR) was used to identify the number of components and the presence of functional groups present in the material. FTIR data was collected by FTIR- 8400S Unit (Shimadzu, Japan). The decomposition and the phase change of solid acid composite are identified in the form of Differential Scanning Calorimetry (DSC), Thermogravimetric Analysis (TGA), Differential Thermal Analysis (DTA), and Derivative Thermogravimetric (DTG). DSC data were obtained by the (DSC-

60) Unit (Shimadzu, Japan) system in the temperature range of 20 to 400 °C at a heating rate of 05 °C /min under Nitrogen flow. TGA, DTA, and DTG were analyzed by SII 6300 EXSTAR at a rate of 10°C/minutes under airflow 200 ml/minutes.

3. Results And Discussion

3.1 X-ray diffraction (XRD)

X-ray diffraction (XRD) patterns of the pure CsH_2PO_4 , composites electrolytes 0.9CDP-0.1 TiO_2 , 0.8CDP-0.2 TiO_2 , 0.7CDP-0.3 TiO_2 , and 0.6CDP-0.4 TiO_2 were observed in the range of 2θ from 20° to 60° as shown in Fig. 1.

The sharp and well resolved diffraction peaks of CDP obtained at the 2θ values of 23.70°, 29.19°, 36.93°, 38.02°, 46.18°, 48.42°, 50.15°, which indicates the high crystalline nature of CDP. These diffraction peaks correspond to (011), (111), (220), (221), (401), (411), and (131). The diffraction patterns of CsH_2PO_4 were identified as the monoclinic phase with space group $\text{P2}_1/\text{m}$. Titanium oxides showed highly intense and sharp peaks at $2\theta = 25.44^\circ$, 38.02°, 48.23°, 54.13°, and 55.28° corresponding to Miller indices (101), (112), (200), (105), and (211). Monoclinic CsH_2PO_4 and anatase TiO_2 were indexed for two components according to JCPDS card No. 84-0122 and 84-1286 respectively [24, 25]. By increasing the concentrations of TiO_2 , the intensity of the peaks is reduced which suggests the rise in the degree of the amorphousity in the composites. The interaction between Cs and Ti in the composites is being displaced from their lattice sites. The displacement caused the dislocation and imperfection; hence, the intensity of the diffracted X-ray peaks is identified. This phenomenon leads to ion diffusivity with ionic conductivity and stability because of a rise in the amorphous nature of the composites [26, 27]. Thus, XRD patterns of the composite electrolytes show the appearance of two independent phases (CsH_2PO_4 and TiO_2) in disordered and dispersed states.

3.2 FESEM and EDX Analysis

EDX and FESEM images of CDP and TiO_2 are shown in Figs. 2 and 3. The surface morphology of pure CDP and TiO_2 showed by FSEM in Fig. 2(a, c and d) and Fig. 3(a, c, and d) respectively. FESEM compose almost spherical, hexagonal, and clustered to form larger aggregates on the surface with different sizes, and it is observed CDP and TiO_2 homogeneous decorated. The chemical composition of pure CDP and TiO_2 was investigated by EDX analysis as shown in Fig. 2(b) and Fig. 2(c).

The obtained results clearly illustrate that the CDP and TiO_2 were well prepared, which also supported the XRD analysis. The EDX spectrum indicated the presence of the Cesium, phosphorus, oxygen in CDP, and titanium, oxygen in TiO_2 , and have the value of weight percent and atomic percent indicated in Table 1 (a and b).

Table 1. The value of weight percentage and atomic percentage of (a) CDP (b) TiO₂ in the EDX spectrum.

Element	Weight%	Atomic%
O K	32.85	70.78
P K	13.80	15.37
Cs L	53.34	13.85
Totals	100.00	

a

Element	Weight%	Atomic%
O K	48.77	74.03
Ti K	51.23	25.97
Totals	100.00	

b

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared transmittance spectra of the pure CDP and composites electrolytes CDP/TiO₂ were taken in the range of 400 cm⁻¹ to 4000 cm⁻¹ to confirm the presence of anions PO₄⁻³ hydrogen and other bonds as shown in Fig. 4.

On the breaking of the hydrogen bonds, CDP showed high conductivity at the temperature of 230 °C. CDP was stable at room temperature due to the paraelectric phase. The IR spectra consist of high-frequency well-separated H modes between 3600 and 1300 cm⁻¹. Stretching P-OH and Bending P-O modes belong to 1300 cm⁻¹ to 800 cm⁻¹. Cs-O and O-P-O belong to 800 cm⁻¹ to 400 cm⁻¹ [28]. The ABC structure of the stretching vibrations appears due to the Fermi resonance and observed for the ν(OH)- 2791 cm⁻¹, δ(OH)- 2332 cm⁻¹, and γ(OH)- 1700 cm⁻¹. The strong absorption of the samples in the region 900–1200 cm⁻¹ of the IR spectra can undoubtedly be assigned to the components of the PO₄ while the four bands at 1216 cm⁻¹, 1110 cm⁻¹, 1080 cm⁻¹, and 930 cm⁻¹ are attributed to the P–O stretching modes in the H₂PO₄⁻ anion that is compatible to reported data. The generated bond due to Cs...O–H is observed at 549 cm⁻¹. FTIR spectrum of TiO₂ observed at 3516 cm⁻¹, 1691 cm⁻¹, and 1260 cm⁻¹ corresponding to the

stretching vibration of the O-H group, bending modes of the water Ti-OH group, a Ti-O group, respectively, in TiO_2 . Ti-O-Ti bonds in TiO_2 lattice shown in the range of $700 - 500 \text{ cm}^{-1}$ [29, 30]. We observed after adding TiO_2 the intensity of composite electrolytes decreases with the increase of doped TiO_2 concentration. This indicates that the amorphous region in the composite material was increased, which was in agreement with the XRD results and also be observed the small shift in some bonds.

3.4 Conductivity

Temperature dependence Arrhenius plots of pure CDP and its four composites are shown in fig .5.

Figure 5 demonstrates that a phase transition of CDP occurs at the temperature of 230°C , and the conductivity increasing by ~ 3 orders of magnitude from the monoclinic phase ($10^{-6} \text{ S cm}^{-1}$) to the cubic phase ($2.0 \times 10^{-2} \text{ S cm}^{-1}$). CDP dehydrated above the temperature of 250°C matched with [18], so conductivity starts to decrease. If the CDP pellet is confined hermetically in a tide and sealed container, the dehydration is greatly reduced. The proton conductivity slightly increased concerning temperature range between 235 to 260°C [3, 30]. We observed that the conductivity of CDP at a lower temperature is more than its composites, while at a higher temperature the conductivity of its composites is more than CDP. As the value of x is increasing the arc of the curve is being linear at a higher temperature, which showed the stable value of the conductivity and agrees with XRD, FTIR, and thermal analysis discussion. The addition of TiO_2 increases the stable conductivity of phosphoric acid composites due to the grain boundaries and imperfect interconnections between the acid and TiO_2 [8]. Composite electrolyte 0.9 CDP/0.1 TiO_2 exhibited high conductivity $1.7 \times 10^{-2} \text{ S cm}^{-1}$ in the temperature range of $240 - 280^\circ\text{C}$ for 45 hours of a pellet which was bounded hermetically in a small container as shown in Fig. 6.

Time dependence of the proton conductivity measured on a pellet which was sealed in a small container. 0.8CDP/0.2 TiO_2 exhibited high conductivity $1.2 \times 10^{-2} \text{ S cm}^{-1}$ in the temperature range of $240 - 290^\circ\text{C}$ for 50 hours as shown in Fig. 7.

0.7CDP/0.3 TiO_2 exhibited $7.0 \times 10^{-3} \text{ S cm}^{-1}$ in the temperature range $240 - 300^\circ\text{C}$ and 0.6CDP/0.4 TiO_2 exhibited $1.0 \times 10^{-3} \text{ S cm}^{-1}$ in the temperature range of $240 - 310^\circ\text{C}$ in open atmosphere as shown in Fig. 5. Similar results were presented for other types of materials at different molar and weight ratio. N. Mohammad et.al reported that the conductivity of CDP is $1.9 \times 10^{-2} \text{ S cm}^{-1}$ [15]. CDP ionic conductivity was found $2.30 \times 10^{-4} \text{ S cm}^{-1}$ at 200°C at the cold sintering process [1]. A proton-conductive electrolyte based on a $\text{CsH}_2\text{PO}_4/\text{SiP}_2\text{O}_7$ the maximum conductivity achieved was 44 mS cm^{-1} at 266°C [19]. $\text{CsH}_2\text{PO}_4 - \text{SiO}_2$ composites with modified silica exhibited high proton conductivity $10^{-3} - 10^{-2} \text{ S cm}^{-1}$ at $130 - 250^\circ\text{C}$ and have higher thermal stability at lower water vapor partial pressures compared with the pure salt [6]. Conductivity was measured for pure CDP and composites CDP/ TiO_2 at different temperatures.

3.5 Thermal Analysis (DSC, TGA, DTA, DTG)

DSC thermal analyses of CDP and its composites electrolytes with a constant heating rate (5 °C /minute) at different composition ratios are shown in Fig. 8.

Dehydration reaction occurs [32] in the following way

Figure 8 confirmed that CDP phase transition monoclinic to cubic occurred at the temperature of 230 °C and another phase transition, which is corresponding to dehydration at 250 °C [15]. CDP shows endothermic peaks at 150, 230, 250 °C. The sharp peak at 150 °C is quasi-irreversible because hydrogen-bonded in CDP are ferroelectrics, it occurs due to the presence of a small amount of $\text{CsH}_5(\text{PO}_4)_2$ [33]. In pure CDP dehydration start after 250 °C while four composites 0.9CDP-0.1TiO₂, 0.8CDP-0.2TiO₂, 0.7CDP-0.3TiO₂, 0.6CDP-0.4TiO₂ showed dehydration behavior disappears as the value of x increased.

The results of the TGA were performed under an ambient atmosphere, as shown in Fig. 9 (a).

Weight loss of 7.2, 3.1, and 1.95% at the temperature of 370, 270 and 230 °C for CDP, respectively. The 3.5% weight loss was found at 300, 289, 250, 235 and 230 °C for 0.9CDP/0.1TiO₂, 0.8CDP/0.2TiO₂, 0.7CDP/0.3TiO₂, 0.6CDP/0.4TiO₂ and pure CDP, respectively, which indicate that the temperature decreases with the same weight loss with increases the amount of x. The introducing of TiO₂ with CDP removes the two and three stage character of weight loss. The weight loss of CDP is due to dehydration, and it started with the formation of $\text{CsH}_2\text{P}_2\text{O}_7$. The amount of weight loss with temperature agrees with previous results [7, 34, 35]. In the case of four composites, dehydration is slowed, which is indicating that the chemical interaction between CDP and TiO₂. Overall weight loss is decreasing with increasing x value and found that the minimum weight loss for the composite 0.6CDP/0.4TiO₂. Our result shows that the thermal behavior and stability increase with increases the value of x.

According to DTA plots, CDP showed main peaks at 150, 230, 332, and 354 °C due to the formation phase of $\text{CsH}_5(\text{PO}_4)$, phase transition, formation of dimmers, and polymers, respectively. After the transition temperature the dehydration process slowdown in Fig. 9 (b) and matched with other results [1, 36, 37].

It is also observed that pure CDP peaks after 250 °C disappeared for 0.8CDP/0.2TiO₂, 0.7CDP/0.3TiO₂, and 0.6CDP/0.4TiO₂ composites.

In the DTG curve Fig. 9 (c) also showed the variation of amorphization and phase composition. The dehydration peaks also disappeared as shown in DSC, DTA curves, and supported each other. DSC, TGA, DTA, DTG is favorable with conductivity, XRD, and FTIR.

4. Conclusions

We have observed the structural, thermal, and proton conductivity behavior of $(1-x) \text{CsH}_2\text{PO}_4/x\text{TiO}_2$ ($0 \leq x \leq 0.4$) composites electrolytes for the fuel cell. Based on the evaluation of the literature and our recent conductivity measurements, CDP undergoes a superprotonic transition at 230°C . Three orders of magnitude ionic conductivity increases in the unmixed sample at the transition temperature. It was also observed that CDP with low additives of TiO_2 (contents $x = 0.1$ and 0.2) appeared in good agreement with ionic conductivity and stability. The highest ionic conductivity $1.7 \times 10^{-2} \text{ S cm}^{-1}$ has measured the composites $0.9\text{CDP}/0.1\text{TiO}_2$ at 270°C , which is more stable for long-term durability than pure CDP. It was achieved the protonic conductivity of $0.9\text{CDP}/0.1\text{TiO}_2$ and $0.8\text{CDP}/0.2\text{TiO}_2$ over a time span $t = 45$ and $t = 50$ hours, respectively, which is confined hermetically in a small container. A mixture of CDP and TiO_2 was useful for protonic conductivity between the temperature range from 240 to 310°C , this result favors to establish fuel cell technology. Thermal analysis (DSC, TGA, DTA, and DTG) revealed enhancement of the thermal stability of CDP as TiO_2 was introduced. The high ionic conductivity and thermal stability of these composites make them attractive for use in different chemical devices and fuel cells.

Declarations

Acknowledgments

The authors are thankful to the M.J.P Rohilkhand University Bareilly (India) for providing me facilities. The authors are also thankful to the Material Science Research Lab, Department of Physics, Gurukul Kangri University Haridwar (India), and Indian Institute of Technology Roorkee to provide necessary facilities.

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Figures

Figure 1

XRD patterns of pure CsH_2PO_4 powdered and composites $\text{CsH}_2\text{PO}_4/\text{TiO}_2$.

Figure 2

FESEM and EDX images of CDP; (a) 20μm (b) EDX (c) 2μm (d) 10μm.

Figure 3

FESEM and EDX images of TiO_2 ; (a) 50µm (b) EDX (c) 200nm (d) 1µm.

Figure 4

O-H modes, Stretching P-O, bending P-OH, O-P-O modes and Cs-O modes in FTIR spectra CDP and comparison its composites 0.9CDP/0.1TiO₂, 0.8CDP/0.2TiO₂, 0.7CDP/0.3TiO₂ and 0.6CDP/0.4TiO₂ in the range of 400cm⁻¹ to 4000 cm⁻¹.

Figure 5

Arrhenius plots of Temperature dependence conductivity for CDP and its composites 0.9CDP/0.1TiO₂, 0.8CDP/0.2TiO₂, 0.7CDP/0.3TiO₂ and 0.6CDP/0.4TiO₂.

Figure 6

Time dependence of the ionic conductivity for the sealed pellet of 0.9CDP/0.1TiO₂ composite electrolytes.

Figure 7

Time dependence of the proton conductivity for 0.8CDP/0.2TiO₂ in a small confined region.

Figure 8

Differential Scanning Calorimetry (DSC) curves for CDP and its composites.

Figure 9

(a)TGA (b) DTA (c) DTG Curves of CDP, 0.9CDP/0.1TiO₂, 0.8CDP/0.2TiO₂, 0.7CDP/0.3TiO₂, and 0.6CDP/0.4TiO₂ at a rate of 10o C/minutes under air flow 200 ml/minutes.