Main Group Chemistry 15 (2016) 125–130
DOI 10.3233/MGC-150191
IOS Press

Effect of telluric acid addition on thermal behavior of cesium dihydrogen phosphate

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Abstract. $x CsH_2PO_4 \cdot (1\text{-}x) Te(OH)_6$ composites have been synthesized for the different compositions, x = 0.02, 0.04, 0.05, 0.06, 0.08 (labeled composites A-E). The composites were characterized by Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), Thermogravimetry (TG) and Differential Thermal Analysis (DTA). Telluric acid, $Te(OH)_6$, added to cesium dihydrogen phosphate (CsH_2PO_4) significantly effects the structure, particle size and thermal stability of the composite material. Enhanced thermal stability could lead to use of CsH_2PO_4 as an electrolyte in low temperature fuel cells.

Keywords: Solid acids, low temperature fuel cells, composite materials, amorphous materials

1. Introduction

Solid acids are compounds which show properties between that of a normal acid and a normal salt. Cesium dihydrogen phosphate, CsH_2PO_4, is a member of the potassium dihydrogen phosphate (KH_2PO_4-type) family. Under sufficient humidification, CsH_2PO_4 transforms from a monoclinic to a stable, cubic phase at 228°C and 1 atm total pressure and exhibits high proton conductivity ($>10^{-2}$ Scm^{-1}) above this phase transition, known as the superprotonic phase transition [1, 2]. Due to its high conductivity in the superprotonic state and relatively high decomposition/melting point (ca. 200–230°C), CsH_2PO_4 has become an attractive candidate for fuel cells operating at low and intermediate temperatures.

However, conditions limit the temperature range for superprotonic phase transition in CsH_2PO_4. Under dry conditions, it decomposes to form polymerization products at temperatures above 200°C [2–6] and its conductivity decreases dramatically.

$$CsH_2PO_4 \longrightarrow \tfrac{1}{2}Cs_2H_2P_2O_7 + \tfrac{1}{2}H_2O \longrightarrow CsPO_3 + \tfrac{1}{2}H_2O \quad (1)$$

The narrow temperature range and chemical instability of the superprotonic phase limits CsH_2PO_4 use in fuel cell applications. Therefore, stabilization of the high conductive phase at a wide temperature range is very important for practical uses of CsH_2PO_4.

In this study, we have investigated the effect of telluric acid addition into CsH_2PO_4 on thermal stability.

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2. Experimental section

Five different composition of $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ (x = 0.02, 0.04, 0.05, 0.06 and 0.08) were synthesized. The composites are identified as composite A, B, C, D and E, respectively. In all synthesis, required amount of telluric acid (H_6TeO_6) (99%, Fluka) and cesium carbonate (Cs_2CO_3) (%99.9, Sigma-Aldrich) were dissolved in a minimum amount of distilled water, separately. The phosphoric acid (H_3PO_4) (85 wt. % in H_2O, Sigma-Aldrich) solution was stoichiometrically added to the cesium carbonate solution. The resulting solution was stirred for one hour and then added into H_6TeO_6 solution. The mixed solution was evaporated slowly at approximately 65°C overnight and the gel-like product was kept in an oven at 110°C for 2 days.

Scanning electron microscopy (SEM) was carried out by CamScan Apollo 300 Field-Emission and x-ray diffraction data was recorded at ambient conditions using a Philip Xpert Pro with Cu Kα radiation. Thermal gravimetry (TG) and differential thermal analysis (DTA) were done with Perkin Elmer Diamond system at a scan rate of 5°C min^{-1} in heating cycle and that of 10°C min^{-1} in cooling cycle.

3. Results and discussion

Figure 1 demonstrates the SEM images of the synthesized $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ composites (x = 0.02, 0.04, 0.05, 0.06 and 0.08). The composite A is the one including the most amount of telluric acid as having a $CsH_2PO_4/Te(OH)_6$ molar ratio of 1:4. 1000X and 4000X magnified images of composite A can be seen in Fig. 1a. The amorphous and larger particles in the range of 10–20 micron might be CsH_2PO_4 considering it occurs from the atoms with larger diameters than that of $Te(OH)_6$. 1–5 micron size particles' structure is in good agreement with the monoclinic structure of $Te(OH)_6$. The composite B with a $CsH_2PO_4/Te(OH)_6$ molar ratio of 2:3 has smaller particles in size than the composite A (Fig. 1b). Decreasing the telluric acid in the composite might cause the smaller particle size in the composite, as well as an unrequired side product can be responsible of the change in both particle size and structure. In the composite B, instead of the amorphous and monoclinic structures obtained in the composite A, the platelet/stick shaped anortic structures take the place of amorphous and monoclinic ones. As seen in Fig. 1c, the structure in the composite C becomes amorphous with an equal molar ratio of $CsH_2PO_4/Te(OH)_6$ and the nanoparticles are also seen on the surface of the amorphous structure. As is clear from the Fig. 1d, increased $Te(OH)_6$ amount in the composite enhances the amorphous structure. The composite E, which has a $CsH_2PO_4/Te(OH)_6$ molar ratio of 4:1, is the composite with the highest $Te(OH)_6$ content and even the amorphous structure dominates in the composite, it might be said that a crystalline structure start to be formed again at this $CsH_2PO_4/Te(OH)_6$ ratio.

The XRD result of the composite A does not indicate any crystalline structure in the composite and presents an amorphous structure (Fig. 2a). However, SEM result of the composite A clearly shows the presence of monoclinic structure besides the amorphous one. This occurrence can be explained by the broad peak of the amorphous structure between 23–33° might block the peaks from the crystalline structure. The composite B is the only composite shows no presence of an amorphous structure (Fig. 2b) and in good agreement with $Cs_3P_3O_9 \cdot H_2O$ structure (ICSD, 026-0398). The lattice constants are a = 10.9200 Å, b = 8.0850 Å and c = 8.2450 Å. The temperature control problem with hot plate heaters might be responsible of that formation of the undesired $Cs_3P_3O_9 \cdot H_2O$, as solid acids can be easily dehydrated to their other side products. 5–10°C decrease in the evaporation temperature can sort the formation of the side products out. $Cs_3P_3O_9 \cdot H_2O$ formation have not been seen in other $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ composites. The amorphous structure dominates the structure in the composite C (Fig. 1c), however the sharp peak around 44–45° indicates the presence of a crystalline structure, which might be

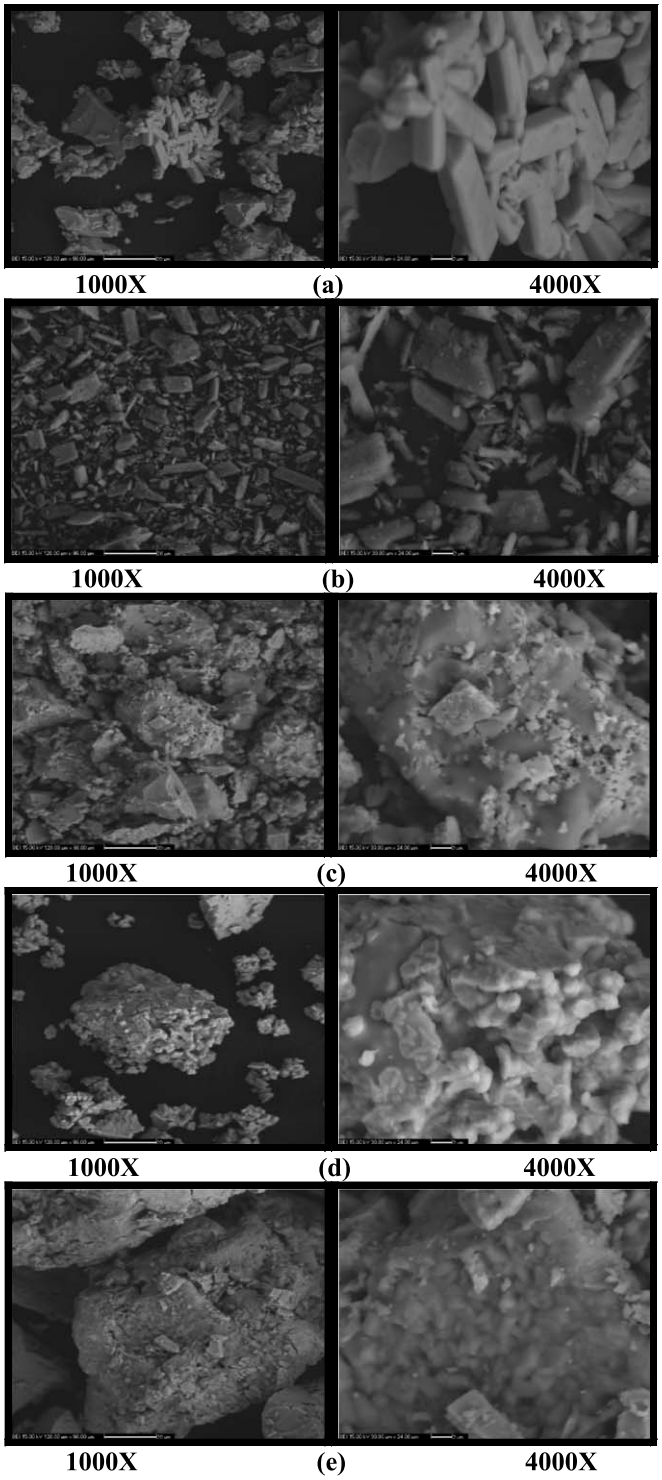


Fig. 1. SEM images of $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ composites under 1000X and 4000X magnification (composite A, x = 0.02; B, x = 0.04; C, x = 0.05; D, x = 0.06; E, x = 0.08).

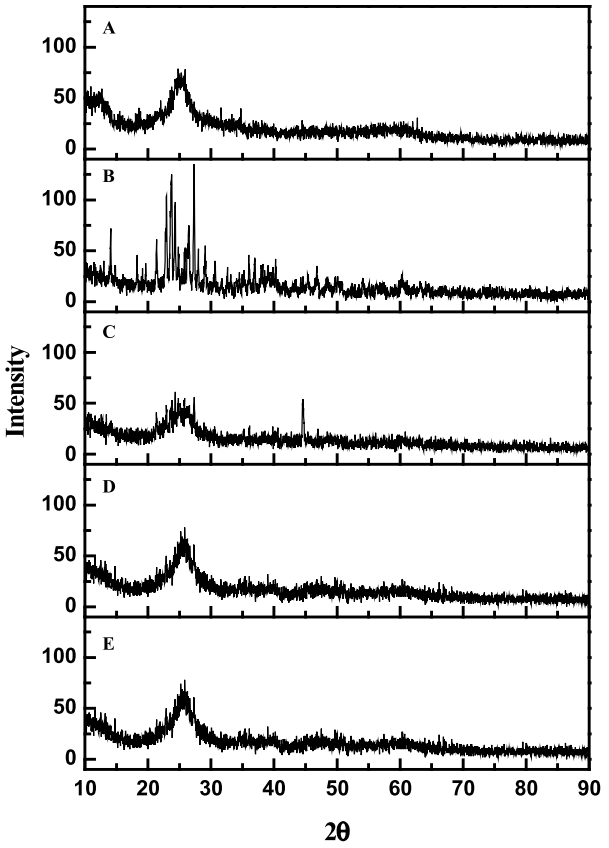


Fig. 2. XRD results of $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ composites. (composite A, x = 0.02; B, x = 0.04; C, x = 0.05; D, x = 0.06; E, x = 0.08).

attributed to the presence of CsH_2PO_4 or the formation of side products like TeO_2 or Te_2O_5. Amorphous structure without any presence of crystal structure is seen in the composites D and E.

Figure 3 gives the thermal analysis of the synthesized composites. Cooling of the all composites were interrupted due to an unknown reason occurred in the thermal analysis system. In the DTA analysis of the composite A, an endothermic slight peak is seen around 30°C with a mass loss of 0.25%. This weight loss is related to the release of humidity. Heating above this temperature, the crystallization of CsH_2PO_4 occurs till 133°C. An unusual weight loss of 1.6% through the crystallization process can be attributed to the release of water from the surface of the compound (like $CsH_2PO_4 \cdot xH_2O$). Neither endothermic nor exothermic peak is seen in DTA analysis over the crystallization process. This might be attributed to the existence of slow crystallization process and a clearer DTA analysis can be observed at higher scan rates than 5°C min^{-1}. DTA analysis at the scan rate of 5°C min^{-1} is not enough to clearly see all endothermic and exothermic steps for all composites. The weight loss above 133°C is likely due to the melting of telluric acid and this observation is in good agreement with the melting point of telluric acid (136°C). The fast weight loss which occurred at 330°C is ascribed to the melting of CsH_2PO_4 (345°C). This mass loss is accompanied by a slight endothermic peak in DTA analysis. The crystalline structure of the composite B is previously identified as $Cs_3P_3O_9 \cdot H_2O$ with XRD results. The weight loss of the composite B above 139°C with an endothermic peak around 142°C is defined as melting of telluric acid. Above 289°C, the weight loss and the endothermic effect is likely the decomposition of $Cs_3P_3O_9 \cdot H_2O$. TG curve of the composite C shows two decomposition steps.

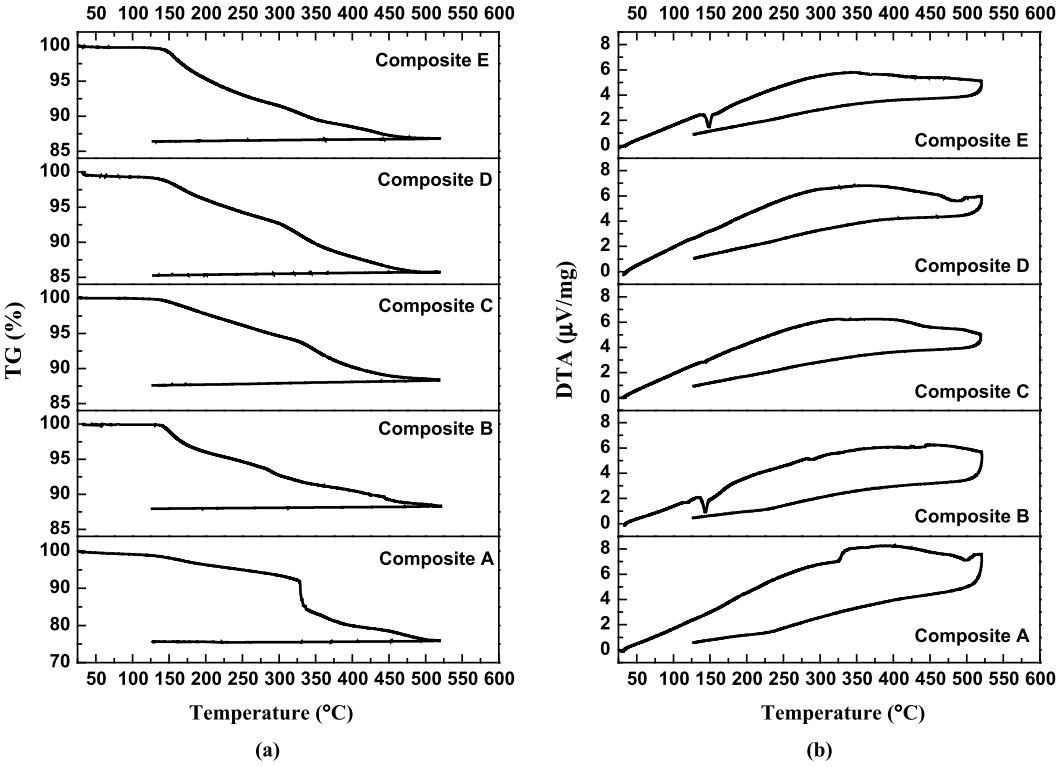


Fig. 3. TG (a) and DTA (b) analysis of the of $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$ composites. (composite A, x = 0.02; B, x = 0.04; C, x = 0.05; D, x = 0.06; E, x = 0.08).

Similar to the composites A and B, the weight loss above 130°C with a slight endothermic effect around 143°C is attributed to the melting of telluric acid. Second step with an onset temperature of 336°C is an agreement with the melting of CsH_2PO_4. It seems CsH_2PO_4 might be thermally stable in the composite C up to its melting point. The thermal analysis of the composite D shows a weight loss up to 131°C attributed to releasing surface water through crystallization. Above this temperature, TG curve of the composite D gives multiple decomposition steps. Melting of telluric acid and decomposition of CsH_2PO_4 are likely responsible of these decomposition steps. As similar to the other composites, a weight loss with an onset temperature of 140°C in the composite E is referred to the melting of telluric acid. An endothermic peak at 147°C is also in agreement with this weight loss. The other decomposition steps are attributed to the decomposition of CsH_2PO_4.

4. Conclusion

Different compositions were synthesized and characterized for $x CsH_2PO_4 \cdot (1-x) Te(OH)_6$. The ratio of $CsH_2PO_4/Te(OH)_6$ was found to be effective on thermal stability of the composites. The composite C with an equal molar amount of CsH_2PO_4 and $Te(OH)_6$ showed a promising thermal stability compared to CsH_2PO_4, which has a decomposition temperature of 200–230°C. It seems that CsH_2PO_4 in the composite C does not decompose up to its melting point and this may give an opportunity for the composite C to be used as electrolyte up to its melting point. A further study of its conductivity is needed to support its potential as an electrolyte for fuel cells.

Acknowledgments

The authors would like to thank Yıldız Technical University for the support of this study. This study is funded by Scientific Research Project Coordination of Yıldız Technical University (#2013-07-01-GEP02).

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