Effects of temperature and humidity on electrical properties of proton conducting KH$_2$PO$_4$ / SiO$_2$ composites

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Abstract. In the present work the temperature and humidity effects on electrical properties of KH$_2$PO$_4$/SiO$_2$ composites have been studied. Composite nature of the system has been confirmed by the XRD patterns. Wagner’s polarization method confirms the ionic conduction in the prepared systems. Temperature and humidity dependent ac conductivity was measured by using complex impedance spectroscopy in the frequency range 10 Hz to $10^5$ Hz. In pure KH$_2$PO$_4$ the conductivity is influenced by the hopping of the proton through defects while in KH$_2$PO$_4$/SiO$_2$ composite systems, the conductivity of composite system is governed by hydrophilicity below 130°C. In the present composite systems, absorption of KH$_2$PO$_4$ takes place at the surface of silica which produce defects near the salt KH$_2$PO$_4$/oxide SiO$_2$ interface. The transition temperature of composite was found to be decreased in comparison to the pure KDP.

1. Introduction

The initial investigations of MH$_2$XO$_4$ class of compounds were mainly related to the ferroelectric transition similar to that discovered in KH$_2$PO$_4$ at 123 K [1]. After the discovery of the superprotonic phase transition in CsHSO$_4$ at 142°C [2,3], high temperature properties of the entire class of compounds began to be examined. MH$_2$PO$_4$ type compounds (M= alkali cation or NH$_4$) constitute the families of solid proton electrolytes. At high temperature, these compounds, show a phase transition from normal conductor to the superionic conductor. A sharp increase in electrical conductivity by several orders of magnitude is associated with this phase transition. Many researchers have studied the structural and transport properties of CsHSO$_4$/SiO$_2$ and CsH$_2$PO$_4$/SiO$_2$ composites systems [4-8]. They have investigated that addition of SiO$_2$ in CsHSO$_4$ system increases the value of electrical conductivity 2 to 2.5 orders of magnitude in comparison to pure CsHSO$_4$. In these families conductivity is governed by the conduction of protons through defects. Potassium dihydrogen phosphate (KDP) is a thoroughly studied solid at room temperature by many workers. Thermal properties of potassium dihydrogen phosphate have also been studied by several groups. In the present work, influence of temperature and humidity on electrical properties of KH$_2$PO$_4$/SiO$_2$ composites have been studied. For study the electrical measurements we have adopted complex impedance spectroscopy.
2. Experimental
The two phase \((1-x)KH_2PO_4/xSiO_2\), where \(x = 0.0, 0.1, 0.3, 0.5\) and 0.7 composites were prepared by solid state reaction method. The constituents \(KH_2PO_4\) (Merck, purity 98%) and fumed silica (\(SiO_2\)) of particle size 7 nm (Sigma Aldrich, purity 99%) were taken in the desired weight ratio and mixed together. A homogeneous powder mixture was prepared by grinding and mixing for about 2 hrs. The fumed silica was used as chemically inert phase in the composite systems. The prepared powder thus obtained were pressed in the form of pellets of 10 mm diameter by hydraulic palletizing machine under the pressure of 5 tons/cm² for further measurements. Silver paint were used as electrodes at the surface of pallets. Conductivity measurements were carried out by means of ac impedance spectroscopy with HIOKI 3522-50 LCR HITESTER impedance analyzer in the frequency range from 10 Hz to 100 kHz.

3. Results and discussion
In the present study we have used following techniques for characterization of composite system (i) X-Ray diffraction for structural characterization. (ii) Wagner’s polarization for measurement of ionic transference number. (iii) Complex impedance spectroscopy for measurement of electrical conductivity.

3.1 XRD Analysis
Well defined sharp crystalline peaks are observed in XRD pattern of pure \(KH_2PO_4\) as well as of the composite system. The comparison of XRD patterns of pure \(KH_2PO_4\) with fumed silica (\(SiO_2\)) composite shows that all the peaks observed in the composite system belong to pure \(KH_2PO_4\). These observations show absence of any global reaction between the host and dispersoid and hence confirm the formation of a composite system.

![Figure 1. X-ray diffraction patterns of \((1-x)KH_2PO_4/xSiO_2\) composites](image)

3.2 Transference number measurement
To confirm the ionic nature of composite we have adopted Wagner’s polarization method. In the Wagner’s polarization technique, the sample is sandwiched between two ions blocking electrodes. We have used thick silver paint as a blocking electrode. When a dc voltage (1.5 volt) is applied across the sample, current decreases very quickly with time and become zero because all the ions are blocked. There are no ions remain to carry a charge so current reached to a value at zero. The ionic transference number comes out to be 1 that confirms the conduction in the samples is due to movement of ions i.e. prepared samples are purely ionic conductors.

3.3 Temperature dependence of conductivity
The bulk conductivity of each compositions was calculated by using the relation

\[
s = \frac{\sigma}{RA}
\]
where \( t \) and \( A \) are the thickness and surface area of cross-section of the pellets respectively and \( R \) is the bulk resistance determined from impedance plots. Conductivity measurements were carried out by means of ac impedance spectroscopy in the frequency range 10 Hz to 100 KHz. The conductivity of different compositions of pure KH₂PO₄ and \((1-x)\text{KH₂PO₄}/\alpha\text{SiO₂}\) composite were evaluated from the frequency dependent of impedance plots (cole-cole plots). Fig. 3 shows the impedance plots of 90KH₂PO₄/10SiO₂ composite at different temperatures. Impedance plots, consist a semicircle in the higher frequency region with a straight tail in lower frequency region. The extrapolation of semicircle on \( Z' \) axis gives the value of the bulk resistance \( R \). The diameter of semicircles decreasing with increasing in temperature i.e. conductivity increases with increase in temperature. Fig. 4 represents the conductivity of pure KH₂PO₄ and different compositions of its composites with fumed silica in the temperature range 300 K to 450 K. It is found that at room temperature, the conductivity of composite is slightly greater than that of pure KH₂PO₄. It may be due to absorption of water content by SiO₂ and evaporates above 130 °C because above this temperature conductivity is decreased in comparison to pure KH₂PO₄. In pure KH₂PO₄ the conduction takes place due to hopping of protons between hydrogen vacancies at temperature below 180 °C [9]. In the present composite, it is assumed that silica absorbs the KH₂PO₄ at its surface producing the defects near the interface of KH₂PO₄ and oxide. In the composite sample the conduction takes place due to Proton hopping through these defects [2].
There is no significant change in the conductivity in low temperature regime from RT- 120 °C however in pure KH$_2$PO$_4$ there is a gradual increase in conductivity from RT-160 °C. The steep change in conductivity in all the compositions of composite occurs at lower temperature i.e. around 120 °C although in pure KH$_2$PO$_4$ it occurs at 160 °C. The decreases in transition temperature has also been observed by Ponomareva et al. [2] in (1-\(x\))CsHSO$_4$ + \(x\)SiO$_2$ composite as an effect of SiO$_2$ addition in CsHSO$_4$. According to them, as the concentration of SiO$_2$ increase in CsHSO$_4$, amorphisation of the hydrate occurs and this leads to decreases in phase transition temperature and relative change of conductivity at phase transition. The phase transition becomes diffusive and gradually decreasing. In our case, we have also observed decrease in the transition temperature, as well as decreases in relative change in ionic conductivity at transition temperature. At high temperature, after the transition, rate of change in conductivity is observed to be same and increasing with temperature. As compared to pure KH$_2$PO$_4$, transition temperature as well as a rate of change of conductivity is observed to be decreases as observed in the case of silica dispersed composite. The variation in conductivity in the low temperature region may be attributed to the protons due to presence of surface adsorbed water and structural protons. The initial increase in conductivity up to temperature 95 °C is due to thermally activated process. Between 95 °C to 120 °C, decrease is attributed to desorption of surface adsorbed water. It is hypothesized that since in composite with \(x = 0.1\), the structural protons are more in comparison to \(x = 0.3, 0.5\) and 0.7, therefore after desorption of surface adsorbed water, the conductivity of composite with \(x = 0.1\) is more than that of other compositions. Therefore for \(x = 0.1\), the variation is almost similar to that of pure KH$_2$PO$_4$ governed by hopping of hydrogen ions from one hydrogen vacancies to the other. However, in other compositions, due to smaller number of structural protons and more surface adsorbed water in comparison to \(x = 0.1\), the decrease in conductivity is more pronounced between 95 °C to 120 °C. Above the temperature 120 °C, the steep increase in conductivity may be associated with partial decomposition of KDP in the composite systems as is explained in the case of pure KDP.

3.4 Humidity dependence of conductivity

The variation of conductivity of various compositions of the composite were also measure as a function of relative humidity. For the measurement, the measurement cell containing composite electrolyte pellets were placed in the sealed desiccator. The humidity level in the desiccator was first decreased upto 10 % by putting charged silica gel in desiccator and then was increased up to 65 % by replacing silica gel with water. Humidity levels were read with the help of hygrometer which is also placed inside the desiccator. The variation of conductivity for pure KDP and various compositions of composites is shown in the fig. 5. The ionic conductivity of composites increases with increasing relative humidity. A change of about 2 orders have been observed in the conductivity on changing the humidity level from 10 to 65 %. The dependence of conductivity on RH further indicates the role of surface adsorbed water in conduction in the composites. Further, this is to mention that above observations are carried out at dynamic humidity levels therefore, above variations are only indicative and not conclusive.

Conclusion

The composite systems of (1-\(x\)) KH$_2$PO$_4$ /\(x\)SiO$_2$ were prepared using solid state route by physical grinding of the starting materials. From the Wagner’s polarization method, it is confirmed that conduction is purely ionic. The following conclusions are obtained from conductivity measurements of KH$_2$PO$_4$ and those silica composites.

1. X-ray investigations of the samples have shown that there is no reaction between the salt and SiO$_2$, and hence forming composites.
2. The ionic transference numbers of (1-\(x\)) KH$_2$PO$_4$ /\(x\)SiO$_2$ has been found to be decreasing with increasing SiO$_2$ concentration however with \(x = 0.0 - 0.5\), composites have been found to be predominantly ionic conductor.
3. In KH$_2$PO$_4$/SiO$_2$ composite systems, the conductivity is governed by hydrophilic nature of silica which induces the conductivity below the phase transition.
4. The ionic conductivity of pure KH$_2$PO$_4$ and that of composites increase with increasing temperature from $\sim$10$^{-8}$ S/cm to $\sim$10$^{-4}$ S/cm. Low temperature variation in conductivity is almost same for all compositions.

5. In all composites the transition temperature was found to be decreased in comparison to the pure KDP.

6. The ionic conductivity of composites is strongly dependent on the relative humidity.

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