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Proton conducting plastic crystal electrolytes based on pivalic acid

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Abstract

New materials based on the plastic crystalline phase of pivalic acid were prepared, and their conductivities measured, in order to assess their potential for application as membranes for fuel cells. Pivalic acid has a very low conductivity of approximately 10^{-13} S cm⁻¹ in the neat form. The objective of this study was to attempt to increase the ionic conductivity of pivalic acid through the addition of bases of varying strengths. Of the bases studied, the heterocyclic molecule, imidazole is the most effective, and upon the addition of 5 mol%, a soft, transparent material with a conductivity of 3.9×10^{-5} S cm⁻¹ at 293 K was obtained. Differential scanning calorimetry was used to study the phase equilibrium in the pivalic acid–imidazole system. The presence of a plastic crystal phase over a temperature range of 21 K was observed in the pivalic acid-rich region.

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Polymer electrolyte membrane fuel cells are currently the most viable candidate to replace combustion engines for portable applications. Despite the ability of the electrolytes to deliver good properties at moderate and near-ambient temperatures, many technical problems can arise from operating at lower temperatures [1]. The primary problem that these membranes suffer from is the dependence of their properties (conductivity, mechanical strength, etc.) on humidity, limiting the performance of the cells to temperatures below the dew point of water [2]. Alternative non-aqueous proton conducting materials are under-development, with particular interest in heterocyclic compounds such as imidazole which can act as either a proton acceptor and a proton donor. This property allows for fast proton conduction by Grotthuss mechanism [3]. Materials incorporating imidazole were previously prepared with either free bases [4] or ionic liquids [5,6] being incorporated into a polymeric matrix or having imidazole chemically-attached to a polymer chain [7] or an oligomer [8].

Interest in plastic crystals has been revived in the last two decades after the recognition of their potential use as new

class of solid electrolytes [9–11]. They are characterized by the existence of high degree of structural disorder originating from the rotation or disorientation, of individual molecules within an ordered crystalline lattice [12]. This type of dynamic disorder is an ideal environment to support fast proton conduction due to the enhanced size and mobility of defects in plastic crystal phases compared to conventional crystals [13].

Previous work on plastic crystals exhibiting proton conductivity was focused on either the doping of non-aqueous proton conducting ionic liquids based on imidazole [14] or organic acids in the plastic crystalline phase of succinonitrile [15]. In the former, flexible materials with high conductivities reaching 1.5 mS cm⁻¹ at 298 K were obtained. In a radically new approach, a new family of compounds known as solid acids, such as cesium hydrogen sulfate (CsHSO₄) have been investigated [16]. They show a plastic transition at intermediate temperatures (323–423 K) with conductivities reaching 10^{-3} to 10^{-2} S cm⁻¹. Work by Haile et al. have shown that despite the fact that the acids are in principle, a viable alternative, they still suffer from many technical problems such as the reduction of sulphur, the softness of the compounds, and their solubility in water upon accidental exposure [17].

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Pivalic acid, *t*-butyl carboxylic acid, $(\text{CH}_3)_3\text{CCO}_2\text{H}$, is a well-known plastic crystal material which shows a plastic phase near room temperature. The plastic phase extends between the solid–solid transition from a crystal to plastic crystal at 280 K to its melting point at 310 K [18]. It adopts a face centered cubic structure and its carboxylic group has a $\text{p}K_{\text{a}}$ of ~ 5 [19,20].

The conductivity of neat pivalic acid was measured at 293 K by the standard impedance spectroscopy technique and found to be very low at $2.5 \times 10^{-12} \text{ S cm}^{-1}$. A similar value was obtained by Sherwood and co-workers [21], which they attributed to the dimeric character of pivalic acid within the plastic crystal phase. They concluded that the predominance of non-conductive proton exchange rather than conductive (free) proton transfer is mainly responsible for the observed low conductivities.

In order to increase the conductivity, it is essential to disrupt the dimeric structure by attempting to break the hydrogen bonds between the two carboxylates. For this purpose we have added small amounts of various bases to the neat acid and measured the conductivity of the resultant materials. Table 1 shows the solubility and the conductivity, at 293 K, of all of the prepared materials with 5 mol% additive. The materials were prepared by mixing, in a small vial, the appropriate amounts of pivalic acid and the additive and then heating the mixture above the melting point of the acid. We have observed that strong bases like KOH dissolve in the acid but produce a material with a conductivity of only $6 \times 10^{-10} \text{ S cm}^{-1}$, and hence provide a modest one-and-a-half orders of magnitude increase. Weaker bases like potassium pivalate, a conjugate base of pivalic acid, have resulted into slightly higher conductivities reaching $1.3 \times 10^{-9} \text{ S cm}^{-1}$. The addition of heterocyclic bases like pyrrolidine and homopiperolizine have given approximately similar conductivities being 2 and $4 \times 10^{-9} \text{ S cm}^{-1}$, respectively. Similarly, a material with a *t*-butylamine base has given a conductivity of $4 \times 10^{-9} \text{ S cm}^{-1}$.

Imidazole, a heterocyclic organic molecule with a $\text{p}K_{\text{a}}$ of 7 conducts protons in the solid state via a Grotthuss mechanism. This involves proton hopping and reorientation of protonated molecules within a hydrogen-bonded network. Imidazole has the ability to work as a proton donor and acceptor due to its ability to auto-dissociate. The addition of imidazole to pivalic acid has proven to be the most effective of all bases studied.

Table 1
Solubility and conductivity, at 293 K, of various bases (5 mol%) in pivalic acid

Compound	Solubility/conductivity
KOH	$6 \times 10^{-10} \text{ S cm}^{-1}$
K^+ -pivalate	$2.4 \times 10^{-9} \text{ S cm}^{-1}$
Pyrrolidine	$2 \times 10^{-9} \text{ S cm}^{-1}$
Homopiperolizine	$4 \times 10^{-9} \text{ S cm}^{-1}$
<i>t</i> -Butyl amine	$4 \times 10^{-9} \text{ S cm}^{-1}$
Imidazole	$3.9 \times 10^{-5} \text{ S cm}^{-1}$
Imidazole (10%)	$5.4 \times 10^{-4} \text{ S cm}^{-1}$
Guanidine	Insoluble
Urea	Insoluble
Poly(ethyleneoxide)	Insoluble

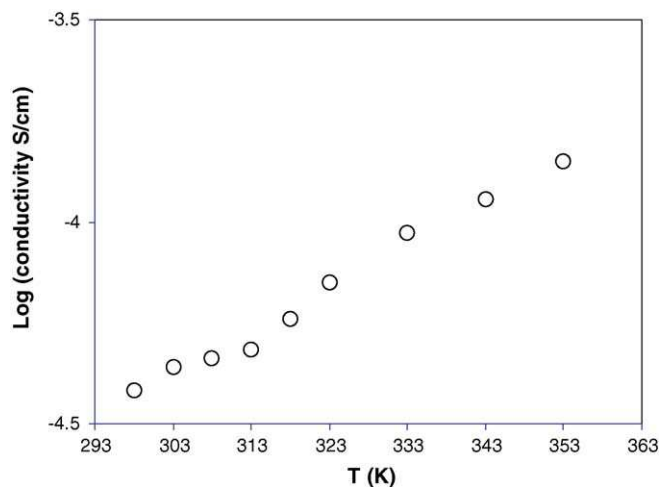


Fig. 1. Temperature-dependence of the conductivity of (5% IM-PA).

Adding a small quantity of imidazole (5 mol%) to the acid gave a transparent and very soft compound (labeled 5% IM-PA). The conductivity of which was found to be $3.9 \times 10^{-5} \text{ S cm}^{-1}$ at 293 K, and increased to $5.19 \times 10^{-5} \text{ S cm}^{-1}$ at 308 K, as can be seen in Fig. 1. Generally, the conductivity increased as a function of temperature going through a short plateau on melting at 304 K, before it continued increasing monotonically.

The mechanism with which imidazole increases the conductivity of pivalic acid; we hypothesize, stems from the ability of imidazole to hydrogen bond with the dimer, and further strengthen the bond to a full proton transfer leading to the formation of imidazolium species. This is a more stable structure for the proton due to the resonance structures available for the cation, which in turn, could either donate its proton to a free imidazole creating a dynamic proton exchange through hydrogen-bonded networks. The formation of higher aggregates (1:2 and possibly 1:3) resulting from the interaction of a 1:1 complex with an acid dimer are also possible resembling in this case mixtures of pivalic acid and triethylamine [22,23]. Although imidazole is less basic than triethylamine ($\text{p}K_{\text{b}}$ 11), it is basic enough to open the dimeric cycle. Mixtures of imidazole and strong acids like bis(trifluoromethanesulfonyl)imide $(\text{CF}_3\text{SO}_2)_2\text{NH}$ amide [24], HBF_4 (HPF_6 , HClO_4) [25] or H_2SO_4 [2] were reported previously. The phase diagram of the imide mixture revealed the formation of a eutectic between the equimolar salt and either imidazole or the acid. In our case, although the eutectic is most likely to form with a melting point lower than ambient temperature, no bulk liquid was observed, suggesting that it could be, as we previously suggested, [26] nano-encapsulated within the long extended dislocations, known to exist in plastic crystalline phases.

DSC scans were recorded for the pivalic acid–imidazole system with compositions ranging from 0 to 100 mol% as shown in Fig. 2, and summarized in Table 2. In the neat form, pivalic acid showed the typical two peaks corresponding to the crystal-to-plastic crystal transition and melting at 290 and 310 K, respectively. Upon the addition of imidazole the two temperatures were lowered but retained the plastic crystalline phase over a tempera-

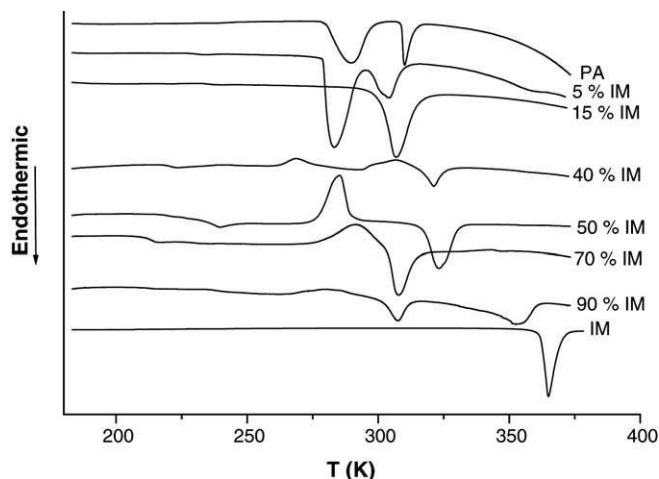


Fig. 2. DSC thermograms of IM-PA compositions with different mole fraction of IM. The heating rate is 10 K min⁻¹.

ture range of approximately 21 K up to the 12.5 mol% imidazole composition, where after the plastic crystalline phase disappears. There seems to be a transient region that is manifested in the unexpected increase in melting point of the 15 mol% composition and, to a lesser extent of the 12.5 mol%.

The DSC data were used to construct the complete phase diagram, which is depicted in Fig. 3 by taking values of the temperature at which the endothermic peaks took place.

It can be seen that at the equimolar ratio a salt with a melting point of 323 K was formed. This has given rise to a eutectec in the imidazole-rich domain at 293 K and another in the pivalic acid-domain at 308 K. This behaviour is typical of imidazole–acid mixtures and similar phase diagrams were reported for imidazole with H₂SO₄ [2], or HTFSI [24] or HBF₄ [25] systems.

Finally, it can be concluded that soft, materials with moderate ionic conductivities can be prepared by adding small amounts of imidazole to pivalic acid. This report is of significant importance as it opens the door for the fabrication of electrochemical devices that function at room temperature with less dependance on relative humidity.

Table 2
Thermal properties for IM-PA compositions

% IM	T_{pc} (K)	T_c (K)	T_e (K)	T_m (K)
100				365
90		279	307	352
80		289	309	341
70		290	308	
60		293	306	316
50		285		323
40		263	293	321
30			294	301
20			293	298
15				306
12.5	281			304
10	281			302
5	283			304
0	290			310

T_{pc} : plastic crystal transition temperature; T_c : crystallization temperature; T_e : eutectec temperature; T_m : melting temperature.

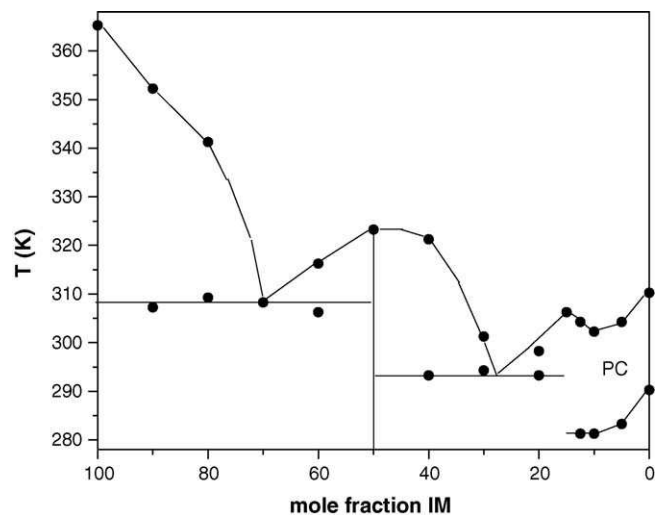


Fig. 3. Phase diagram of the system IM-PA (pc: plastic crystal form).

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