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Pentapyridinium 18-Silver Iodide, a "Two-Dimensional" Solid Electrolyte*

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The new solid electrolyte pentapyridinium 18-silver iodide, $(C_5H_5NH)_5Ag_{18}I_{23}$, effectively allows the current-carrying Ag^+ ions to move in only two dimensions. Comparison with the other solid electrolyte in the C_5H_5NHI-AgI system, namely $(C_5H_5NH)Ag_5I_6$, demonstrates that three-dimensionally interconnecting diffusion pathways are more favorable to high conductivity.

We report a new solid electrolyte in the pyridinium-iodide–silver-iodide system in which the current carriers (the Ag^+ ions) are forced to stay within layers perpendicular to the hexagonal c axis of the crystal. There are no paths by which the Ag^+ ions can move between these layers, which are separated by layers of (effectively) $[(C_5H_5NH)_3I]^{2+}$ ions. As a result, the average conductivity of the material is low. This is further corroboration of the thesis that three-dimensional connectivity is probably best for highly conducting solid electrolytes.

There are two compounds in the system of pyridinium iodide and silver iodide (PyI-AgI) which are now known to be solid electrolytes. The relation of the conductivity-versus-temperature behavior to the crystal structure and Ag^+-ion site distribution of $(C_5H_5NH)Ag_5I_6$ has been previously reported.[1] $(C_5H_5NH)Ag_5I_6$ is a three-dimensional solid electrolyte and has a room-temperature average conductivity of 0.077 $(\Omega\ \mathrm{cm})^{-1}$, almost an order of magnitude higher than that, 0.008 $(\Omega\ \mathrm{cm})^{-1}$, of $(C_5H_5NH)_5Ag_{18}I_{23}$, the two-dimensional solid electrolyte (Fig. 1).

Figure 1(a) is a top view of the iodide-ion arrangement in the crystal (space group, $P\bar{6}2m$; $a=13.62$, $c=12.58$ Å, $Z=1$) of $Py_5Ag_{18}I_{23}$.[2] The paths for the Ag^+ ions are shown in Fig. 1(b) and result from the sharing of faces of iodide tetrahedra. Figure 1(c), which is a side view of the structure, illustrates clearly how the Ag^+ ions are constrained to move between layers of (effectively) $[(C_5H_5NH)_3I]^{2+}$ ions. There are no paths for Ag^+-ion diffusion crossing these layers [see also Fig. 1(d)]. Two-fifths of the $(C_5H_5NH)^+$ ions are stacked along the hexagonal c axes.

For comparison, a top view of $PyAg_5I_6$ is shown in Fig. 2. This crystal (space group, $P6/mcc$, $a=12.03$, $c=7.43$ Å, $Z=2$) has three-dimensional pathways for Ag^+-ion diffusion. (These pathways

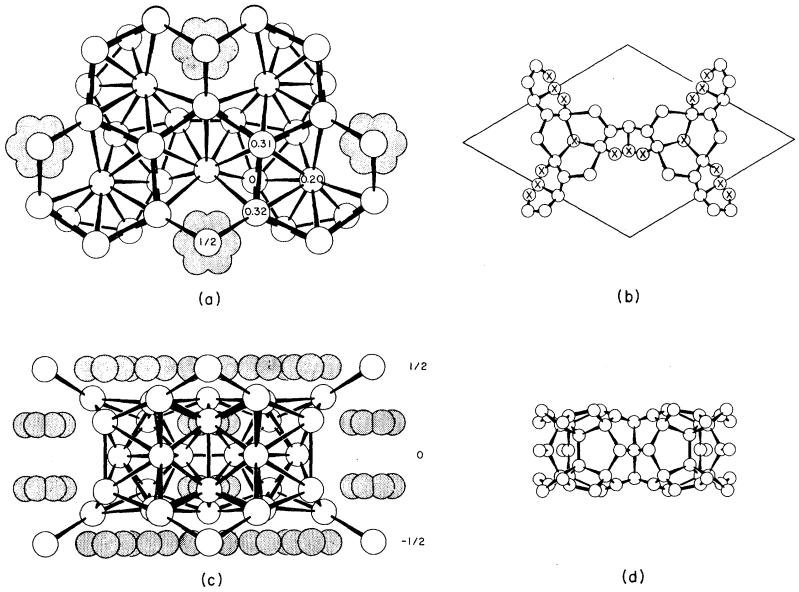

FIG. 1. (a) Top view of iodide-ion arrangement is $Py_5Ag_{18}I_{23}$. The pyridinium ions (stippled) on the hexagonal axes are also shown. (b) Top view of Ag^+-ion paths in $Py_5Ag_{18}I_{23}$. The equilibrium Ag^+-ion sites (located at or near iodide tetrahedra centers) are shown. A cross indicates a connection between upper and lower halves of the Ag^+ path network within the conducting layer. See also (d). (c) Side view of the iodide arrangement in $Py_5Ag_{18}I_{23}$. The pyridinium ions (stippled) in the $\pm\frac{1}{2}c$ levels of the unit cell are shown. These together with the I^- ions at $\pm(0, 0, \frac{1}{2})$ block movement of Ag^+ ions in the c-axis direction. (d) Side view of the Ag^+-ion paths in $Py_5Ag_{18}I_{23}$.

are therefore more difficult to visualize.) The $(C_5H_5NH)^+$ ions are *all* stacked along the hexagonal c axes. Details on pathways in $PyAg_5I_6$ have already been given elsewhere.[1]

$PyAg_5I_6$ has a transition at 50°C from a region of low disorder to one of high disorder.[1] In the higher-temperature region, h_m, the enthalpy of activation of motion, is 0.21 eV. This is the value of h_m found between room temperature and 100°C for $Py_5Ag_{18}I_{23}$.[2] At 55°C, the (average) specific conductivities of $PyAg_5I_6$ and $Py_5Ag_{18}I_{23}$ are 0.29 and 0.015 $(\Omega\ \mathrm{cm})^{-1}$, respectively, differing by a factor of 19.

A strict comparison of conductivities cannot be made [except for isostructural compounds, e.g., $RbAg_4I_5$,[3,4] KAg_4I_5, and $(NH_4)Ag_4I_5$, in which case nothing really new is learned] because the crystal structures are so different. $Py_5Ag_{18}I_{23}$ has seven crystallographically nonequivalent sets of equilibrium sites for the Ag^+ ions, $PyAg_5I_6$ only three; the former contains only face-sharing tetrahedra, the latter both octahedra and tetrahedra sharing faces with each other and among themselves but in a very different manner from that in $Py_5Ag_{18}I_{23}$. The respective Ag^+-ion concentrations[5] $(0.89 \text{ and } 1.07)\times10^{22}\ \mathrm{cm}^{-3}$ are quite different as are the Ag^+-ion equilibrium-site concentrations[6] $(2.72 \text{ and } 3.65)\times10^{22}\ \mathrm{cm}^{-3}$. On

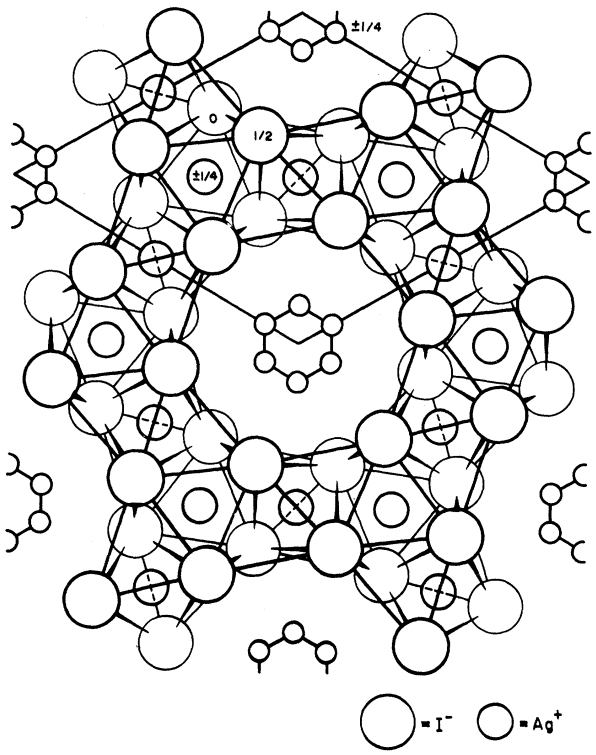

FIG. 2. Top view of the crystal structure in $PyAg_5I_6$ at -30°C. As temperature increases, Ag^+ ions increasingly move into the tetrahedra which are empty in this figure. (From Ref. 1.)

the other hand, the two-dimensional solid electrolyte *implies* lower concentrations of Ag^+ ions and equilibrium sites, simply because it must contain ions or atoms which *block* the motions of the current carriers in one of the crystal dimensions.

It can readily be shown[2] that the total volume of the crystal occupied by the pathways themselves is lower for the two-dimensional solid electrolyte than for any of the three-dimensional solid electrolytes, $(C_5H_5NH)Ag_5I_5$, $RbAg_4I_5$, $[(CH_3)_4N]_2Ag_{13}I_{15}$, whose structures[1,4,7] have been determined. Both the carrier concentrations and the conductivities of each of these three-dimensional solid electrolytes are higher than those of $Py_5Ag_{18}I_{23}$. This implies that those three-dimensional solid electrolytes that have lower conductivities than $Py_5Ag_{18}I_{23}$ will have lower carrier concentrations, lower volume fractions occupied by the conducting pathways, and probably more complex pathways.

Sodium β-alumina, a material which is also a two-dimensional solid electrolyte, does not attain a high conductivity until relatively high temperature; at 100°C, for example,[8] σ_1 is 0.077 $(\Omega\ \mathrm{cm})^{-1}$ [note that Whittingham and Huggins[9] report $\sigma_1 = 0.0382\ (\Omega\ \mathrm{cm}^{-1})$] ; for $Py_5Ag_{18}I_{23}$ it is[10] 0.05 $(\Omega\ \mathrm{cm})^{-1}$.

The results and comparisons given here demonstrate the high probability that three-dimensional pathways for diffusion of the ionic current carriers are most favorable for high-conductivity solid electrolytes. It is to be emphasized that simplicity and numerous interconnections of these pathways enhance the conductivity. {For example, compare the crystal structures of $RbAg_4I_5$[4] with those of $[(CH_3)_4N]_2Ag_{13}I_{15}$[9] and of the two compounds of pyridinium.}

Crystals of $Py_5Ag_{18}I_{23}$ were grown by G. P. Espinosa. Measurements of average specific conductivity were made by S. A. Wilber.

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[2]Details on the crystal-structure determination and measurements of conductivity and further discussion thereof are to be published.

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[5]It should be emphasized that in $Py_5Ag_{18}I_{23}$, as well as in all other AgI-based solid electrolytes for which accurate determinations have been made, the equilibrium distribution of Ag^+ ions over crystallographically nonequivalent sites is markedly nonuniform.

[6]These are the estimated values at 55°C. The lattice constants of $Py_5Ag_{18}I_{23}$ have not been measured at this temperature, but were assumed to increase by the same factor as those of $PyAg_5I_6$ which have been measured (Ref. 1). The 55°C concentrations are actually only about 1% lower than the room-temperature values.

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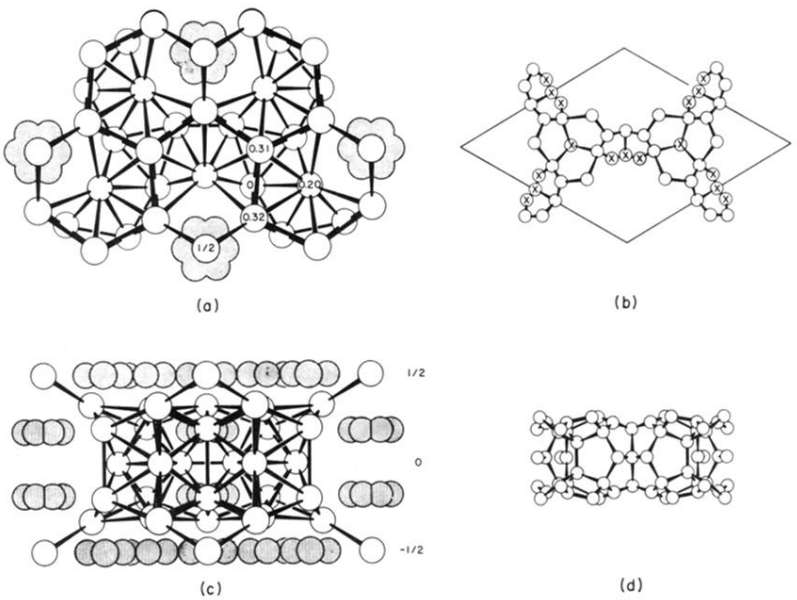
[10]Only $\langle\sigma\rangle$ of $Py_5Ag_{18}I_{23}$ was measured, from which $\sigma_1 = 1.5\langle\sigma\rangle$.



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