Hopping conductivity in lithium-exchanged pillared layered tin phosphate materials

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Abstract

Hopping conductivity in lithium-exchanged alumina pillared layered tin phosphate materials is analysed on the basis of the coupling model. The electrical conductivity is correlated with the lithium content and the basal distance of the pillared materials. Characteristic parameters such as dc and ac activation energies, and the attempt and coupling frequencies show a marked dependence on the basal distance and the lithium content. The migration entropy of the hopping process is greater for samples with higher Li contents and lower basal distances. The conductivity time correlation function has a stretched exponential (or KWW) shape, in which the coupling parameter decreases to a minimum value for the sample with the highest basal distance.

Keywords: Hopping conductivity; Tin phosphate; Layered structure; Pillared materials; Complex Correlated System (CCS)

1. Introduction

Pillared layered phosphates (PLP) are novel porous solids with attractive properties as absorbents [1–3] and catalysts [4,5]. In these materials, nanostructures of metal oxides “bridge” disorganized sheets of the layered phosphate, and consequently, they are usually poorly crystallized materials, although their pore-size distributions are quite narrow. Most of them present high exchange capacities, close to those of smectite clays. The presence of exchangeable cations makes possible the existence of ionic conductivity. In previous works [6,7], we reported the electrical properties of some alumina PLP. At low temperature (298–523 K) the conductivity is predominantly protonic due to the presence of zeolitic water. Above 523 K, the carrier is the exchangeable ion; the conductivity is reversible and the equivalent circuit is formed by two subcircuits, assigned to conduction in large pores and small pores (localised in the interlayer region).

Significant advances in order to establish correlation among the diffusing ions have been made in the last few years [8]. In general, complex correlated systems (CCS) are related to diffusion of ions in glasses or polymers in which the charge carriers show a strong interaction. Ion exchanged metal oxide PLP materials can be considered to be like CCS too, because the diffusing ions are interacting with each other and with the pillars. The time dependence and the dynamic properties of these compounds could be very

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1.- Preparation of the starting colloidal phosphate: \( \alpha\text{-Sn[NM}_{\text{4}}\text{H(PO}_{\text{4}}\text{)}_{\text{2}}\text{.}4\text{H}_{\text{2}}\text{O} \)

\[
\begin{align*}
\alpha\text{-Sn(HPO}_{\text{4}}\text{)}_{\text{2}}\text{.}2\text{H}_{\text{2}}\text{O} & \xrightarrow{\text{aq. suspension}} \alpha\text{-Sn(HNPrA)(PO}_{\text{4}}\text{)}_{\text{2}}\text{.}n\text{H}_{\text{2}}\text{O} & \xrightarrow{[\text{NM}_{\text{4}}\text{Cl}]_{\text{2}}} \alpha\text{-Sn[NM}_{\text{4}}\text{H(PO}_{\text{4}}\text{)}_{\text{2}}\text{.}4\text{H}_{\text{2}}\text{O} \\
\text{n-propylamine (nPrA)} & \xrightarrow{\text{2 hours, } 25^\circ\text{C}} & \text{1 day, } 25^\circ\text{C}
\end{align*}
\]

2.- Preparation of the pillaring solution

\[
\begin{align*}
0.2 \text{ M NaOH} & \xrightarrow{0.2 \text{ M AlCl}_{\text{3}}.6\text{H}_{\text{2}}\text{O}} \text{Flocculated material} & \text{HOAc} & \xrightarrow{\text{Pillaring solution}} \text{pH=4.2-4.3} \\
\text{OH}^-/\text{Al}^+ = 2.5 & & \text{OAc}^-/\text{Al}^+ = 2.1
\end{align*}
\]

3.- Intercalation and pillaring

\[
\begin{align*}
\alpha\text{-Sn[NM}_{\text{4}}\text{H(PO}_{\text{4}}\text{)}_{\text{2}}\text{.}4\text{H}_{\text{2}}\text{O} & \xrightarrow{\text{Pillaring solution}} \text{I l~tration} \\
\text{Calcination at } 400^\circ\text{C} & \xrightarrow{\text{Alumina-pillared tin phosphate}} \text{Ion exchange with } 0.1 \text{ M LiCl} \\
\text{Li-exchanged alumina-pillared tin phosphate} & \xrightarrow{\text{Scheme 1.}} \text{similar to those of glasses and polymers.}
\end{align*}
\]

The aim of the present work is to verify whether the electrical behaviour of different lithium-exchanged alumina pillared layered tin phosphate materials fit in a theoretical model. The coupling model and other related theories are considered.

2. Materials and experimental methods

2.1. Preparation of lithium-exchanged pillared layered tin phosphates

The pillared layered tin phosphate materials were prepared following the method described elsewhere [6]. Different aliquots of a buffered aluminium oligomer solution were contacted with agitation under reflux for one day, with a colloidal suspension of \( \alpha\text{-Sn[NM}_{\text{4}}\text{H(PO}_{\text{4}}\text{)}_{\text{2}}\text{.}4\text{H}_{\text{2}}\text{O} \), and then cooled at room temperature. The solids were filtered off, washed with water, dried in air, calcined for two hours at 673 K and analysed. Table 1 shows the composition and the interlayer distance of the studied samples. These materials present B.E.T. surface areas close to 200 m² g⁻¹ and are usually mesoporous solids with a small contribution of micropores. The alumina pillared materials were exposed to ammonia vapours and then fully ion-exchanged with a 0.1 molar LiCl solution. Scheme 1 shows the preparation procedure.

2.2. Physical measurements

All materials were characterised by XRD (Siemens D501 diffractometer, Cu Kα radiation, graphite monochromator), thermal analysis (Rigaku Thermoflex instrument, 10 K min⁻¹ as heating rate) and chemical analysis. Adsorption–desorption of N₂ was measured on a conventional volumetric appara-
Ac conductivity measurements were carried out on compact discs with ionically blocking gold electrodes using a Solartron 1255 frequency response analyser which was controlled by computer; the frequency range was 1 Hz to 1 MHz. The compact discs, 13 mm in diameter and 1 mm thick were prepared by pressing the powder material at 6 ton cm$^{-2}$. The experimental data were corrected by software and the influence of connecting cables and other parasitic capacitances was eliminated [9].

3. Results and discussion

When heated above 473 K, the original α-tin phosphate, α-Sn(HPO$_4$)$_2$$\cdot$H$_2$O, collapses, and is transformed to pyrophosphate, by condensation of P-OH groups of adjacent layers. The conductivity in the collapsed layered phosphates is attributed to the presence of mobile protons on the external surface [10]. On the other hand, when metal oxides are inserted within the interlayer region, the structure is much more disordered and remains open, at least up to 773 K, for ion exchange and adsorption. The presence of exchangeable cations gives rise to the appearance of ionic conductivity at high temperature. To study the electrical properties of ion-exchanged alumina pillared α-tin phosphate, four Li$^+$-exchanged pillared materials, with different chemical compositions and interlayer distances were selected (see Table 1). The corrected data of ac conductivity for the different materials were fitted by a non-linear least square method (NLLS) [11]. For all samples the equivalent circuit may be modeled by two subcircuits ($R_1$ and $R_2$) in parallel with a condenser. Both subcircuits consist of a constant phase element (CPE) associated in parallel with a resistor. The admittance of the constant phase element, expressed as $Y(i\omega)^n$, presents two $n$ values, close to 0.5 (for large pores) and 0.7 $\leq n \leq$ 1.0 (for small pores) [5].

In Fig. 1, the imaginary part of the complex electrical modulus is plotted against the normalized frequency. At low frequency, the relaxation may be associated with conduction in large pores ($R_1$) and at higher frequency, with conduction in small pores ($R_2$) [6]. This behaviour is general for all studied samples. Fig. 2 shows the variation of the normalized imaginary modulus in the high frequency region for the sample with the highest basal distance (sample H). This curve presents a stretched exponential shape, which is indicative of the existence of interactions among the exchangeable ions and the surface of pillars and adjacent layers, which occur in the interlayer region, where the majority of exchange sites are localised. The electrical conductivity of the Li-exchanged alumina pillared tin phosphate materials (Fig. 3) decreases with temperature up to 520 K and then increases gradually up to 773 K. This behaviour implies two different charge carriers, protons from
frequency independent in the low frequency region, and frequency dependent in the high frequency region. This frequency dispersion of the conductivity has been found in many complex condensed matter systems, in which the conductivity involves a hopping process of the charge carriers [12].

According to Almond and West [13] the ionic conductivity may typically be expressed (excluding electrode and intergranular effects) as:

$$\sigma'(\omega) = \sigma_{dc} + Y\omega^n,$$

where $\sigma_{dc}$ and $Y\omega^n$ are the dc and ac contributions respectively. $Y$ is a function of the temperature and $n$ varies between $0 < n < 1$ [14]. When the carrier concentration is thermally activated, the activation energy is composed of two terms: $E_a$, which is the activation energy for the mobile ion hopping process, and $E_c$ that for the mobile ion concentration [13]. The dc conductivity may then be expressed as:

$$\sigma_{dc} T = \sigma_0 \exp\left[\frac{(E_a + E_c)}{kT}\right]. \tag{1}$$

The experimental data fit this equation as can be seen in Fig. 5.

Recognizing that ion-exchanged-PLP materials are weak electrolytes, two distinctive carrier population are assumed to exist, "mobile" and "immobile" carriers. In the weak electrolyte model almost all carriers are bound at various traps and only those that are thermally excited contribute to the electrical conductivity [15].

In a random medium the current density resulting from a step function electric field excitation will not be constant. Firstly, the most mobile ions respond, leading to a higher current, just after the excitation. Later, these mobile ions may encounter high potential energy barriers and the ionic conductivity decreases up to a limit value. This means, in the frequency domain, that the conductivity becomes frequency independent in the low frequency region, and frequency dependent in the high frequency region. This frequency dispersion of the conductivity has been found in many complex condensed matter systems, in which the conductivity involves a hopping process of the charge carriers [12].

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Similarly, the ac contribution may be expressed as [12]:

\[ YT = \sigma_0 \exp \left[ \frac{E_a (1 - n) + E_c}{kT} \right]. \tag{2} \]

The experimental data for the four samples fit quite well to Eqs. (1) and (2). Plots for sample B are reported as an example in Fig. 6.

Table 2 lists the activation energies \( E_a \) and \( E_c \) for the four studied samples; \( E^*_a \) values representing the activation energy for an isolated hopping process (microscopic barrier energy [16]) are also included in Table 2 for comparison. \( E^*_a \) is related to \( E_a \) by the equation:

\[ E^*_a = (1 - n) E_a. \]

Both, \( E_a \) and \( E^*_a \) decrease with increasing basal distance \( (d_{001}) \) of the pillared materials, presenting a minimum value for the sample H. This behaviour can be attributed to a relaxation effect in CCS [17].

The empirical equation relating \( E_c \) with the Li\(^+\) concentration, \( C(\%) \), was found to be:

\[ E_c = 0.194 - 2.51 \times 10^{-5} C^{4.359} \]

(for \( C = 0 \), \( E_c \) has a maximum value of 0.194, which is very close to that of sample B with the minimum lithium content (2.20 g of Li per 1000 g of pillared phosphate)). Conversely to \( E_a \) and \( E^*_a \), \( E_c \) increases with the basal distance.

Assuming that the charge carriers are the same for dc and ac, the real ac conductivity may be expressed as:

\[ \sigma(\omega) = Y(\omega_p)^n, \]

\( \omega_p \) is the ionic hopping frequency which can be obtained directly from ac conductivity data, and may be expressed as an Arrhenius plot:

\[ \omega_p = \omega_0 \exp (-E_a/kT). \]

Here \( \omega_0 \) is the effective attempt frequency of the ion moving from its site to the nearest neighboring site, which is related to the lattice vibration frequency, \( \omega_0 \), by the following equation:

\[ \Delta S^m = k \sum \ln(\omega_c/\omega_0). \]

\( \Delta S^m \) is the migration entropy for the hopping process. In this equation, \( \omega_c \) and \( \omega_0 \) represent the frequencies of the hopping ion sitting at the bottom and the saddle point respectively [18]. \( \Delta S^m \) can be calculated using both the Meyer–Neldel [19] rule and the Dienes equation [19]. The Meyer–Neldel plot for the Li-exchanged alumina pillared tin phosphate materials is shown in Fig. 7. The linear dependence of the logarithm conductivity prefactor upon activation energy suggests that all samples studied belong to the same family of compounds. The characteristic temperature, \( T_d \), obtained from this plot (520 K) is the same as that deduced from TG curves. At this temperature, the zeolitic water in the pillared material is completely lost [6]. With this \( T_d \) value, \( \Delta S^m \) is calculated from the Dienes expression. \( \omega_0, \Delta S^m \), and \( \omega_0 \) values are listed in Table 2. In comparing N, S and B

<table>
<thead>
<tr>
<th>Sample</th>
<th>( E_a ) (eV)</th>
<th>( E^*_a ) (eV)</th>
<th>( E_c ) (eV)</th>
<th>( \omega_c ) (rd s(^{-1}))</th>
<th>( \omega_0 ) (rd s(^{-1}))</th>
<th>( \omega_p ) (s)</th>
<th>( \Delta S^m/k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>1.12</td>
<td>0.069</td>
<td>0.050</td>
<td>3.15 \times 10^{12}</td>
<td>6.49 \times 10^{11}</td>
<td>4.66 \times 10^{-15}</td>
<td>1.58</td>
</tr>
<tr>
<td>S</td>
<td>0.91</td>
<td>0.058</td>
<td>0.120</td>
<td>1.46 \times 10^{9}</td>
<td>3.94 \times 10^{8}</td>
<td>3.85 \times 10^{-12}</td>
<td>1.31</td>
</tr>
<tr>
<td>H</td>
<td>0.64</td>
<td>0.051</td>
<td>0.180</td>
<td>3.42 \times 10^{6}</td>
<td>1.08 \times 10^{6}</td>
<td>7.27 \times 10^{-9}</td>
<td>1.15</td>
</tr>
<tr>
<td>B</td>
<td>1.00</td>
<td>0.055</td>
<td>0.190</td>
<td>5.23 \times 10^{8}</td>
<td>1.49 \times 10^{8}</td>
<td>7.03 \times 10^{-9}</td>
<td>1.25</td>
</tr>
</tbody>
</table>
or N, S and H samples, one finds higher $\Delta S^m$ values for samples with higher Li contents and lower basal distances, where the hopping probability should be greater. Comparison of the H and B samples appears to indicate that the basal distance has a greater influence on $\Delta S^m$ than the Li$^+$ content, since an increment of the basal distance of 0.8 Å against an increment of the Li$^+$ content of more than 50% lead to a reduction of the $\Delta S^m$ value of 0.1 units.

In PLP the interlayer mobile ion interacts with each other ion and with the pillars, so that the relaxation is that of a complex correlated system. The coupling model is based on the fact that the ion motion is slowed down by interactions with other ions. In this Model, the hopping frequency, $\omega_0$, corresponding to the motion of a single ion can only be maintained for short times. After a characteristic time, $\omega_0^{-1}$, which is temperature independent, the interactions between the ions slow down the hopping rate, which adopts a time-dependent form:

$$\omega(t) = \omega_0 (\omega_c t)^{-n}.$$ 

In CCS, if the elementary diffusion process is characterized by a jump from one site to a nearest neighboring site, the cooperative relaxation can be described as a continuous-time random walk (CTRW) process with a waiting-time distribution:

$$\psi(t) = -d\phi/dt$$
$$d\phi/dt = -\omega_p \phi \quad \omega_c t < 1,$$

$$d\phi/dt = -\omega(t) \phi \quad \omega_c t > 1.$$ 

The normalized conductivity time correlation function $\phi(t)$ can be expressed as the Kohlrausch-Williams-Watts (KWW) [21,22], or “stretched exponential” function. It is well represented by

$$\phi(t) = \exp\left[-\frac{(t/t_p^*)^{\beta}}{\beta}ight] \quad \omega_c t < 1,$$
$$\beta = 1 - n,$$

where $t_p^*$ is an effective relaxation time which is found to vary with temperature according to the Arrhenius law:

$$t_p^* = \tau_\infty^* \exp\left(\frac{E_a}{kT}\right),$$

where

$$\tau_\infty^* = \left[\beta \omega_0 \omega_0^{-1}\right]^{1/\beta}$$

and

$$\phi(t) = \exp\left[-\frac{(t/t_p)}{\beta}\right] \quad \omega_c t > 1.$$ 

It can be seen in Table 2, that the coupling time increases with basal distance of the material. In CCS, the relaxation rate of an ion is independent up to the time $t_c$, after which the rates are correlated by ion-ion interactions. Fig. 8 shows the variation of the normalized conductivity time correlation function for sample S. The longitudinal dimension of the pores increases with the basal distance and therefore, the normalized conductivity time correlation function for the sample S at different temperatures: (●) 650 K, (○) 700 K, (+) 775 K.
ion has additional free space for motion. Consequently, one may expect that the correlation time for interaction with other ions and the pillars will increase with increasing basal distance.

4. Conclusions

Alumina pillared layered tin phosphates are porous solids with relatively high cation exchange capacity and electrical properties similar to those of glasses and polymers. The hopping conductivity data for lithium are well described by a coupling model.

The electrical conductivity presents a marked dependence upon the lithium content. The activation energies, attempt frequency, and migration entropy decrease with increasing basal distance, due to a lower interaction between diffusing ions themselves and with the pillars in larger pores. The decay function exhibits a stretched exponential shape and its coupling parameter also decreases with the basal distance.

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References