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Probing the mobility of lithium in LISICON: Li^+/H^+ exchange studies in Li_2ZnGeO_4 and $Li_{2+2x}Zn_{1-x}GeO_4$

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We investigated Li^+/H^+ exchange in the lithium ion conductors (LISICONS) [$Li_{2+2x}Zn_{1-x}GeO_4$; $x = 0.5$ (I) and $x = 0.75$ (II)] and their parent, γ-Li_2ZnGeO_4. Facile exchange of approximately $2x$ lithium ions per formula unit occurs with both the LISICONS in dilute acetic acid, while the parent material does not exhibit an obvious Li^+/H^+ exchange under the same conditions. The results can be understood in terms of lithium ion distribution in the crystal structures: the parent Li_2ZnGeO_4, where all the lithium ions form part of the tetrahedral framework structure, does not exhibit a ready Li^+/H^+ exchange; LISICONS, where lithium ions are distributed between framework (tetrahedral) and nonframework sites, undergo a facile Li^+/H^+ exchange of the nonframework site lithium ions. Accordingly, Li^+/H^+ exchange in dilute aqueous acetic acid provides a convenient probe to distinguish between the mobile and the immobile lithium ions in lithium ion conductors.

Introduction

Facile ion exchange is one of the manifestations of high mobility of lithium in metal oxides.[1] All ionic conductors are good ion exchangers although the converse may not be true, because ion exchange is a necessary but not sufficient condition for fast ion conduction.[2] The implication is that ion exchange could serve as a convenient probe for investigation of lithium ion mobility in solids, although quantitative prediction of ionic conductivity/diffusion coefficients may not be easy on the basis of ion exchange studies.

A strong correlation between lithium ion exchange on the one hand and lithium ion mobility under redox conditions has been established in certain anion close packed oxide structures. For example, it is known that oxides of the α-$NaFeO_2$ structure type (such as α-$LiAlO_2$ and α-$NaCrO_2$) undergo facile Li^+/H^+ exchange and Na^+/Li^+ exchange respectively,[3,4] while $LiCoO_2$ with the same structure undergoes redox deinsertion/insertion of lithium, making it the choice positive electrode material for lithium battery.[5] Interestingly, β-$LiAlO_2$ and γ-$LiAlO_2$, which possess structures based on a distorted hcp anion array wherein lithium and aluminium ions occupy tetrahedral sites, do not exhibit Li^+/H^+ exchange.[3]

LISICONS, $Li_{2+2x}Zn_{1-x}GeO_4$ ($-0.36 \leqslant x \leqslant 0.87$),[6,7] are a well-known family of lithium ion conductors exhibiting high lithium ion conduction ($\sigma \sim 0.13$ S cm^{-1} at 300 °C), which are derived from the parent γ-Li_2ZnGeO_4, by $Zn^{2+} \rightarrow 2Li^+$ substitution. Both the parent and the LISICONS possess structures closely related to β-/γ-$LiAlO_2$. The structure of Li_2ZnGeO_4 consists of a distorted hcp anion array wherein Li, Zn and Ge ions occupy one-half of the tetrahedral sites (Fig. 1). LISICONS, $Li_{2+2x}Zn_{1-x}GeO_4$ ($x = 0.50$ and $x = 0.75$), adopt essentially the same structure[6–8] where the substitution $Zn^{2+} \rightarrow 2Li^+$ introduces additional (interstitial) lithium ions into the structure, which occupy octahedral sites (Fig. 1). The actual structure of LISICONS is complex, consisting of lithium-stoichiometric regions and lithium-rich defect clusters,[9] the complexity arising from the inherent instability of the materials. It is believed that the high conductivity of LISICONS arises from the interstitial site lithium ions. On the basis of the structure and ionic conductivity data of Li_2ZnGeO_4 and LISICONS, we considered that Li^+/H^+ exchange would provide a convenient probe to distinguish between the mobile (supernumerary or interstitial) and the immobile (framework) lithium ions in these materials. To our knowledge, the Li^+/H^+ exchange in Li_2ZnGeO_4 or its LISICON derivatives has not been reported in the literature. Accordingly, we investigated the Li^+/H^+ exchange in the two well-known LISICON compositions, $Li_3Zn_{0.5}GeO_4$ and $Li_{3.5}Zn_{0.25}GeO_4$, together with the parent material, Li_2ZnGeO_4.

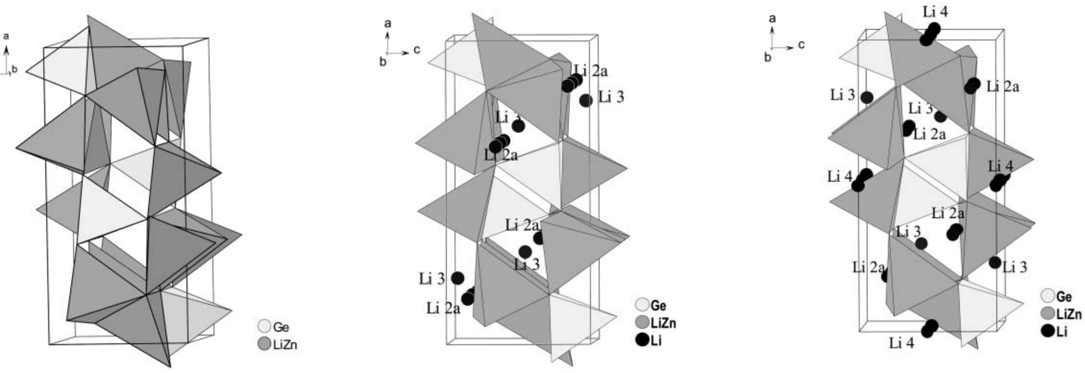

Fig. 1 Crystal structures of (left) γ-Li_2ZnGeO_4, (middle) LISICON I, and (right) LISICON II. Extraframework lithium ions are shown in the structures of I and II.

Experimental

$Li_{2+2x}Zn_{1-x}GeO_4$ ($x = 0, 0.5, 0.75$) were prepared from stoichiometric mixtures of Li_2CO_3, ZnO (predried at 600 °C for 24 h) and GeO_2. While the synthesis of Li_2ZnGeO_4 was done at 1100 °C, the syntheses of lithium rich $x = 0.5$ and $x = 0.75$ members were carried out at a lower temperature (810 °C) for 24 h. Li^+/H^+ exchange was investigated in 0.02–0.05 M acetic acid for 15 h for Li_2ZnGeO_4 and in 0.02 M acetic acid for 12–15 h for $x = 0.5$ and $x = 0.75$ members. The acid exchanged products were washed with distilled water and dried in air. All the samples were stored over anhydrous $CaCl_2$ in a desiccator.

The samples were characterized by powder X-ray diffraction (Siemens D5005 X-ray diffractometer, CuK_α radiation), IR spectroscopy (Perkin Elmer 1000FT spectrometer), TGA (Cahn TG-131 system) and SEM/EDX (JEOL JSM 5600 LV Scanning Electron Microscope). The lithium contents of the samples were determined by flame photometry.

Results and discussion

Powder XRD patterns (Fig. 2) showed the formation of single-phase Li_2ZnGeO_4 and $Li_{3.0}Zn_{0.5}GeO_4$(I) and $Li_{3.5}Zn_{0.25}GeO_4$(II). The lattice parameters (Table 1) derived from the powder XRD data using least squares refinement are in agreement with values reported for these phases in the literature (JCPDS 38-1082, 32-0608).[8] Flame photometric analyses of the lithium contents of the samples are consistent with the nominal compositions (Table 2).

We investigated Li^+/H^+ exchange of Li_2ZnGeO_4 and its LISICON derivatives I and II in aqueous acids and found that 0.02–0.05 M acetic acid is the appropriate medium to carry out the exchange, without leaching other cations. After Li^+/H^+ exchange, the dry products were analyzed for lithium content and the results are given in Table 2. The results show that while no Li^+/H^+ exchange occurs with Li_2ZnGeO_4 even after prolonged treatment with 0.05 M acetic acid, considerable exchange occurs with LISICON oxides. The actual lithium contents of the two LISICON oxides I and II after acid treatment are close to the ideal compositions, $Li_2Zn_{0.5}GeO(OH)$ and $Li_2Zn_{0.25}GeO_{2.5}(OH)_{1.5}$ (the actual compositions are given in Table 2). The results indicate that approximately $2x$ lithium ions per formula unit are exchanged from the LISICONS I ($x = 0.5$) and II ($x = 0.75$) ($Li_{2+2x}Zn_{1-x}GeO_4$).

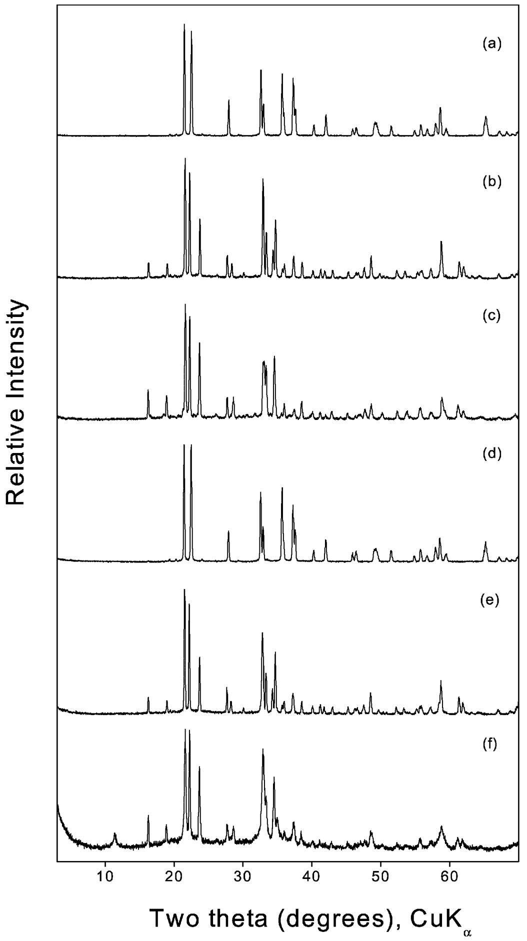

Fig. 2 Powder XRD patterns of (a) Li_2ZnGeO_4, (b) LISICON I, and (c) LISICON II. In (d), (e) and (f), we give the XRD patterns of (a), (b) and (c) after acid treatment.

Powder XRD patterns of the acid exchanged products (Fig. 2) show that there is very little change in the lattice parameters of Li_2ZnGeO_4 after acid treatment, and this is consistent with the lithium content analysis that showed no Li^+/H^+ exchange in

Table 1 Lattice parameters of $Li_{2+2x}Zn_{1-x}GeO_4$ before and after Li^+/H^+ exchange

		Lattice parameters			
Composition	Space group	a/Å	b/Å	c/Å	β/°
Li_2ZnGeO_4	$P2_1/n$	6.361(1)	5.431(1)	5.027(1)	90.07(2)
$Li_{3.0}Zn_{0.5}GeO_4$	*Pnma*	6.283(1)	10.861(1)	5.161(1)	—
$Li_{3.5}Zn_{0.25}GeO_4$	*Pnma*	6.256(2)	10.859(1)	5.152(1)	—
Li_2ZnGeO_4[a]	$P2_1/n$	6.363(1)	5.438(1)	5.030(1)	90.07(2)
$Li_2Zn_{0.5}GeO_3(OH)$[b]	—	6.308(1)	10.866(2)	5.167(1)	—
$Li_2Zn_{0.25}GeO_{2.5}(OH)_{1.5}$[c]	—	12.491(3)	10.870(2)	10.375(2)	—

[a] Product obtained after treatment of Li_2ZnGeO_4 in 0.05 N CH_3COOH for 15 h. [b] Product obtained after treatment of $Li_3Zn_{0.5}GeO_4$ in 0.02 N CH_3COOH for 12 h. [c] Product obtained after treatment of $Li_{3.5}Zn_{0.25}GeO_4$ in 0.02 N CH_3COOH for 12 h.

Table 2 Chemical compositions of $Li_{2+2x}Zn_{1-x}GeO_4$ and their acid treated derivatives based on lithium content

	% Li		% Li		
Nominal composition	Found	Calculated	Found	Calculated[a]	Composition after acid exchange
Li_2ZnGeO_4	6.40	6.43	6.38	6.43	$Li_{1.98}ZnGeO_{3.98}(OH)_{0.02}$
$Li_3Zn_{0.5}GeO_4$	10.20	10.95	7.43	7.53	$Li_{1.97}Zn_{0.5}GeO_{2.97}(OH)_{1.03}$
$Li_{3.5}Zn_{0.25}GeO_4$	13.65	13.71	8.16	8.24	$Li_{1.98}Zn_{0.25}GeO_{2.48}(OH)_{1.52}$

[a] Calculated for the ideal compositions, Li_2ZnGeO_4, $Li_2Zn_{0.5}GeO_3(OH)$ and $Li_2Zn_{0.25}GeO_{2.5}(OH)_{1.5}$.

these materials. The XRD pattern of the acid exchanged product of I largely resembles that of the parent with a slight increase in the lattice parameters (Table 3). The pattern of the acid exchanged product of II, which shows an additional low angle reflection ($d \sim 7.5$ Å), could be indexed on a LISICON type cell with doubling of the a and c parameters (Table 4).

Table 3 Powder XRD data for LISICON I after acid treatment

hkl	d_{obs}/Å	$d_{cal}{}^{a}$/Å	I_{obs}
020	5.435	5.433	16
011	4.672	4.666	14
120	4.122	4.116	100
101	4.001	3.997	89
111	3.749	3.751	48
121	3.222	3.219	24
200	3.155	3.154	14
031	2.966	2.966	8
220	2.725	2.727	66
131	2.683	2.684	35
211	2.612	2.613	24
002	2.583	2.583	42
140	2.492	2.495	14
221	2.411	2.412	20
022	2.333	2.333	14
141	2.248	2.246	10
122	2.186	2.188	11
231	2.160	2.160	9
032	2.101	2.103	9
051	2.002	2.103	9
320	1.961	1.961	8
241	1.911	1.912	11
222	1.874	1.875	20
232	1.750	1.750	9
331	1.716	1.715	8
340	1.663	1.662	8
113	1.644	1.642	10
152	1.609	1.608	9
260	1.571	1.570	17
133	1.510	1.510	17
213	1.497	1.497	13
233	1.395	1.395	7

[a] $a = 6.308(1)$, $b = 10.866(2)$, $c = 5.167(1)$ Å.

Table 4 Powder XRD data for LISICON II after acid treatment

hkl	d_{obs}/Å	$d_{cal}{}^{a}$/Å	I_{obs}
011	7.546	7.505	21
020	5.434	5.435	35
012	4.696	4.681	28
220	4.103	4.100	100
202	3.994	3.990	100
212	3.751	3.746	71
222	3.219	3.216	28
400	3.119	3.122	25
040	2.718	2.717	85
232	2.683	2.682	49
412	2.596	2.598	64
141	2.567	2.572	33
240	2.495	2.492	22
042	2.407	2.407	29
214	2.340	2.339	23
242	2.247	2.246	16
224	2.192	2.192	17
432	2.153	2.152	14
034	2.108	2.109	15
052	2.002	2.005	14
602	1.929	1.932	14
442	1.906	1.906	17
424	1.873	1.873	22
060	1.812	1.811	13
434	1.747	1.747	15
016	1.708	1.707	13
262	1.648	1.649	17
614	1.605	1.605	16
460	1.567	1.567	27
236	1.513	1.514	19
416	1.498	1.498	17
822	1.442	1.441	12
644	1.394	1.393	11

[a] $a = 12.491(3)$, $b = 10.870(2)$, $c = 10.375(2)$ Å.

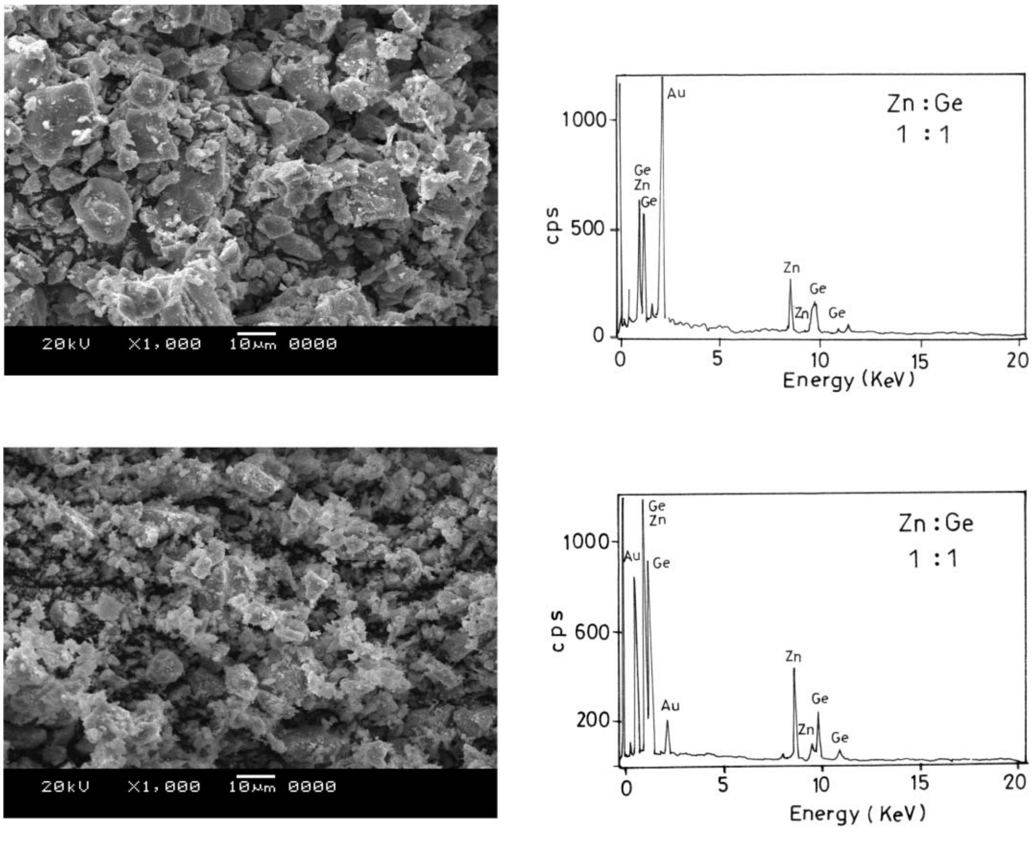

Fig. 3 (Left) SEM images of Li_2ZnGeO_4 before (top) and after (bottom) acid treatment. The corresponding EDX spectra are shown on the right.

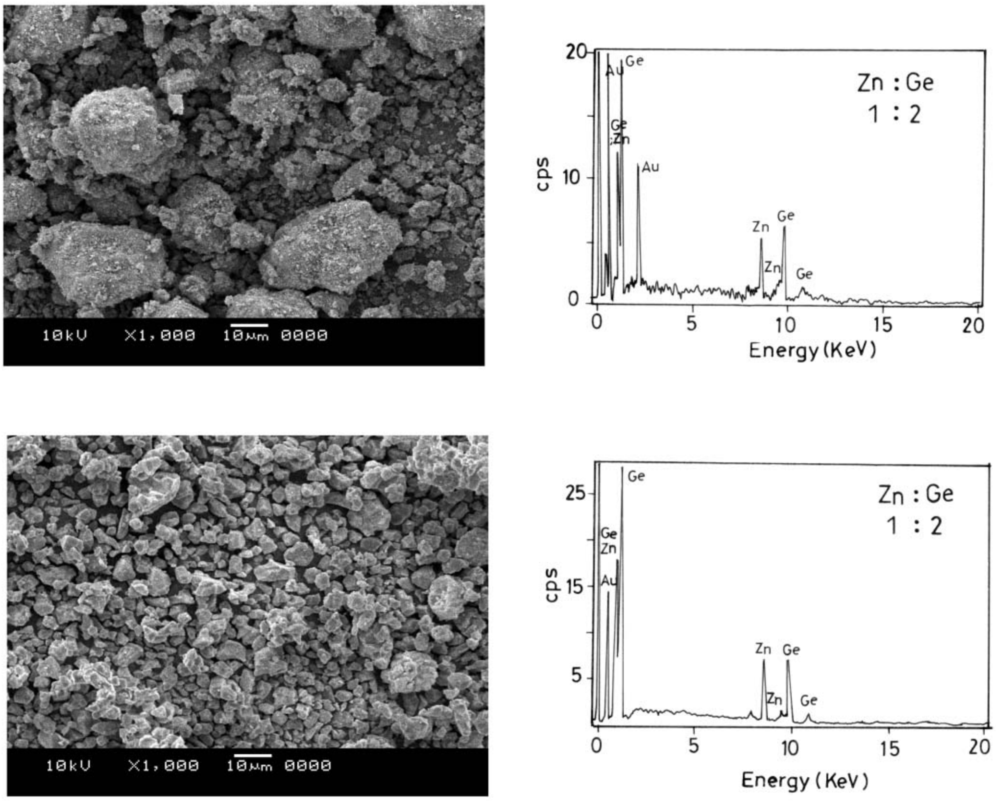

Fig. 4 (Left) SEM images of LISICON I before (top) and after (bottom) acid treatment. The corresponding EDX spectra are shown on the right.

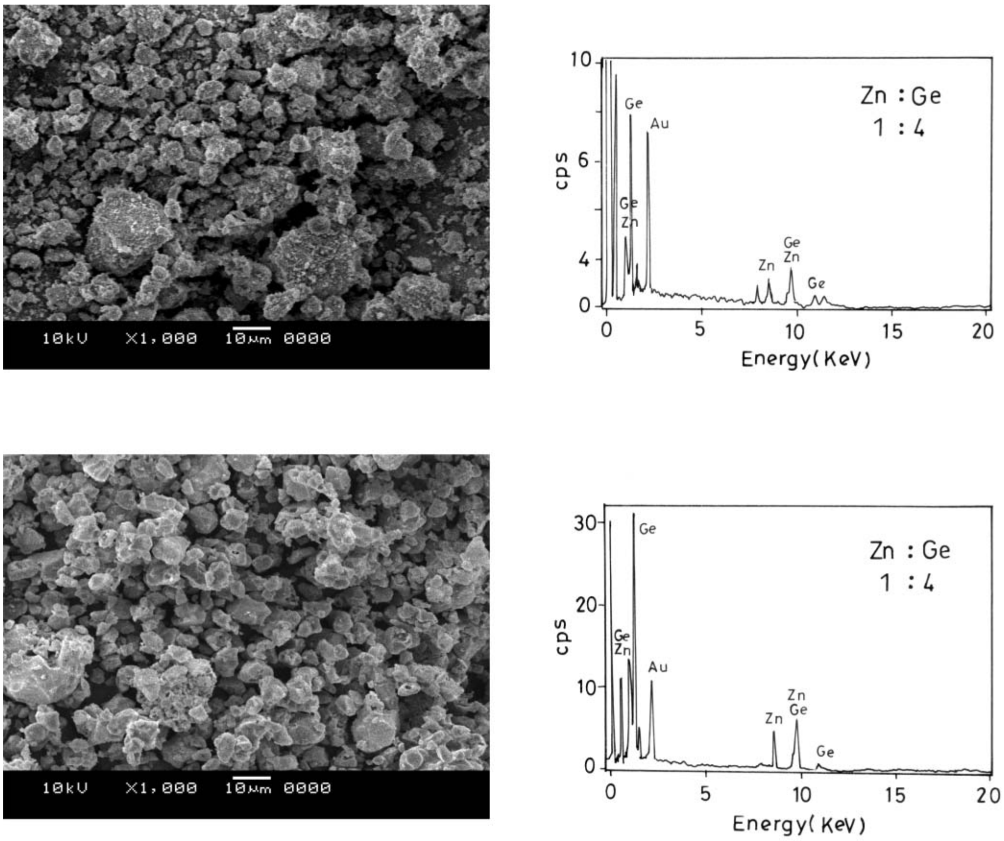

Fig. 5 (Left) SEM images of LISICON II before (top) and after (bottom) acid treatment. The corresponding EDX spectra are shown on the right.

We have also characterized the acid-exchanged materials and their parents by SEM/EDX. The results show that essentially there is no change in the composition and morphology of Li_2ZnGeO_4 after acid treatment (Fig. 3). On the other hand, there is a definite change in the morphology of I and II after acid treatment (Figs. 4 and 5). The EDX analyses however show that in all the cases the ratio of Zn : Ge remains intact after acid treatment.

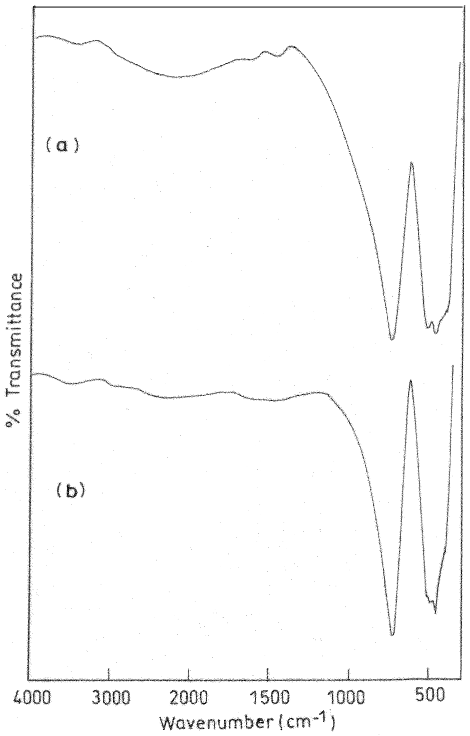

Fig. 6 IR spectra of γ-Li_2ZnGeO_4 before (a) and after (b) acid treatment.

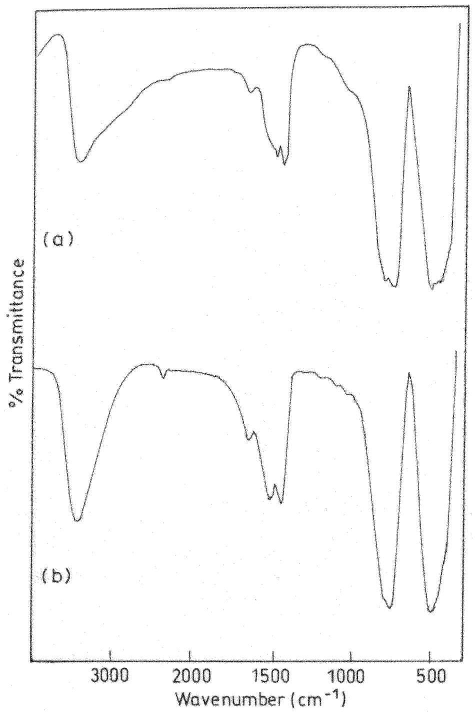

Fig. 7 IR spectra of LISICON I (a) and LISICON II (b) after acid treatment. The doublet around 1500 cm^{-1} could be due to surface carbonate species.

The IR spectra of Li_2ZnGeO_4 before and after acid treatment essentially remain unchanged (Fig. 6), consistent with other investigations. The spectra mainly consist of strong bands centered around 725, 500 and 460 cm^{-1}, which are respectively due to GeO_4, ZnO_4 and LiO_4 tetrahedra respectively.[10] On the other hand, the IR spectra of I and II show considerable changes after acid treatment (Fig. 7). While the sharp bands centered around 750 and 500 cm^{-1} more or less remain as in the parent materials, new strong/sharp bands appear in the 3400–3450 cm^{-1} and 1500–1650 cm^{-1} region, which indicate the presence of hydroxy groups arising from Li^+/H^+ exchange.

The Li^+/H^+ exchange results of Li_2ZnGeO_4 and the LISICONS could be rationalized on the basis of their crystal structures. γ-Li_2ZnGeO_4, which is isostructural with γ-Li_3PO_4,[11] consists of an anion array that is intermediate between hcp and tetragonal packing, where Li, Zn and Ge occupy one-half of the tetrahedral sites (Fig. 1). The Li^+ and Zn^{2+} are distributed over two sets of tetrahedral sites which share common edges. The GeO_4 tetrahedra are isolated, sharing corners with (Li/ZnO_4) tetrahedra. Absence of Li^+/H^+ exchange in γ-Li_2ZnGeO_4 is consistent with the tetrahedral coordination of Li^+ in this material. The interlinking of tetrahedra in the structure is such that it does not provide a continuously connected pathway for Li^+ migration. Accordingly, this material does not exhibit Li^+/H^+ exchange in dilute acetic acid and also it is a poor lithium ion conductor.[7]

The Li^+/H^+ exchange behaviour of LISICONS is different, however. Both the LISICONS I and II readily exchange approximately 1.0 and 1.5 Li^+ per formula unit. Formation of I and II from γ-Li_2ZnGeO_4, involving $Zn^{2+} \rightarrow 2\ Li^+$ substitution, suggests replacement of Zn^{2+} by Li^+ at the tetrahedral sites, with the additional Li^+ going into interstitial/octahedral sites. A neutron diffraction study[8] has shown that the cation distribution in the LISICON structures is not so straightforward. For LISICON I, part of the supernumerary lithium goes into a new interstitial site [Li(3)]. This interstitial site lithium displaces some Li^+ from site (2) to a new tetrahedral site (2a). A similar distribution of lithium occurs with LISICON II as well, wherein there is yet another lithium site [Li(4)] with small occupancy. The overall lithium distributions for both the LISICONS I and II are given in Table 5.

If we consider that Li(2a) and Li(3) only are exchanged in LISICON I during the acid treatment, the composition of the solid after acid treatment would be $Li_{2.15}Zn_{0.5}GeO_4H_x$. Similarly if we assume that Li(2a), Li(3) and Li(4) in LISICON II are exchanged during the acid treatment, the composition of the acid-treated material would be $Li_{2.28}Zn_{0.25}GeO_4H_y$. These compositions compare favourably with the actual compositions of the acid treated materials based on lithium content analysis (Table 2). Considering the limitations of lithium analysis by flame photometry as well as the uncertainties in the composition/distribution of lithium obtained from the neutron diffraction study and also the differences arising from

Table 5 Distribution of lithium in various crystallographic sites in the LISICONS I and II (after ref. 8)

LISICON I $Li_3Zn_{0.5}GeO_4$ ($Z = 4$)[a]

Lithium site	Occupancy	Lithium content
Li(1) at 4c	0.89 × 4	3.56
Li(2) at 8d	0.63 × 8	5.04
Li(2a) at 8d	0.17 × 8	1.36
Li(3) at 4c	0.27 × 4	1.08

Total lithium content per unit cell = 11.04

LISICON II $Li_{3.5}Zn_{0.25}GeO_4$ ($Z = 4$)[a]

Lithium site	Occupancy	Lithium content
Li(1) at 4c	0.92 × 4	3.68
Li(2) at 8d	0.68 × 8	5.44
Li(2a) at 8d	0.24 × 8	1.92
Li(3) at 4c	0.34 × 4	1.36
Li(4) at 4b	0.06 × 4	0.24

Total lithium content per unit cell = 12.64

[a] Space group: *Pnma*.

sample preparation/history, we believe the agreement between the expected and the actual lithium contents of the acid exchanged LISICONS should be regarded as satisfactory. Accordingly, the Li^+/H^+ exchange studies suggest that the Li^+ ions at nonideal/nonframework sites in the LISICONS are exchanged readily, while the lithium ions at the framework sites of the parent Li_2ZnGeO_4 structure remain intact. We are led to the natural conclusion that it is the exchangeable Li^+ in the LISICONS that contributes to the high ionic conductivity of these materials. The ion exchange studies described herein therefore provide a convenient probe to distinguish between the mobile and the immobile lithium ions in LISICONS.

Conclusions

We have described Li^+/H^+ ion exchanges studies of LISICONS and their parent oxide, Li_2ZnGeO_4. While the parent oxide does not undergo obvious Li^+/H^+ exchange in dilute acetic acid, considerable exchange of lithium occurs with the LISICONS. Quantitative estimation of the lithium contents of the acid-exchanged LISICONS reveals that the lithium ions occupying nonframework/interstitial sites are most likely exchanged during the acid treatment. The investigations suggest that Li^+/H^+ exchange could provide a convenient probe to distinguish between the mobile and the immobile lithium ions in lithium-ion conductors.

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