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Conventional lithium-ion batteries provide exceptionally high energy densities, making them the most popular option for mobile/portable applications. Nevertheless, safety issues and limitations on the operating voltages associated with the use of liquid electrolytes as anionic media for Li-ion diffusion between the electrodes, have led to the proposed introduction of all-solid-state batteries, where this liquid electrolyte is replaced by a Li-ion solid-state conductor. The use of solid-state electrolytes would allow access to higher operating voltages and could address many safety concerns. There are several candidate systems as solid-state electrolytes, with four families being the most widely studied: the air stable NASICON-like LiMM\(^{+}\)(PO\(_4\))\(_3\) structures, lithium containing garnet materials with ionic conductivity up to 1.3 mS cm\(^{-1}\), Li\(_{2}\)\(_{3}\)La\(_{2}\)\(_{3}\)Li\(_{4}\)TiO\(_{12}\) perovskites in the same range of conductivities, and the most recent thio-LISICON Li\(_{10}\)Ge\(_{2}\)S\(_{12}\) materials with conductivities topping the 10 mS cm\(^{-1}\) matching those of liquid electrolytes. However, despite achieving ionic conductivities comparable with those of liquid electrolytes, different drawbacks – such as instability at low voltages or large grain-boundary resistances, have hampered their full implementation. Thus, the search for new candidate materials remains a challenge for the realization of next generation of Li-ion batteries.

The structure of the Li\(_{6}\)Hf\(_{2}\)O\(_{7}\) shown in Figure 1 contains Li\(^+\) ions in 5-fold oxygen coordination in a square pyramid geometry and Hf\(^{4+}\) ions octahedrally coordinated by oxide. The lithium ions form a pair of chains through the structure. This monoclinic phase can be achieved by introducing interstitial lithium ions, the structural characterization of these materials has been examined and showed good performance for CO\(_2\) gas capture extending interest in this material beyond its ability as an ionic conductor.

We report here the microwave-assisted synthesis of the Li\(_{6}\)Hf\(_{2}\)O\(_{7}\) material, its aliovalent doping with Li\(^{+}\) and Y\(^{3+}\) ions to introduce interstitial lithium ions, the structural characterization of these materials and the influence of this doping on the ionic conductivity of these compounds.

**Experimental**

**Synthetic procedures.**—All reagents were used as supplied: LiOH·H\(_2\)O (98%) from Sigma-Aldrich and H\(_2\)O\(_2\) (99.99%), In\(_2\)O\(_3\) (99.997%) and Y\(_2\)O\(_3\) (99.9%) from Alfa Aesar.

Figure 1. Crystal structure of the Li\(_{6}\)Hf\(_{2}\)O\(_{7}\) material with C2/c space group of symmetry. Li\(^+\) ions are shown in green; O\(^-\) anions are shown in red and Hf\(^{4+}\) are shown in blue with their octahedral coordination environment explicitly shown.
For the microwave-assisted solid-state synthesis of the In- and Y-doped \( \text{Li}_x\text{Hf}_2\text{O}_7 \) materials, stoichiometric amounts of reagents were mixed and ball milled for 20 minutes at 20 Hz with stainless steel milling media. The resulting fine powder was pelletized at 3 tonnes under uniaxial pressure. The pellet material was heated at 700°C for 6 hours in a 2.45 GHz CEM Phoenix hybrid microwave furnace for the decomposition of the precursor materials. Subsequently, the material was reground and pelletled for a second heat-treatment carried out in air at 850°C for 4 hours in the same microwave furnace with a low heating rate of 2°C min\(^{-1}\) to reduce lithium vaporization. For higher doping levels of \( x \geq 0.10 \) an additional heat-treatment of 850°C for 4 hours was used to increase sample purity.

**Structural characterization.—** The purity and crystal structures of these samples was assessed using powder X-ray diffraction. A PANalytical X’Pert PRO Diffractometer was used for this purpose using Cu-Kα radiation in the 20 range 15–60° and a step size of 0.016°. These data were analyzed by Rietveld refinement with the Generalized Structure Analysis System (GSAS), along with the graphical user interface EXPGUIT.22

**Scanning electron microscopy and energy-dispersive X-ray spectroscopy.—** Particle size and morphology were examined using scanning electron microscopy (SEM) images acquired with a Philips XL30 ESEM microscope equipped with an Oxford Instruments Energy 250 energy dispersive spectrometer. Samples were ground and a tiny amount of the fine powder was deposited over a carbon-taped sample holder and gold-coated prior to analysis. Copper tape was employed as an EDX calibration standard and the voltage of the incident beam was 20 keV.

**Electrochemical impedance spectroscopy.—** Transport measurements were performed on a Solartron 1260 Impedance Analyzer using an ac rms voltage of 200 mV in the frequency range of 1–10\(^6\) Hz and a temperature range between RT and 424°C in 50°C intervals. The as-synthesized powders were cold-pressed under uniaxial pressure at 3 tons and the resultant pellets were heated for 4 hours at 850°C, obtaining 1–2 mm thick pellets with a diameter of 10 mm. Platinum electrodes were connected using a suspension of ca. 1 μm platinum particles on opposing faces of the pellet.

**Results and Discussion**

**Synthesis and structural characterization.—** In order to create Li non-stoichiometry on the material, the substitution of \( \text{Hf}^{4+} \) ion with trivalent ions was undertaken, with the anticipation that charge balance would be maintained by the incorporation of additional Li\(^+\) into the structure. Of the various trivalent ions in the periodic table, \( \text{In}^{3+} \) and \( \text{Y}^{3+} \) were the most suitable ions to dope the \( \text{Li}_x\text{Hf}_2\text{O}_7 \) due to their relatively close ionic radius to \( \text{Hf}^{4+} \) (\( \text{In}^{3+} = 0.80 \) Å, \( \text{Y}^{3+} = 0.90 \) Å and \( \text{Hf}^{4+} = 0.71 \) Å)30 together with the redox stability of the ions, required for any solid-state electrolyte for lithium-ion battery applications.

Compositions from the series’ \( \text{Li}_{6+x}\text{Hf}_2\text{In}_x\text{O}_{7} \) and \( \text{Li}_{6+x}\text{Hf}_2\text{Y}_x\text{O}_{7} \) were synthesized by a novel microwave-assisted solid-state route we have developed previously for the synthesis of other solid-state electrolyte materials for lithium-ion batteries.34 The use of microwave radiation in solid-state synthesis has been demonstrated as an energy efficient synthetic route which enables the use of lower temperatures and shorter times compared with conventional solid-state synthetic routes.35 Our synthesis is facilitated by the presence of starting materials, such as the LiOH precursor,26 that strongly couple with microwaves and with materials with high dielectric constants such as the \( \text{HfO}_2 \) that can effectively couple with microwave radiations at high temperatures, in a similar way to the \( \text{ZrO}_2 \) precursor.37,38

Undoped \( \text{Li}_6\text{Hf}_2\text{O}_7 \) and doped compounds up to \( x = 0.05 \) were obtained as single phase samples at a temperature of 850°C. This required only four hours for the synthesis compared with several days required by conventional methods previously reported.20 Due to the dominance of the diffraction profile by the \( \text{Hf}^{4+} \) cations and the low symmetry of the structure the atomic coordinates and anion occupancies were fixed at the published values. The minimal scattering from Li\(^+\) meant it was not possible to identify the location of the additional Li\(^+\) in the structure. Rietveld refinement of the lattice parameters and profile coefficients shows that this simple approach gives a good agreement between the experimental data and a calculated model for the C2/c space group (Fig. 2). The cell parameters obtained from the Rietveld refinements resulted in an \( a = 10.4157(2) \) Å \( b = 5.9678(1) \) Å and \( c = 10.1589(2) \) Å with a β angle of 100.385(1°) leading to a cell volume of 621.13(2) Å\(^3\) for the undoped material.

For higher dopant levels up to \( \text{Li}_6\text{Hf}_1.9\text{In}_{0.1}\text{O}_{7} \) and \( \text{Li}_{6}\text{Hf}_{0.9}\text{Y}_{0.1}\text{O}_{7} \) an additional four hours of heating at 850°C was needed in order to achieve single phase materials. The solubility limit for the \( \text{In}^{3+} \) doping was identified at concentrations higher than 0.15, when the secondary phase \( \text{LiInO}_3 \) starts to appear and further heating led to decomposition of the target material. In the case of the \( \text{Y}^{3+} \) doping the solubility limit is reached just above \( x(\text{Y}) = 0.10 \), with appearance of additional peaks at this composition. These peaks could not be indexed by a reduction in space group symmetry, nor do they arise from any of the starting materials or obvious binary or ternary oxides that may result in this system. The lower solubility of this cation in the structure is presumably due to the larger deviation from the radius of \( \text{Li}^{+} \) exhibited by \( \text{Y}^{3+} \) compared to \( \text{Hf}^{4+} \).

Inspection of the diffraction patterns shown in Figure 3 shows no gross changes in the Bragg scattering suggesting the structure is largely unchanged. It should be clearly understood that due to the negligible X-ray scattering arising from \( \text{Li}^{+} \) in the presence of the dominant scatterer \( \text{Hf}^{4+} \) these data give no insight into the placement of the additional lithium in the structure. It may be assumed that \( \text{Li}^{+} \) exists at interstitial sites, but this remains conjecture at this stage.

There are no dramatic changes in the structures derived from Rietveld analyses, with the most significant being a decrease in the monoclinic distortion with \( \text{Y}^{3+} \) doping as manifested in the β lattice parameter shown in Figure 4. In the case of the In\(^{3+} \) doping, there were no significant changes in the structure. Again, these results are as anticipated after consideration of the ionic radii of \( \text{In}^{3+} = 0.80 \) Å, and \( \text{Hf}^{4+} = 0.71 \) Å, and with the radius of \( \text{Li}^{+} = 0.76 \) Å.

EDX analyses of \( \text{Li}_6\text{Hf}_{1.9}\text{In}_{0.1}\text{O}_{7} \) and \( \text{Li}_{6}\text{Hf}_{1.9}\text{Y}_{0.1}\text{O}_{7} \) estimated the relative atomic ratios of In:Hf as 0.09 and Y:Hf = 0.05.

Figure 2. Rietveld refinement against X-ray diffraction data collected from the undoped \( \text{Li}_6\text{Hf}_2\text{O}_7 \) material. The monoclinic structure gives a good agreement with the data. \( R_{wp} = 12.75\% \) and \( R_p = 9.41\% \).

**Figure 2.** Rietveld refinement against X-ray diffraction data collected from the undoped \( \text{Li}_6\text{Hf}_2\text{O}_7 \) material. The monoclinic structure gives a good agreement with the data. \( R_{wp} = 12.75\% \) and \( R_p = 9.41\% \).
Figure 3. Diffraction patterns collected from the (a) Li$_{6+x}$Hf$_{2-x}$In$_x$O$_7$ and (b) Li$_{6+x}$Hf$_{2-x}$Y$_x$O$_7$. The peaks arising from impurity phases at the highest dopant levels are indicated.

which are in good agreement with the values of 0.09 and 0.04 that are anticipated from the targeted stoichiometries.

A powdered sample of Li$_6$Hf$_2$O$_7$ shows agglomerates of microparticles between 10 and 50 microns with no specific morphology as shown in Figure 5. A fractured pellet for the Li$_{6.15}$Hf$_{1.85}$In$_{0.15}$O$_7$ material shows large grains with good connection between them. Despite that, the density of this material was only $\approx$78% of the theoretical density. Further sintering at higher temperatures in order to achieve higher densities resulted in decomposition of the material, possibly due to lithium evaporation.

An elemental compositional map was generated from a cracked pellet of the material that showed the highest conductivity, Li$_{6.10}$Hf$_{1.90}$Y$_{0.10}$O$_7$. Figure 6 shows that this map indicated a uniform distribution of Hf, Y and O across the pellet without any apparent segregation or inhomogeneity.

Figure 4. Monoclinic distortion ($\beta$-angle) variation following the substitution of Hf$^{3+}$ ions with Y$^{3+}$. A progressive decrease is observed due to the bigger size of the Y$^{3+}$ ions compared to Hf$^{3+}$.

Figure 5. SEM image of (a) the as-synthesized Li$_6$Hf$_2$O$_7$ and (b) the pelleted Li$_{6.15}$Hf$_{1.85}$In$_{0.15}$O$_7$ material prepared for EIS analyses.

Figure 6. An elemental map of the Hf, Y and O distributions on a fractured pellet that had been studied by impedance analysis. This is generated from EDX measurements and false colored to indicate the contributions from Hf (green), Y (blue) and O (red).

Ionic conductivity behavior.—The ionic transport properties of the undoped and doped materials were analyzed by means of impedance analysis and a typical Nyquist plot for the undoped material at 174°C is shown in Figure 7. A clear semicircle is observed at higher frequencies due to intra-grain ionic conductivity. The linear lower frequency response is typical of the blocking of Li$^+$ due to the use of platinum electrodes, indicating the ionic nature of the impedance. In order to obtain the value for the resistance of the material, these data were fitted using an equivalent circuit of a resistor, due to the resistance to ionic conduction, with a parallel constant phase element due to double layer polarization. The capacitance resulting from the fit is in the order of $10^{-12}$ F, indicating the observed
resistance is mainly due to bulk conductivity,\textsuperscript{41} and the conductivity is $1.95 \times 10^{-2} \text{ mS cm}^{-1}$.

In order to obtain further information about the ionic conduction phenomena in these materials, the activation energies of all the phase pure compositions were determined by variable temperature conductivity measurements. Arrhenius analysis of the data from the undoped material is shown in Figure 8. This indicates that the activation energy for ionic diffusion in Li$_6$Hf$_2$O$_7$, 0.97(4) eV, which lies between the values reported for the isostructural Li$_6$Zr$_2$O$_7$ by Goodenough and co-workers\textsuperscript{27} of 0.84 eV and the 1.25 eV obtained by Rao et al.\textsuperscript{28} Since there is more than one variable parameter within each study (e.g., synthetic conditions, density, set-up employed on the measurements, etc.), it is difficult to draw direct comparisons based on these values alone. Also, the activation barrier presented here represents the total conductivity which is highly dependent on the sample microstructure. A detailed study between both isostructural families of materials would be required in order to provide a better understanding regarding the role of the Hf and Zr atoms in the ionic conductivity of these materials.

For the In doped material, the ionic conduction at 174°C is progressively enhanced with the insertion of the In$^{3+}$ dopant, until it is increased by one order of magnitude at 174°C for the $x$(In) = 0.15. The activation energy for ionic conductivity is decreased by a 28% compared to the undoped parent material. In all the cases the evolution of ionic conductivity with temperature agrees accurately with an Arrhenius behavior as shown in Figure 8.

The introduction of Y$^{3+}$ also increased the ionic conductivity proportionally to Y$^{3+}$ doping stoichiometry as shown in Figure 9, again giving an order of magnitude higher for the $x$(Y) = 0.10 composition at 174°C. Due to the increased ionic conductivity, for the Y-doped material, reliable data could be acquired at room temperature. The activation energy is significantly altered by this doping reaching a value as low as 0.42(3) eV for the $x$(Y) = 0.10 composition as shown in Figure 9. The transport properties of all of these compounds are collected in Table I and Figure 10.
and displays two clear behaviors as the frequency is varied.

In the absence of structural information on the location of the additional Li\(^{+}\) ions inserted into the material it is only possible to speculate on the origin of this decrease in activation energy. If interstitial Li\(^{+}\) ions are introduced then a step change in activation energy would be expected due to the introduction of a new pathway for Li\(^{+}\) migration. The more gradual trend observed here suggests that increasing values of \(x\) may be causing incremental increases in electrostatic repulsion and destabilising Li\(^{+}\) and so reducing the barrier to ion motion.

The relationship of the conductivity with the frequency is shown in Figure 10 and displays two clear behaviors as the frequency is varied. At low to intermediate frequencies the conductivity is approximately constant due to the dominance of the jump relaxation of Li ions by \(dc\) conductivity, leading to a plateau-like region on the graph. This region displays a slight curvature at very low frequencies due to the polarization arising from the increasing resistance to lithium diffusion at the Li-blocking Pt electrodes when decreasing the frequency of the \(ac\) field. The second region at higher frequencies indicates a rapid increase in charge transport that can be attributed to the forward and backward movements of the ions under the influence of the rapid \(ac\) field.\(^{42-44}\)

This behavior is in agreement with the Jonscher universal power law\(^{45}\) (Eq. 1) presenting both of the components, the \(\sigma_{dc}\) corresponding to the plateau region and the linear region corresponding to the \(\sigma_{ac}\) – multiplied by a proportionality constant A. The value for conductivity in the plateau region is increased as the doping concentration increases, indicating the positive impact on the ionic conductivity of the dopant ions.

\[
\sigma(f) = \sigma_{dc} + A f^n
\]

The frequency exponent \(n\) has been calculated from fits of the frequency dependent range. The variation of the \(n\) exponent with respect to the doping (Table II) is clear, where a decrease in the \(n\) exponent with increasing amount of the dopant is observed indicating a lower contribution of the forward-backward jumps in favor of macroscopic ionic diffusion. These values for the \(n\) exponent are close to unity, similar to the values reported for other crystalline lithium ion conductor materials, such as the Li-NASICON structures.\(^{46}\)

### Table I. Ionic conductivity and activation energy data for Li\(_{6+x}\)Hf\(_{2-x}\)In\(_{2}\)O\(_7\) and Li\(_{6+x}\)Hf\(_{2-x}\)Y\(_2\)O\(_7\) materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ionic Conductivity at 174°C (mS cm(^{-1}))</th>
<th>Activation Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(<em>{6.00})Hf(</em>{2.00})O(_7)</td>
<td>1.95 \times 10(^{-2})</td>
<td>0.97(4)</td>
</tr>
<tr>
<td>Li(<em>{6.05})Hf(</em>{1.95})In(_{0.05})O(_7)</td>
<td>2.17 \times 10(^{-2})</td>
<td>0.77(1)</td>
</tr>
<tr>
<td>Li(<em>{6.10})Hf(</em>{1.90})In(_{0.10})O(_7)</td>
<td>9.88 \times 10(^{-3})</td>
<td>0.74(3)</td>
</tr>
<tr>
<td>Li(<em>{6.15})Hf(</em>{1.85})In(_{0.15})O(_7)</td>
<td>1.33 \times 10(^{-4})</td>
<td>0.68(3)</td>
</tr>
<tr>
<td>Li(<em>{6.20})Hf(</em>{1.80})In(_{0.20})O(_7)</td>
<td>3.32 \times 10(^{-5})</td>
<td>0.68(2)</td>
</tr>
<tr>
<td>Li(<em>{6.25})Hf(</em>{1.75})In(_{0.25})O(_7)</td>
<td>2.46 \times 10(^{-6})</td>
<td>0.42(3)</td>
</tr>
</tbody>
</table>

### Table II. Values of the frequency exponent \(n\) for the Li\(_{6+x}\)Hf\(_{2-x}\)In\(_{2}\)O\(_7\) and Li\(_{6+x}\)Hf\(_{2-x}\)Y\(_2\)O\(_7\) materials.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(n) exponent value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(<em>{6.00})Hf(</em>{2.00})O(_7)</td>
<td>1.29(1)</td>
</tr>
<tr>
<td>Li(<em>{6.05})Hf(</em>{1.95})In(_{0.05})O(_7)</td>
<td>1.23(1)</td>
</tr>
<tr>
<td>Li(<em>{6.10})Hf(</em>{1.90})In(_{0.10})O(_7)</td>
<td>0.93(2)</td>
</tr>
<tr>
<td>Li(<em>{6.15})Hf(</em>{1.85})In(_{0.15})O(_7)</td>
<td>0.94(1)</td>
</tr>
<tr>
<td>Li(<em>{6.20})Hf(</em>{1.80})In(_{0.20})O(_7)</td>
<td>1.07(2)</td>
</tr>
<tr>
<td>Li(<em>{6.25})Hf(</em>{1.75})In(_{0.25})O(_7)</td>
<td>0.80(2)</td>
</tr>
</tbody>
</table>

Figure 10. Activation energy for ionic diffusion as calculated from Arrhenius fitting for the different amounts of In (a) and Y doping (b) of the LiHf\(_{2}\)O\(_7\) material. A clear decrease is observed with increasing amount of dopant.

Figure 11. Ionic conductivity of the (a) In- and (b) Y-doped LiHf\(_{2}\)O\(_7\) materials as a function of the frequency measured for the different amounts of dopant. Fits to the frequency dependent range data are indicated by a solid line of the same color as the fitted data set.
Conclusions

We have demonstrated the successful synthesis and characterization of Li$_6$Hf$_2$O$_7$ by an energy-efficient microwave-assisted synthetic approach. An aliovalent doping strategy has been employed using Y$^{3+}$ and In$^{3+}$ to increase the number of lithium per formula unit, and so improve the ionic conductivity of the material. Powder X-ray diffraction has been used to follow the dopant insertion within the crystal structure. In this manner, it was found that the upper solubility limits of the dopants is x(In) = 0.15 for Li$_6$Hf$_2$O$_7$, and x(Y) = 0.10 for Li$_{6+x}$Hf$_2$O$_7$Y$_{1-x}$O$_2$. The ionic conductivity of the phase pure materials has been studied by means of impedance spectroscopy, showing a decrease of the energy barrier for ionic conductivity from 0.97 eV for the undoped material to 0.62 eV for the 0.15 In-doped material and a value of 0.42 eV for the 0.10 Y-doped compound. This low value compares favorably to other promising solid-state electrolyte materials. This demonstrates the potential of disorder in relatively simple crystal structures to generate new materials for solid-state electrolytes applications.

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