Short communication

LiCoPO₄ mechanical properties evaluated by nanoindentation


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Abstract

LiCoPO₄ is a promising cathode material for use in high voltage Li-ion batteries. One of the problems with LiCoPO₄ is limited cycle life. One possible cause for the limited cycle life of LiCoPO₄ is mechanical degradation. As a consequence, the mechanical properties, elastic modulus, E, and fracture toughness, KIC, of hot-pressed dense (~98%) polycrystalline (15–20 μm) single phase LiCoPO₄ were investigated. E for the hot-pressed LiCoPO₄ specimen is ~137 GPa while the E value for the LiCoPO₄ specimen after annealing at 600 °C is ~106 GPa. The fracture toughness of the hot-pressed LiCoPO₄ sample is ~0.41 MPa m¹/₂, which increased to ~0.53 MPa m¹/₂ after annealing. These low KIC values reveal that LiCoPO₄ is a brittle material. It is believed that the decrease in E and increase in KIC with annealing is associated with a reduction in residual stress.

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1. Introduction

LiCoPO₄ is of considerable interest as a new Li-ion battery cathode material owing to its high specific energy density of ~800 Wh/kg, which is >30% more than the commercialized, isostructural, LiFePO₄ cathode material [1]. One of the problems with LiCoPO₄ is limited cycle life [2–5]. One possible cause for the limited cycle life of LiCoPO₄ is mechanical degradation (e.g., particle fracture). Mechanical degradation has been suggested for the limited cycle life of LiFePO₄ [6], LiCoO₂ [7], LiNi₁/₃Mn₁/₃Co₁/₃O₂ [8] and LiₓMn₂O₄ [9]. Recently, Woodford et al. [9] have developed a model to predict the cycle life of oxide cathodes based on mechanical degradation. This model predicts the cycle life as a function of particle size and charging rates. In order to use this model and other micromechanical models [10–14] to predict the cycle life of a cathode material, knowledge of the material’s mechanical properties such as the elastic modulus, E, and fracture toughness, KIC, is required. Hence, it is the purpose of this short note to present the first results to the best of our knowledge on the mechanical properties of LiCoPO₄, with the intent that this information can be used in micromechanical models to predict the cycle life and determine what microstructural variables can be varied to increase the cycle life of LiCoPO₄.

2. Experimental

2.1. Processing and characterization

LiCoPO₄ powder was prepared via a citrate complexation route [15], Co(OH)₂, LiH₂PO₄, and citric acid, 1, 1.01, 1.02, molar ratio, respectively, were mixed into deionized water until all solids were dissolved. The resulting solution was evaporated to dryness via a microwave oven. The resulting dried mass was removed, ground lightly with mortar and pestle and heated in air at a rate of 10 °C min⁻¹ to 600 °C and the reactant mixture was held at this temperature for 12 h.
Dense discs of LiCoPO₄ were prepared by hot-pressing the powders at 800 °C at 62 MPa pressure for 0.5 h in graphite dies under air with an argon shielding gas. Rectangular parallelepipeds were cut perpendicular to the pressing direction using a low-speed diamond saw for density and mechanical property measurements. In addition, one rectangular parallelepiped sample was given an additional heat-treatment of 600 °C for 4 h under air to relieve any possible residual stresses that developed during cooling of the hot-pressed sample.

The relative density of the LiCoPO₄ rectangular parallelepipeds was determined by dividing the bulk density, determined from the weight and volume, by the theoretical density. Phase purity was evaluated using X-ray powder diffraction. Data were collected using a Rigaku Ultima III diffractometer (Cu Kα radiation). The microstructure of the hot-pressed LiCoPO₄ samples was examined on fracture surfaces using scanning electron microscopy (FEI environmental SEM). No surface coatings were applied to examine the fractured samples, but accelerating voltages of 2 or 5 kV were used to minimize surface charging.

2.2. Mechanical testing

Nanoindentation testing was chosen to determine the mechanical properties, because it is a convenient method used to measure these properties from small volumes of material [16–19]. Flat and polished LiCoPO₄ samples were prepared for nanoindentation testing using standard metallographic sample preparation procedures. A nanoindenter (Ubi1, Hysitron Co., Minneapolis, MN) with a Berkovich diamond tip was used to indent homogeneous regions of the sample's polished surface to determine $E$, hardness, $H$, and $K_{IC}$. The elastic modulus was calculated from the load-displacement curve during unloading using the Oliver–Pharr method [18,19]. Fracture toughness was determined using the pop-in method [7,20–22]. At least five different indents were made on both the hot-pressed and annealed samples. The applied load to produce impressions ranged from 1 to 6 mN. Quartz was used as the standard reference material to calibrate the instrument. As an additional check, values of $E$ and $H$ were also determined by nanoindentation performed using an Agilent Nano Indenter G200 by Analytical Services Laboratory of Nanomechanics Incorporated (Oak Ridge, TN) on a different section of the same hot-pressed sample. Poisson’s ratio, $\nu$, of 0.25, a typical value for ceramics [23], was used in the calculations.

3. Results and discussion

3.1. Characterization

Fig. 1 shows the X-ray diffraction pattern of the LiCoPO₄ sample after hot-pressing. All diffraction lines of LiCoPO₄ can be indexed based on an olivine structure with a $Pnma$ space group. No second phases were detected.

A representative SEM micrograph of a fracture surface from the hot-pressed LiCoPO₄ sample is shown in Fig. 2. From Fig. 2 several important points are noted. Firstly, the sample is highly dense, very little porosity is observed, in agreement with the relative density of ~98%, determined from the physical dimensions, weight and the theoretical density calculated from the crystal structure. Secondly, no secondary phases were observed at the grain boundaries. Thirdly, the linear intercept grain size is between 15 and 20 μm. Finally, the fracture mode is mixed transgranular and intergranular. In summary, the hot-pressed LiCoPO₄ material is single phase (no second phases), highly dense (~98%) with good bonding across the grain boundaries (evidence of transgranular fracture).

3.2. Elastic modulus

The $E$ value for the hot-pressed LiCoPO₄ sample is 136.7 ± 3.1 GPa (Table 1). This value is in excellent agreement...
with $E = 140.7 \pm 8.9$ determined by Nanomechanics, Inc., on a different section of the same hot-pressed sample. The $E$ value for the LiCoPO$_4$ specimen after the 600 °C heat-treatment is $105.6 \pm 4.1$ GPa (Table 1). Unfortunately, no experimental LiCoPO$_4$ values exist for $E$ measured by other experimental techniques such as; acoustic resonance to compare to the $E$ values for LiCoPO$_4$ determined by nanoindentation in this study. However, theoretical predictions for the bulk modulus, $K$, for LiCoPO$_4$ exist. Using density functional theory Shang et al. [24] predict a $K$ value of 91.6 GPa. Amador et al. [25] also using density functional theory predict a $K$ value for LiCoPO$_4$ of 73 GPa. From these $K$ values, the elastic modulus can be estimated using the following equation, below assuming isotropic behavior [26]:

$$E = 3K (1-2v) \quad (1)$$

Inserting the above predicted $K$ values into Eq. (1) with $v = 0.25$ yields $E = 137$ GPa ($K = 91.6$ GPa) and $E = 110$ GPa ($K = 73$ GPa). The experimental $E$ values for the hot-pressed (137 GPa) and annealed (106 GPa) LiCoPO$_4$ samples fall within the range of predicted $E$ values (110–137 GPa). The lower $E$ of the annealed LiCoPO$_4$ sample compared to the as hot-pressed sample could be a result of two things. Annealing could cause a change in microstructure and/or a reduction in residual stresses that developed during cooling to room temperature after hot-pressing. X-ray diffraction of the annealed sample revealed a similar X-ray diffraction pattern to the hot-pressed sample, single phase (i.e., no new phases formed). SEM examination revealed a similar grain size in both samples. Density measurements for both same samples were similar suggesting, no change in porosity. Thus, no microstructural changes occurred during annealing. Consequently, it is likely that the lowering of $E$ for LiCoPO$_4$ that occurs on annealing is a result of a reduction in residual thermal stresses. It is known that for non-cubic crystals, such as LiCoPO$_4$ with an orthorhombic structure, that residual stresses can develop in polycrystalline samples during cooling as a result of anisotropic thermal expansion coefficients [9,27–29].

### 3.3. Hardness and bonding

The hardness value for the LiCoPO$_4$ specimen after hot-pressing is $9.10 \pm 0.4$ GPa (Table 1). This value is in excellent agreement with value for $H = 9.37 \pm 1.08$ determined by Nanomechanics, Inc., on a different section of the same hot-pressed sample. The hardness value for the heat-treated LiCoPO$_4$ is $9.2 \pm 0.2$ GPa (Table 1). The hardness values did not seem to change with annealing. This result is in agreement with the observation that the microstructure was the same for both hot-pressed and annealed LiCoPO$_4$ samples.

Gilman [30] and Chin et al. [31] reported that the ratio of the hardness to the shear modulus, $G$, for crystals is relatively constant for different types of bonding: For covalent, ionic and metallic bonding, $H/G \sim 0.1$, $H/G \sim 0.01$, and $H/G \sim 0.006$, respectively [30,31]. The hardness and elastic modulus data can be used to calculate the Gilman–Chen parameter ($H/G$) for LiCoPO$_4$ to determine the dominant type of bonding. The shear modulus can be estimated from the $E$ values using the following equation [26]:

$$G = E/(2(1+v)) \quad (2)$$

A value of $v = 0.25$ was used to calculate $G$. The $H/G$ value for the as hot-pressed and annealed LiCoPO$_4$ is $\sim 0.17$ and $\sim 0.21$, respectively, suggesting that the dominant bonding type is covalent. This result is in agreement with the strong covalent nature of the bonding within the phosphate framework of the olivine structure of LiCoPO$_4$ [32,33].

### 3.4. Fracture toughness

Precise measurement of the crack length is considered the most critical step in determining $K_{IC}$ of a brittle material when using an indentation technique. Since crack lengths when using nanoindentation can be small (e.g., submicron), direct crack length measurements using optical or scanning electron microscopy are not that accurate [20]. As a consequence, this study employed the pop-in method. In the pop-in method the crack length is determined from the nanoindentation load–displacement curves without the need for direct imaging of the indentation to determine crack length [7,20,21]. $K_{IC}$ is calculated using the following equation [7,20,34]:

$$K_{IC} = k \left( \frac{E}{H} \right)^{0.5} \left( \frac{p}{c^{0.3}} \right) \quad (3)$$

where $k$ is a constant $= 0.016$ for a Berkovich indenter [21,34], $p$ is the applied load, and $c$ is the crack length from the center of the indent to the crack tip, which is calculated from the load–displacement curves using the following equation [7,20]:

$$c = \sqrt{2h_m + \left( \frac{Q}{H} c - \sqrt{2} \right) h_k} \quad (4)$$

where $Q$ is a material independent constant of 4.55 [7,20]. A polynomial curve fitting routine was used to determine the displacement values of $h_m$ and $h_k$, which are defined as, the maximum pop-in penetration displacement at maximum load and the extra penetration displacement resulting from entry of the indenter into the crack, respectively [7,20,21].

An SEM image of a typical indent and the resulting cracks emanating from the indent corners in hot-pressed LiCoPO$_4$ made using a Berkovich diamond indenter is shown in Fig. 3. From Fig. 3 it can be seen that the radius of the indent impression is $\sim 1 \mu$m, while the crack lengths emanating from the indent corners are $\sim 2$ to $3 \mu$m, yielding total crack lengths from the center of the indent to the crack tip $\sim 3$ to $4 \mu$m. The fracture toughness of the hot-pressed LiCoPO$_4$ sample is $0.41 \pm 0.09$ MPa m$^{1/2}$ (Table 1). The fracture toughness of LiCoPO$_4$ after annealing increased by

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$ (GPa)</th>
<th>$H$ (GPa)</th>
<th>$K_{IC}$ (MPa m$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot-pressed LiCoPO$_4$</td>
<td>136.7 ± 3.1</td>
<td>9.1 ± 0.4</td>
<td>0.41 ± 0.09</td>
</tr>
<tr>
<td>Annealed LiCoPO$_4$</td>
<td>105.6 ± 4.1</td>
<td>9.2 ± 0.2</td>
<td>0.53 ± 0.12</td>
</tr>
</tbody>
</table>
The increase in fracture toughness after annealing is likely due to the reduction in tensile stresses that developed during cooling after hot-pressing as a result of the anisotropic thermal expansion coefficients associated with the olivine structure [9,27–29] since, the microstructure (e.g., grain size, porosity) of both samples is similar.

No $K_{IC}$ values exist for any Li-olivine cathodes to compare the LiCoPO$_4$ values to. However, LiCoPO$_4$ fracture toughness results can be compared to typical values for ceramics. In general ceramics exhibit fracture toughness values from ~0.5 to 5 MPa m$^{1/2}$, with values for single crystals between ~0.5 and 2 MPa m$^{1/2}$ and for polycrystals between ~2 and 5 MPa m$^{1/2}$ [28]. Since, the total crack length for both LiCoPO$_4$ samples is in general less than 4 $\mu$m (Fig. 3), compared to grain sizes which are between 15 and 20 $\mu$m (Fig. 2), the $K_{IC}$ values (~0.4–0.5 MPa m$^{1/2}$) measured in this study most likely represent single crystal fracture toughness values. In which they are near the low end of single crystal values (~0.5 to 2 MPa m$^{1/2}$). This observation suggests that LiCoPO$_4$ is a brittle material like glass.

From the $K_{IC}$ values for LiCoPO$_4$ the fracture surface energy, $\gamma$, can be determined using the following equation [27,28,34,35]:

$$\gamma = K_{IC}^2/2E \tag{5}$$

Inserting values of $K_{IC}$ ~0.47 MPa m$^{1/2}$ and E~122 GPa (the average value for the two LiCoPO$_4$ samples) into Eq. (5) yields $\gamma$ ~1 J/m$^2$. This value is in very good agreement with fracture surface energy values of ~0.5 to 3 J/m$^2$ commonly exhibited by single crystal ceramics [35]. This result adds further confirmation that the $K_{IC}$ values for LiCoPO$_4$ measured in this study are likely associated with single crystal fracture toughness values.

4. Conclusions

Dense (relative density ~98%) single phase LiCoPO$_4$ with a grain size between 15 and 20 $\mu$m was prepared by hot-pressing. The mechanical properties, $E$, $H$ and $K_{IC}$ were determined using nanoindentation on the hot-pressed sample and after annealing. The $E$ value for the hot-pressed LiCoPO$_4$ specimen is ~137 GPa, while the $E$ value for the LiCoPO$_4$ specimen after annealing at 600 °C is ~106 GPa. The $H$ value for LiCoPO$_4$ is ~9.1 GPa. The $H$ values did not vary with heat-treatment. The $K_{IC}$ of the hot-pressed LiCoPO$_4$ sample is ~0.41 MPa m$^{1/2}$, which increased to ~0.53 MPa m$^{1/2}$ after annealing. These $K_{IC}$ values are near the low end of single crystal fracture toughness values, which suggest that LiCoPO$_4$ is a brittle material like glass. It is believed that the decrease in $E$ and increase in $K_{IC}$ with annealing is associated with a reduction in residual stresses that developed during cooling to room temperature after hot-pressing. It is known that for non-cubic crystals, such as LiCoPO$_4$ with an orthorhombic structure, that residual stresses can develop during cooling as a result of anisotropic thermal expansion coefficients.

The $E$, $H$ and $K_{IC}$ values determined in this study to the best of our knowledge represent the first experimentally measured mechanical properties of the high voltage LiCoPO$_4$ cathode material. Such information is needed in micromechanical models to predict the cycle life and determine what microstructural variables can be varied to increase the cycle life of LiCoPO$_4$, so it can be used in Li-ion batteries which will exhibit higher energy than are currently available.

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