Short communication

Mechanical and physical properties of LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC)

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A R T I C L E   I N F O

Article history:
Received 17 February 2017
Accepted 19 March 2017
Available online 31 March 2017

Keywords:
Lithium nickel manganese cobalt oxide
Mechanical properties
Physical properties
Pulse echo technique
Nanoindentation

A B S T R A C T

Lithium Nickel Manganese Cobalt Oxide (NMC) is one of the most common oxide cathode materials for Li-ion batteries. NMC is also under consideration for use in all solid-state batteries. However, differences in the coefficients of thermal expansion (CTE) between NMC and the solid electrolyte during composite electrode fabrication and differential expansion and contraction during electrochemical cycling will cause stresses possibly resulting in electrode fracture and battery capacity fade. As a consequence, we hot-pressed phase-pure polycrystalline NMC with controlled density and accurately measured the mechanical (elastic modulus, shear modulus, Poisson’s ratio and nanoindentation hardness) and physical properties (CTE and thermal conductivity). We believe that this is the first report of the mechanical and physical properties of commercially available NMC and these experimental data are important to predict or increase the cycle life of NMC as a cathode material for state-of-the-art Li-ion and advanced solid-state batteries.

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1. Introduction

Owing to their intrinsic stability, all solid-state ceramic batteries are garnering interest to enable safe, large-format energy storage technology [1,2]. Though there are numerous bulk-scale solid-state cell configurations, the composite oxide electrode is one of the most chemically stable and is non-flammable. The composite oxide configuration consists of a fast oxide-ion conductor, an oxide electrode, and a conductive additive, which are blended/randomized and densified at elevated temperature [2]. Compared to contemporary liquid electrolyte Li-ion batteries in which individual cathode particles are free to expand and contract during cycling, the proposed composite oxide configuration will generate stresses at the solid electrolyte/cathode interface. These stresses are created by the relative expansion and contraction of the cathode as it is lithiated and de-lithiated while the solid electrolyte does not change volume and during cooling from densification temperature due to the CTE difference between the electrolyte and electrode materials. Stresses within electrodes can lead to their fracture, resulting in battery capacity loss and power fade. Thus, there is a need to characterize the mechanical properties of solid electrolytes and electrodes. Previous work characterized the mechanical properties of oxide electrolytes using acoustic analysis, Vickers and nanoindentation [3–5]. However, no reports to date describe the mechanical properties of one of the most common oxide cathodes, LiNi$_{0.33}$Mn$_{0.33}$Co$_{0.33}$O$_2$ (NMC), which is also of interest in all-solid-state composite cathodes. The purpose of this work is to synthesize phase-pure polycrystalline NMC with controlled density and accurately measure the salient elastic and mechanical properties to facilitate the development of solid-state composite cathodes. Since the mechanical properties of single-crystalline cathodes are critical for predicting their cycle lives using computational models [6], hardness and elastic modulus of NMC single-crystals are measured by nanoindentation. To directly measure Poisson’s ratio and the shear modulus, the pulse-echo acoustic technique was used. In addition, the Poisson’s ratio is necessary to determine the elastic modulus using nanoindentation, and the elastic modulus analyzed using pulse-echo is also cross-checked. The CTE and thermal conductivity of NMC are also measured using dilatometry and laser flash diffusivity, respectively. These physical and thermal properties can help better understand the micromechanical environment and to predict the compatibility between NMC and solid-state electrolytes, e.g., LLZO, during densification and electrochemical cycling, respectively.

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http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.048
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2. Experimental procedure

2.1. Densification

As-received NMC powders (Toda America, Battle Creek, MI) were dry-milled for 10 h at 400 rpm in a planetary mill (Retsch GmbH, Haan, Germany). ZrO$_2$ balls with an average diameter of 1 mm were used as milling media. The weight ratio between the ZrO$_2$ ball and the NMC powder was 5:1. The ball-milled powders were hot-pressed into billets (12.7 mm diameter, 4.0 mm thick) using a rapid induction hot-pressing technique at 1253 K and 60 MPa for 75 min under Ar. The relative density was determined using Archimedes’ principle, where cyclohexane was used as the immersion liquid. The NMC specimens were polished using standard metallographic techniques. The final finish used a 1 μm diamond polishing compound (Diamond Paste, South Bay Technology, CA, USA).

2.2. Characterization

X-ray diffraction was performed using a diffractometer (Rigaku Rotating Anode XRD, Tokyo, Japan) with CuKα radiation in a 2θ range of 10–70° at 100 mA and 40 kV. Microstructures of NMC powers and hot-pressed NMC specimens were observed using a Dualbeam SEM/FIB microscope (FEI Helios Nanolab 650, accelerating voltage: 50V–30 kV; beam current: 0.8 pA–26 nA). The average particle or grain size of NMC was estimated from SEM micrographs using ImageJ software [7]. Acoustic properties were analyzed using
Table 1
Mechanical and physical properties of bulk NMC (in comparison with LCO and LLZO).

<table>
<thead>
<tr>
<th></th>
<th>Elastic modulus (E)</th>
<th>Shear modulus (G)</th>
<th>Poisson’s ratio (ν)</th>
<th>Hardness (H)</th>
<th>CTE (αL) [K]</th>
<th>Thermal Conductivity [W/(m·K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>199 ± 12 GPa (Nanoindentation)</td>
<td>78 ± 1 GPa (Pulse echo)</td>
<td>0.25</td>
<td>11.2 GPa (Nanoindentation)</td>
<td>1.2–1.3 (10⁻³[K])</td>
<td>2.9–4.3</td>
</tr>
<tr>
<td></td>
<td>194 ± 2 GPa (Pulse echo)</td>
<td>78 ± 1 GPa (Pulse echo)</td>
<td>0.25</td>
<td>11.2 GPa (Nanoindentation)</td>
<td>1.2–1.3 (10⁻³[K])</td>
<td>2.9–4.3</td>
</tr>
<tr>
<td>LiCoO2 (LCO) [20]</td>
<td>174 ± 25 GPa (Nanoindentation)</td>
<td>60 ± 1 GPa (Nanoindentation)</td>
<td>0.26</td>
<td>9.1 GPa [4] (Nanoindentation)</td>
<td>1.5 (10⁻³[K])</td>
<td>~4.0</td>
</tr>
<tr>
<td>Li7La3Zr2O12 (LLZO) [3]</td>
<td>150 ± 2 GPa (Nanoindentation)</td>
<td>60 ± 1 GPa (Nanoindentation)</td>
<td>0.26</td>
<td>9.1 GPa [4] (Nanoindentation)</td>
<td>1.5 (10⁻³[K])</td>
<td>~4.0</td>
</tr>
</tbody>
</table>

Fig. 3. Representative pulse-echo spectra of bulk NMC: (a) Longitudinal and (b) shear waves. Transducer excitation voltage is on the vertical axis and the acoustic wave propagation time on the horizontal axis. The time between reflections is indicated in μs.

where V is the wave velocity ($V_3$ and $V_1$: shear and longitudinal wave velocities, respectively), h is the thickness of the specimen, and t is the wave travel time through the measured thickness h and is defined as the transit time between subsequent echoes. Since the specimen thickness was ~5.12 mm (the measured mass density $\rho$ was ~4.53 g/cm³), the longitudinal and shear wave speeds were calculated to be ~7152.0 m/s and 4147.2 m/s, correspondingly. Nanoindentation was carried out on a Hysitron TI950 Triboindenter (Minneapolis, MN, USA) loaded with a standard diamond Berkovich indentation tip (highest indentation load: 10 mN). Hardness was determined from at least 10 indentation measurements. The Elastic modulus was calculated from the load-displacement curve during unloading using the Oliver-Pharr method [9]. The elastic modulus and Poisson’s ratio of the Berkovich diamond tip were 1140 GPa and 0.07, respectively. The CTE of the bulk NMC was measured using an industry standard thermomechanical analyzer (Q400, TMA) from 273 to 673 K. Thermal conductivity was measured using a Laser Flash method from 300 to 800 K in a Linseis LFA 1000.

3. Results and discussion

Fig. 1 shows SEM micrographs of NMC powders before and after dry ball-milling. The average primary particle size of as-received NMC was ~8.0 ± 2.4 μm (Fig. 1(a)), while the average secondary particle size was ~482.7 ± 160.3 nm. SEM analysis of the dry ball-milled NMC powders is presented in Fig. 1(b), from which it can be seen that the primary particles were broken into individual particles. Hot pressing the as-received NMC powders resulted in relative densities ~90%, while hot-pressing the ball-milled NMC powders resulted in much higher relative densities, ~96%. Therefore ball-milling improved the sinterability of the as-received NMC powders by breaking up the primary particles into secondary particles.

XRD analysis of the hot-pressed bulk NMC confirmed that NMC maintained the same crystal structure compared to the as-received powder (ICSD: 171750) [10]. An SEM micrograph of a polished surface of hot-pressed NMC is shown in Fig. 2(a), where no obvious pores were apparent (the features were likely to be evidence of par-
particle pullout during polishing and not porosity). The density of the specimen was 4.58 g/cm$^3$, corresponding to a high relative density $\sim$96.0% (theoretical density: 4.77 g/cm$^3$) [10]. An SEM micrograph of the freshly fractured surface is also presented in Fig. 2(b), from which a mixed fracture mode (transgranular and intergranular) is observed with the intergranular mode being dominant. The specimen is dense and the NMC grains are equiaxed. In addition, the average grain size is estimated to be $\sim$4.2 $\pm$ 1.5 $\mu$m, much larger than the secondary particle size, $\sim$0.5 $\mu$m.

To directly measure the Poisson’s ratio and elastic modulus of polycrystalline NMC, pulse-echo was conducted assuming that the specimen is isotropic. The elastic modulus ($E$), shear modulus ($G$) and Poisson’s ratio ($\nu$) are calculated using the following Eqs. [8,11,12]:

\[
E = \rho V_s^2 \\
G = \frac{E}{2(1+\nu)} \\
E = \frac{\rho(1+\nu)(1-2\nu)}{(1-\nu)} V_s^2
\]

where $\rho$ is the mass density of the specimen. Fig. 3 illustrates the representative pulse-echo spectra, where the period $t$ (time gap between subsequent echoes) for the longitudinal and shear waves are $\sim$1.434 and 2.473 $\mu$s, respectively. With $V_L$ and $V_S$ being calculated to be 7152.0 m/s and 4147. 2 m/s, respectively, the $E$, $G$ and $\nu$ are then determined to be $\sim$194.3 GPa, 77.9 GPa and 0.25, respectively, from Eqs. (2)–(4).

To measure the hardness and elastic properties of NMC single crystals and cross-check the pulse-echo results, nanoindentation was also conducted and compared (Fig. 4.) A representative load-displacement curve is shown in Fig. 4(a), where the peak load is 500 $\mu$N and the maximum indentation depth is 22.8 nm; the measured elastic modulus and indentation hardness were 201 GPa and 11.0 GPa, respectively. Fig. 4(b) shows the load dependence of $E$ and $H$ of NMC grains, varying in the range of 179–201 GPa and 9.1–11.7 GPa, respectively. The average $E$ and $H$ obtained at peak loads $\leq$5 mN were $\sim$199 and 11.2 GPa, respectively. In particular, both the $E$ and $H$ of NMC varied in a similar manner; they both decreased with increasing indentation load. The indentation size effect was widely reported in ceramic materials, which may have been due to cracking or dislocation motion caused by deeper pen-

Fig. 4. Nanoindentation results of bulk NMC: (a) Load-displacement curve with a peak load of 500 $\mu$N, (b) elastic modulus and hardness as a function of indentation load, (c) in-situ AFM image showing indentation impressions with a peak load of 5 mN, and (d) AFM image at a peak load of 10 mN. The inset is a corresponding reverse gradient AFM image.
traction of the indenter [13–15]. Fig. 4(c) shows an in-situ atomic force microscopy (AFM) image of indentation impressions under a peak load of 5 mN. No pile-up around the indentations was observed and the average size of the indentation impressions was ~1.0 μm. A typical AFM image of a 10 mN indentation impression is shown in Fig. 4(d), where an uplifted fragment at the lower left side of the indentation indicates cracking. The discrepancy between the elastic moduli measured by nanoindentation (average ~199 GPa at indentation loads ≤5 mN) and pulse-echo (~194 GPa) is only ~2.5%, indicating that dense polycrystalline NMC exhibits almost the same elastic properties as single-crystalline NMC.

The CTE of the bulk NMC was measured to be ~1.2–1.3 (10−5/K) from 353 (measurement was stabilized at over 350 K) to 673 K. In comparison, the theoretical volumetric CTE value of LCO from 350 to 600 K was ~1.2–1.5 (10−5/K) [16], very close to our measurements. Generally, the thermal conductivity of NMC decreased linearly from 4.3 to 2.9 W/(m.K) with increasing temperature from 300 to 800 K. The reported experimental value of thermal conductivity of LCO at 300 K was ~4.0 W/(m.K) [17], similar to those of NMC in this study. A summary of the mechanical and physical properties of NMC is also listed in Table 1, from which it is seen that the mechanical and physical properties of NMC and LCO are similar with NMC having a slightly higher elastic modulus.

Upon cooling, the stress generated between NMC and solid electrolyte materials, e.g. LLZO, can be roughly evaluated by Eq. (5) [18], assuming isotropic elastic behavior of NMC and LLZO,

\[
\sigma = \frac{\Delta \alpha \Delta T}{E_{NMC}} = \frac{\Delta \alpha \Delta T}{E_{LLZO}}
\]

where \( \Delta \alpha \) is the CTE mismatch between NMC and LLZO, ~2.5 (10−6/K); \( \Delta T \) is the difference between sintering temperature and room temperature, e.g. 1123 K; \( E_{NMC} \) and \( E_{LLZO} \) are elastic moduli of NMC (195 GPa) and LLZO (150 GPa), respectively. The calculated stress between the NMC/LLZO interface is ~180 MPa. At present, no fracture stress data is available for NMC and LLZO. However, fracture stress data is available for Y2Al5O12 (a similar cubic garnet to LLZO) ranged from 200–300 MPa [19]. To more accurately predict interface stresses between NMC and solid electrolytes, Finite Element Analysis (FEA) can be used. Thus, we present the first results on the mechanical and physical properties of NMC with the intent that this information can be used to predict the cycle life of NMC as a cathode material and to better design the solid electrolyte/cathode interface to avoid stress-related failures of all-solid-state Li-ion batteries.

4. Conclusions

Phase-pure polycrystalline NMC cathode materials with controlled density (relative density ~96.0%) were synthesized using rapid induction hot-pressing at 1253 K and 60 MPa for 75 min in Ar. The elastic modulus \( E \), shear modulus \( G \), hardness \( H \), and Poisson's ratio \( \nu \) of bulk NMC determined (and cross-checked) by nanoindentation and pulse-echo were ~195 GPa, ~78 GPa, ~11.2 GPa, and 0.25, respectively. In addition, the CTE and thermal conductivity of NMC from 350–675 K were measured to be 1.2–1.3 (10−5/K) and 2.9–4.3 W/(m.K) from 300–800 K, respectively. The internal stress between NMC and a solid-state electrolyte, LLZO, upon cooling was roughly estimated to be 180 MPa based on these experimental data. These experimentally measured mechanical and physical properties of NMC provide valuable information for a better design of Li-ion and advanced solid-state batteries using NMC as a cathode material.

Acknowledgements

EC, NJT, JW, and JS would like to acknowledge support from the Advanced Research Projects Agency-Energy (DE-AR0000653) and the University of Michigan; JW would also like to acknowledge support from the U. S. Army Research Laboratory. EC would like to thank Nicholas Moroz and Travis Thompson for their help on thermal conductivity measurement. HC would also like to acknowledge support of the National Research Foundation (NRF) of Korea (2014R1A2A1A1052513; 2009-0093814).

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