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Original Article

Mechanical properties of the solid electrolyte Al-substituted $Li_7La_3Zr_2O_{12}$ (LLZO) by utilizing micro-pillar indentation splitting test

An-Ni Wang[1], Juliane Franciele Nonemacher*, Gang Yan, Martin Finsterbusch, Jürgen Malzbender, Manja Krüger

Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK), 52425 Jülich, Germany

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ABSTRACT

Garnet structured Al-substituted $Li_7La_3Zr_2O_{12}$ (Al:LLZO) is a promising candidate as electrolyte in all-solid-state Li-ion batteries due to its chemical stability against Li-metal and high voltage cathode materials. In order to ensure long-term stable operation, electrolyte crack growth induced and/or the volume change of the active material on the cathode side needs to be avoided, requiring in particular knowledge of local and global mechanical properties of the electrolyte material. Micro-pillar splitting test was used for the first time on this material to determine the microscopic fracture toughness of single grains and compare it with conventional Vickers indentation fracture toughness (VIF), which represents macroscopic fracture toughness. Both methods yielded comparative results. In conclusion, the micro-pillar splitting test can be used as an advanced locally resolved characterization method that can open up new experimental directions for characterizing and understanding battery materials and enable a targeted approach for material improvements.

1. Introduction

For Li-ion batteries (LIBs), in general, but especial for all-solid-state lithium batteries, the mechanical degradation under cyclic charging appears to be a critical factor affecting the lifetime [1–5]. During the operation of LIBs, the intercalation of ions into and out of the electrodes induces cyclic volumetric expansion and contractions of the electrodes, thereby generating considerable internal stress within the electrode structure [6–9]. This kind of dynamic mechanical alteration governs the coupling of electro-, chemo- and mechanical fields, corresponding to the Li-concentration, diffusion potential, and displacements. This combined effect can eventually lead to the formation of micro-cracks, formation of Li-dendrites and other local structural defects at the electrolyte interface and within electrolyte [1–4]. To avoid Li metal penetration through the electrolyte, a high tolerable shear modulus of the electrolyte of more than twice that of Li metal (4.25 GPa) has been recommended [10–12]; however, more recent studies indicate that this alone is not sufficient as a selection guideline [13–17]. Moreover, grain boundary effects and tri-junction area bonding should be considered [14,18–20]. Especially the charging cycle related formation of micro-cracks, whose formation will be related to the fracture toughness, is commonly expected to reduce the effective ionic conductivity and the rate capability of electrodes and consequently needs to be suppressed to reach long cycle life and higher stability [1,6,19,21]. Therefore, a comprehensive study of fracture toughness and fracture mechanisms especially in the range from micro- to nano-meters is crucial for a targeted, functional optimization and future materials development in this field.

The garnet structured $Li_7La_3Zr_2O_{12}$ (LLZO) is one of the most promising solid electrolytes candidates for all-solid-state lithium batteries due to its high ionic conductivity (up to ~0.1 mS/cm for cubic structure by doping with Ta or Al elements [14,22,23]), low electronic conductivity, good electrochemical compatibility with the Li metal anode [24,25], and possibility to fulfill mechanical stability requirements for battery assembling [26].

Table 1 presents a summary of some recent studies with respect to experimental and numerical results on LLZO mechanical properties [10,26–28], and it should be noted that the number of reports on the fracture toughness are limited and all respective results are based on Vickers indentation fracture (VIF) testing. The conventional VIF method can permit a macroscopic characterization of the fracture toughness although inherent uncertainties related to crack length measurement and equations to be used for different crack shapes have to be considered; however, assessment of crack propagation path trajectories can already reveal some insight into the local fracture behavior.

* Corresponding author.
E-mail addresses: anni.wang@tu-ilmenau.de (A.-N. Wang), j.nonemacher@fz-juelich.de (J.F. Nonemacher).
[1] Technische Universität Ilmenau, Materials for Electrical Engineering and Electronics, WET-ZMN, 98693 Ilmenau, Germany.

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Table 1
Mechanical properties of LLZO using computational and experimental methods summarized from literature.

Materials	Porosity [%]	Grain size [μm]	Testing Method	Young's Modulus [GPa]	Hardness [GPa]	Vickers K_{IC} [MPa m$^{0.5}$]
$Li_{6.91}La_3Zr_{1.98}Al_{0.13}O_{12}$ [This study]	7	100	Nanoindentation Micro-pillar splitting	145.6 ± 7.3	8.5 ± 0.4	1.19 ± 0.13; 0.99 ± 0.05 (Micro-pillar)
$Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$ [26]	36	4.5–5.0	Resonant ultrasound spectroscopy	149.8 ± 0.4; 132.6 ± 0.2	6.3 ± 0.3 (V: 2.9 N); 5.2 ± 0.4 (V: 4.9 N)	–
$Li_{6.17}Al_{0.28}La_3Zr_2O_3$ [10]	~2	5–50	DFT (0 K)	162.6	–	–
			DFT (298 K)	154.5		
			Impulse excitation	146.1 ± 0.8		
			Dynamic indentation	150.3 ± 2.2		
$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ [10]	~2	1–10	DFT (0 K)	154.9	–	–
			DFT (298 K)	147.2		
			Impulse excitation	139.9 ± 2.1		
			Dynamic indentation	153.8 ± 2.7		
$Li_{6.19}Al_{0.27}La_3Zr_2O_{12}$ [29]	15	2.7 ± 1.7	Nanoindentation	~135 GPa	4.7 ± 0.2 (V:0.3 N); 8.1 ± 0.8 (B:125 μN)	2.37 ± 0.1 (Intergranular)
	5	3.2 ± 1.9	–	–	7.4 ± 0.4 (V: 0.3 N); 9.3 ± 0.5 (B:125 μN)	~1.3
	4	3.5 ± 1.8	–	–	~8.8 (V: 0.3 N); ~9.1 (B: 125 μN)	~1.11
	2	3.7 ± 1.8	Nanoindentation	~140 GPa	~9.1 (V: 0.3 N); ~9.1 (B: 125 μN)	0.97 ± 0.1 (Intragranular)
$Li_{6.24}La_3Zr_2Al_{0.24}O_{11.98}$ [28]	3	~5	–	–	–	*0.86–1.63

DFT = density functional theory; V = Vickers indenter, B = Berkovich indenter.
* Toughness calculated from different analytical equations.

As shown by Wolfenstine et al. [28], the fracture toughness obtained using different models for the same LLZO VIF imprint can range from 0.86 to 1.63 MPa m$^{0.5}$ and most importantly neither half-penny nor Palmqvist models appeared in their case to completely address the crack propagation behavior characterized on the basis of FIB-SEM cross-sectional images, raising the need for additional methods that permit a fracture toughness characterization and avoid at the same time complexities associated with complex crack shapes.

Recently, a transition from intergranular to intragranular fracture behavior was found via VIF method in the case of hot-pressed LLZO [29], where the crack propagation changed due to the relative density associated with the presence of intergranular pores and weak grain boundaries. According to this result, LLZO with low density is macroscopically tougher compared to one with higher relative density due to the weak grain boundaries that deflected the crack trajectories away from the direction of maximum driving force. This phenomenon can be particularly relevant for application in terms of processing boundary conditions and target materials properties. It also shows the necessity for identification of the local mechanical properties with respect to the intrinsic material toughness with the aim to assist future structural designs of LLZO-based electrode materials, components and full cells.

Considering the importance of solid state battery materials and in particular their mechanical behavior, the current work presents an investigation on the use of Berkovich indentation to characterize elastic modulus, hardness and fracture toughness of Al-substituted $Li_7La_3Zr_2O_{12}$ (Al:LLZO), whereas elastic modulus and hardness are derived from depth-resolved indentation data, fracture toughness data are determined from crack lengths using conventional VIF method and an advanced micro-pillar splitting method, being the focus of the work.

The micro-pillar indentation splitting testing as a means to measure the toughness was recently developed by Sebastiani et al. based on sharp indentation testing of FIB milled micro-pillars [30,31], in order to solve some of the issues related to fracture toughness determination based on indentation of films. This method for measuring the fracture toughness at small scales is based on fracture by splitting of pillar leading to reproducible loads as determined from pop-in effects in the displacement-load curves. The fracture toughness can be calculated using the following equation:

$$K_c = \gamma \bullet \frac{P_c}{R^{3/2}} \quad (1)$$

where P_c is the critical load at failure, γ is a dimensionless coefficient that includes the influence of elastic-plastic properties, and R is the pillar radius.

In particular for the local materials property assessment, the technique has shown several advantages compared to VIF and other micro-mechanical testing methods currently available. The design of a micro-pillar for testing is relatively simple, there is no necessity for accurate image correction and crack length measurement or for minimizing the materials residual stress [32,33]. Furthermore, when the aspect ratio height to diameter is greater than 1, residual stresses on the upper portion of the pillar and substrate compliance are negligible with respect to the critical load of failure [30,31]. Even though the crack length and geometry are not required, it they be assessed after testing via FIB/SEM analyses and additional information on the crack path can be assessed.

The instability load and pillar radius needed in Eq. (1) are easily measured and fracture toughness can be derived, which highlights the feasibility of this method. In addition, since the pillar splitting can occur at shallow indentation depths and the FIB damage is considered to be surface localized and far from the position of the crack nucleation and propagation, the potential FIB-induced damage is commonly accepted to be less significant compared to other micro-mechanical testing methods, such as single- and double-cantilever bending, which is also the case for battery materials possessing a high ion-conductivity, which would result in larger damage induced by the Ga^+ ions.