Mechanical and electrochemical properties of cubic and tetragonal $Li_xLa_{0.557}TiO_3$ perovskite oxide electrolytes

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ABSTRACT

Solid oxide electrolytes with high Li ion conductivity and mechanical stability are vital for all solid-state lithium ion batteries. The perovskite material $Li_xLa_{0.557}TiO_3$ with various initial Li ($0.303 \leq x \leq 0.370$) is synthesized by traditional solid-state reaction. The cubic and tetragonal structures are prepared with fast and slow cooling, respectively. The results reveal that the Li ion conductivity of the cubic structure is higher. In fact, the bulk conductivity of $1.65 \times 10^{-3}\,S\,cm^{-1}$ is obtained at room temperature for $x = 0.350$. The crystal structure is not affected by the Li_2O quantity. In addition, Young's modulus, hardness, and fracture toughness are determined with indentation method for both structures. The Young's modulus increases with increasing Li_2O. However, hardness and fracture toughness keep a relatively stable value independent of Li_2O quantity.

1. Introduction

Lithium secondary batteries have high discharge voltage, high energy density, long working life, and low self-discharge rate, and therefore have been overwhelmingly utilized in electronic devices such as cell phones, laptop computers and cameras [1,2]. The developments of electric vehicles (EV) and energy storage in power plants are greatly increasing the demand of lithium batteries [3]. Lithium batteries are usually composed of cathodes, anodes, liquid electrolytes, separators and so on [4]. The most commonly used anode material is graphite, since the direct use of Li metal as anode is prohibited due to the dendrite formation in the liquid electrolytes [5]. The liquid electrolyte is made from organic solvent containing a lithium salt, and the organic solvent is flammable [6]. Although the probability of catching fire is very low for a lithium cell, fires and explosions of lithium batteries have frequently been reported throughout the world due to the large quantity of used lithium batteries [7]. Because large number of lithium batteries are assembled together in EVs or power plants, fire or explosion in a lithium battery has the potential to cause a terrible catastrophe [8]. Safety issues have stunted the large-scale application of lithium

batteries [7]. Besides, the liquid electrolyte and separators occupy 40% volume and 25% weight of the lithium batteries, and thus the liquid electrolyte is an obstruction for increasing the energy density of lithium batteries [4]. Furthermore, the temperature range of operation is also limited by the liquid electrolytes [9].

All-solid-state lithium batteries with inorganic solid electrolytes and new structure designs are deemed to solve these problems [7]. Inorganic solid electrolytes have several advantages compared with liquid, polymer or gel electrolytes, such as improved safety, better thermal and chemical stability [7]. All-solid-state lithium batteries have a simpler structure due to the replacement of liquid electrolytes and separators by solid electrolytes, and the Li metal can be directly used as anode material, which permits the achievement of a higher energy density [7].

Inorganic solid electrolytes comprise oxide solid electrolytes and sulfide solid electrolytes [10]. Although the ion conductivity of sulfide solid electrolytes is higher, they have low chemical stability and are prone to react with moisture and oxygen [11,12]. Oxide solid electrolytes have been extensively studied due to their chemical stability [13,14]. In fact, perovskites with general formula $La_{2/3-x}Li_{3x}TiO_3$ are
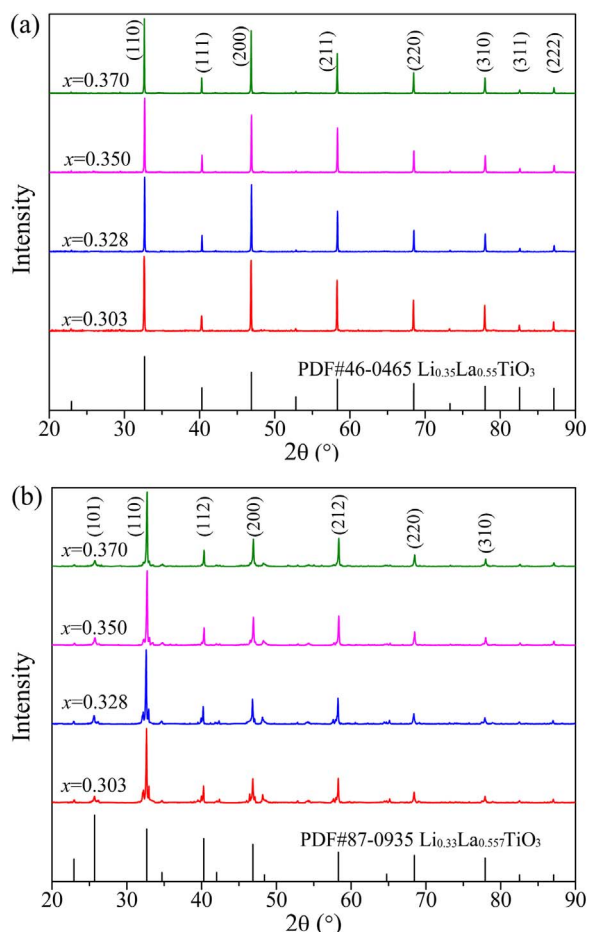

Fig. 1. XRD patterns of $Li_xLa_{0.557}O_3$ samples with various x values, (a) cubic structure, (b) tetragonal structure.
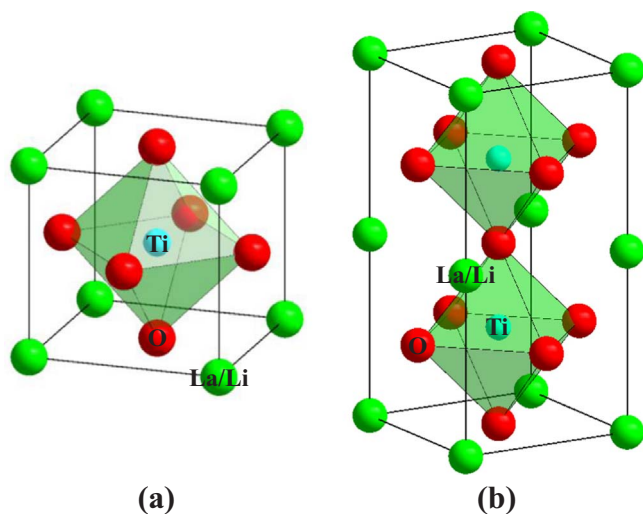

Fig. 2. Unit cells of crystal lattice, (a) cubic structure, (b) tetragonal structure.

among the best oxide solid electrolytes [15]. Numerous papers on this system have been reported since Inaguma et al. firstly reported a high conductivity in $Li_{0.34}La_{0.5}TiO_{2.94}$ [16–20]. Precisely, these compounds have the general formulation $Li_{3x}La_{2/3-x}V_{1/3-x}TiO_3$, where V is A site

vacancies [17]. A pure phase can be obtained in the domain $0.06 < x < 0.14$ [17]. The presence of vacancies at the A-site is favorable for fast Li ions diffusion [21].

$Li_{3x}La_{2/3-x}V_{1/3-x}TiO_3$ materials were found to exhibit a tetragonal, cubic, or orthogonal structure depending on the composition and the preparation conditions [17,20,22,23]. In addition to Li ion conductivity, the solid electrolytes are expected to exhibit high mechanical stability so that they could maintain structural integrity upon the dendrite formation of Li metal. Despite the key importance, the mechanical properties of $Li_{3x}La_{2/3-x}V_{1/3-x}TiO_3$ electrolytes have not received much attention. This paper reports the effects of the preparation condition, as well as the Li content on the micro-structure and properties. The mechanical properties (Young's modulus, hardness, fracture toughness) of both cubic and tetragonal structures are studied using the indentation method.

2. Experiments

The samples are synthesized by traditional solid reaction methods. Reagents of La_2O_3 (99.99%), Li_2CO_3 (99.9%) and TiO_2 (99.9%) are chosen as raw materials. The Li quantity in $Li_xLa_{0.557}TiO_3$ is chosen as 0.300, 0.330, 0.350 and 0.370 for the four samples, respectively. The raw materials are mixed in an agate jar for 6 h with ethanol as the milling agent. The mixed powder is calcined at 1100 °C for 8 h in air. The calcined powder is ball-milled in an agate jar for 10 h with ethanol as the milling agent. The mixture is dried at 120 °C in an oven, and then is uniaxially pressed into disks with a diameter of ∼ 10 mm and a thickness of ∼ 1.2 mm under a pressure of 180 MPa. The disks are sintered at 1200 °C for 10 h in air with a heating rate of 3 K min⁻¹, and the cooling rates are 10 K min⁻¹ and 3 K min⁻¹ for cubic and tetragonal structure, respectively. The crystal structure of samples is characterized by powder X-ray diffraction (XRD) (Ultima IV, Rigaku Corporation, Tokyo, Japan) with Cu-Kα radiation. The XRD patterns are recorded in a 2θ range of 20–90°. The lattice parameters are calculated with Rietveld refinement method. Microstructure is examined using field emission scanning electron microscopy (FE-SEM) (S-4800, Hitachi, Tokyo, Japan). The relative density is measured by Archimedes method. The chemical compositions are determined by inductively coupled plasma optical emission spectrometer (ICP-OES) (ICP-OES; iCAP6000, Thermo Fisher Scientific, Waltham, MA, USA). Assuming a spherical geometry the average grain size of the equivalent diameter was 2.9 ± 0.5 μm.

The Li ion conductivity is measured with alternating current (AC) impedance, where gold is deposited on both sides of polished samples. AC impedance spectra are measured using an impedance analyzer (Agilent 4294A, Agilent Technologies, Santa Clara, CA, USA) in the frequency range of 40–10⁶ Hz. The data are further analyzed by using Z-View impedance software. The Li ion conductivity is calculated from the equation:

$$\sigma = \frac{d}{AR} \tag{1}$$

where d is the disk thickness, A is the area of the disk and R is the sample resistance.

Young's modulus (E), hardness (H), and fracture toughness (K_{IC}) are measured with micro-indentation (CSM: coating and surface measurement, CH) [24]. The indentation fracture toughness K_{IC} is estimated via the relationship:

$$K_{IC} = k \left(\frac{E}{H} \right)^{1/2} \frac{F_m}{c^{3/2}} \tag{2}$$

where c is the crack length, F_m is the load. The constant $k = 0.016$ is selected for Vicker's tip [24]. The load of 1 N was applied for all indentations, and 25 indentation points are analyzed for each sample.