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Influence of operating temperature on $\text{Li}_2\text{ZnTi}_3\text{O}_8$ anode performance and high-rate charging activity of Li-ion battery

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ABSTRACT: $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) is synthesized as an anode material using a facile solid-state-reaction method, and its electrochemical storage properties at different temperatures is investigated along with its ultra-fast-charging activity. X-ray diffraction, Raman spectroscopy, and transmission electron microscopy analyses confirm the formation of spinel LZTO. The LZTO anode half-cell LIB delivers the highest reversible first discharge capacity of 181.3 mAhg^{-1} at a current rate of 0.1 Ag^{-1} . The maximum capacity of 106.97 mAhg^{-1} is obtained within 44 seconds when the LZTO battery is charged at an ultrafast charging rate of 10.0 Ag^{-1} . It shows superior high-rate long-cycle-life stability even at an ultra-high-charging rate, revealing a capacity retention of 106.28% after 100 cycles. The sustainability of the LZTO battery at different temperatures is investigated, and the best results are obtained in a temperature range of $10\text{-}40 \text{ }^\circ\text{C}$ with a capacity variation of about 30%. The electrochemical analyses reveal that the LZTO anode exhibits a capacitive-type storage mechanism at high scan rates. The superior fast

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4 charging performance of the LZTO anode is associated with its spinel structure, which forms
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6 tunnel-like pathways for easy Li ion diffusion.
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11 **KEYWORDS:** *Li₂ZnTi₃O₈ Anode, ultrafast rechargeable charging, Li ion battery*

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24 **1. Introduction**

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26 As high-performance batteries become essential in various industries and everyday life, great
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28 efforts have been made to enhance the battery performance features, such as power density,
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30 energy density, cycle life, cost-effectiveness, and charging time, without sacrificing the safety of
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32 the battery [1-4]. Among various battery technologies, Li-ion batteries (LIBs) are currently
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34 prevalent because of their outstanding advantages, such as higher power density, higher energy
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36 density, and longer cycle life compared with other rechargeable batteries. Nowadays there has
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38 been an enormous demand for high energy density batteries with fast charging ability for electric
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40 vehicles. However, before LIBs can be used in electric vehicles, greater challenges must be
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42 overcome: higher energy density and enhanced reaction kinetics for fast charging, thermal
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44 stability and high rate operation [5]. Because it takes much longer to charge a battery than to fill
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46 a tank with fuel, ultrafast charging may be the answer to wide use of LIBs in electric vehicles.
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48 Some studies have found that the synthesis of active nanomaterials and the incorporation of
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50 carbon into them improved the charging rate by reducing the diffusion distance and internal
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52 resistance [6,7]. In addition, a small modification of the active materials by doping with any
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4 other element could have the same effect in improving the charging rate by reducing the
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7 diffusion length. Ultrafast charging may add a stress to the battery, increasing the battery
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9 temperature. However, it is suggested that a battery can be charged ultra-fast up to 50% of its
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11 capacity and can be moderately charged up to the other half.
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14 Because of good safety and an excellent cycling stability, titanium (Ti)-based complex
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16 materials have been synthesized and investigated as a potential LIB anode. For the last two
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18 decades, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) has been vigorously investigated due to its demonstration of excellent
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20 cycling stability [8-12]. but its low theoretical capacity of 175 mAhg^{-1} , poor electric conductivity,
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22 and high intercalation potential of 1.5 V result in a reduction of the energy density [13, 114]. On
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24 the other hand, the Ti-based complex metal oxides, such as LZTO, have been investigated for
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26 LIBs, and they have demonstrated a large capacity and sound cycling stability [13, 14, 15]. The
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28 Li and zinc (Zn) atoms in the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ structure are located in the tetrahedral sites that form a
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30 tunnel-like pathway for an easy Li-ion insertion process. The theoretical LZTO-structure
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32 capacity of 227 mAhg^{-1} is higher than that of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) and its discharge
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34 voltage of 0.5 V is lower than that of the Li/Li⁺ couple.^{15,16} M-doped $\text{Li}_2\text{ZnTi}_3\text{O}_8$ compounds,
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36 where M is silver (Ag), aluminum (Al), copper (Cu), nickel (Ni) and C, have also been
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38 investigated to effectively improve electrochemical performance by enhancing electronic
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40 conductivity and Li-ion diffusivity [17-21]. So far, the testing of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ based LIB anodes
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42 has included the following synthetic strategies: (i) preparation of nano-sized particles, (ii) metal-
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44 ion doping and (iii) coating with conductive materials. Moreover, the electrochemical
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46 performance, cycle life, and safety of the LIBs are affected by the operation or storage
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48 temperatures. Fast lithiation/delithiation is one of the most important electrochemical properties
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50 of LIBs for high-power applications. The current reports on the LZTO LIB, however, only deal
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4 with its operation at room temperature, and its ultrafast-charging activity has not yet been
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6 studied.

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8 In this study, LZTO was synthesized as an LIB anode material via a solid-state-reaction
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10 method, and its battery performance was tested at different temperatures ranging from -5 to 55
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12 $^{\circ}\text{C}$. The measured maximum-charge storage capacity at a rate of 0.1 Ag^{-1} was $\sim 181 \text{ mAhg}^{-1}$ at
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14 $25 \text{ }^{\circ}\text{C}$ and $\sim 227 \text{ mAhg}^{-1}$ at $40 \text{ }^{\circ}\text{C}$ tolerate the ultra-high-charging rates of 1.0 , and 10.0 Ag^{-1}
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16 delivering the specific capacities of ~ 150 and $\sim 107 \text{ mAhg}^{-1}$.
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23 24 **2. Experimental**

25 26 **2.1. Material Preparation**

27 The LZTO anode material was prepared using a solid-state-reaction method for which
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29 lithium carbonate (Li_2CO_3), zinc oxide (ZnO), and titanium dioxide (TiO_2) served as the raw
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31 materials. These three precursor materials were mixed at a molar ratio of 2:1:3 and were ground
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33 for 3 hr using an agate mortar. The 5 % extra lithium carbonate was used in order to compensate
34
35 lithia loss during synthesis process. The powder was then heated in a muffle furnace at $700 \text{ }^{\circ}\text{C}$
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37 for 12 hr in air before it was cooled to room temperature. The obtained product was again ground
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39 for 30 min and heated at $900 \text{ }^{\circ}\text{C}$ for 12 hr in air; then it cooled down naturally to room
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41 temperature. The final product was filtered using a sheave with a $45\text{-}\mu\text{m}$ pore size to remove the
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43 unevenly sized particles.
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54 55 **2.2. Characterization**

56 The crystallinity of the prepared sample was characterized using X-ray powder diffraction
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58 (XRD) spectroscopy (with PANalytical's X'pert PRO system, The Netherlands) with $\text{Cu K}\alpha$
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4 radiation (wavelength $\lambda = 1.54056 \text{ \AA}$). Micro (μ)-Raman spectroscopy was performed at room
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6 temperature using an argon-ion (Ar^+) laser with an excitation wavelength of 532 nm. The
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8 structural properties of the sample were investigated using transmission electron microscopy
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10 (TEM) (JEM 2010, JEOL Ltd., Japan) with an energy dispersive X-ray (EDX) detector (Oxford
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12 Instruments, U.K), high-resolution transmission electron microscopy (HR-TEM), and selected
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14 area electron diffraction (SAED). The acceleration voltage and the camera length were 300 kV
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16 and 255.8 mm, respectively. The electrochemical properties of the LZTO anode were studied
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18 using cyclic voltammetry (CV), galvanostatic charge-discharge, and alternating-current (ac)
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20 impedance analysis for which the (MPG-2) battery cycler (Bio-Logic Science Instruments,
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22 France) was employed. Temperature-dependent battery performance measurement was
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24 performed in a specially designed oven within an error of $\pm 0.1^\circ$.
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34 **2.3. Battery fabrication**

35 The battery performance of the LZTO anode was investigated using a CR2032-type coin-cell
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37 assembly. The slurry was prepared using $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (80%), carbon black (10%), and a binder
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39 (10% polyvinylidene fluoride in N-methyl-2-pyrrolidone). The LZTO anode electrode was
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41 uniformly coated on Cu foil using a doctor-blade technique. A half-cell was assembled in an
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43 argon (Ar)-filled glove-box using an LZTO disk (15 mm) as a working electrode and Li metal as
44
45 the counter electrode. A 1M LiPF_6 solution that was dissolved in a mixture of ethylene carbonate
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47 and dimethyl carbonate with a 1:1 volume ratio was used as the electrolyte.
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3. Results and discussion

3.1. Structural and microstructural analysis

The XRD pattern of the LZTO sample is shown in Fig. 1 (a). The main diffraction peaks appear at 30.16° , 35.45° , 43.25° , 56.89° , and 62.53° , and these correspond to the (220), (113), (004), (115), and (404) planes of the cubic-spinel structure of LZTO (JCPDS-44-1037), respectively [13, 14, 15]. Moreover, although some of the minor impurity peaks that are associated with rutile titanium dioxide (TiO_2) were also detected at 27.46° and 54.36° , their contribution was very small compared with that of the LZTO. The crystal structure of LZTO is described as $(\text{Li}_{0.5}\text{Zn}_{0.5})^{\text{tet}}[\text{Li}_{0.5}\text{Ti}_{1.5}]^{\text{oct}}\text{O}_4$ [13, 14, 22]. Thus, the Zn and Li:Ti (1:3) atoms are placed in the tetrahedral and octahedral sites, respectively. The Li and Zn atoms that are located in the tetrahedral sites form a three-dimensional tunnel-like network that is beneficial for Li-ion (Li^+) intercalation [15, 16]. Figure 1(b) shows the Raman spectrum of the LZTO sample. The Raman peaks at 403 and 439 cm^{-1} correspond to the Zn-O and Li-O stretching modes of vibration of ZnO_4 and LiO_4 tetrahedra, respectively. The higher-frequency peak at 716 cm^{-1} is associated with the Ti-O symmetric stretching vibration of the TiO_6 octahedral group [18]. The other peaks are associated with the stretching modes of cation-O bonds and the bending of O-cation-O (below 350 cm^{-1}). The XRD and Raman analyses were consistent, revealing the formation of a high-quality LZTO film.

A scanning-electron-microscopy (SEM) image of the LZTO sample is shown in Fig. 1 (c). The LZTO sample has a granular morphology with different grain sizes. The constituent elements of the LZTO sample were determined using energy dispersive X-ray spectroscopy (EDX), as shown in Fig. 1 (d). The inset of Fig. 1 (d) shows the relative atomic ratios of the

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4 major constituent elements: Zn, Ti, and O. The chemical composition of the LZTO film is
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7 $\text{Li}_x\text{Ti}_{3.7}\text{ZnO}_{9.6}$.

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9 The LZTO powder was further subjected to the TEM, HR-TEM and SAED studies to assess
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11 its microstructural properties and to conduct a qualitative phase analysis. Figure 2 shows the
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13 TEM, HRTEM and SAED analyses of the LZTO powder. The large-scale TEM images shown in
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15 Figs. 2 (a) and (b) confirm its granular micro-size morphology, and this is consistent with the
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17 SEM image in Fig. 1(c). Clear lattice-fringe regions are observed in the HR-TEM image (Figs.
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19 1(c)), revealing its good crystallinity. The lattice distances of the (113), (220), and (110) planes
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21 (d_{113} , d_{220} , d_{110}) of the selected area (marked with a box in Fig. 2 (d)) are $2.50 \pm 0.1 \text{ \AA}$, 2.92 ± 0.1
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23 \AA , and $5.9 \pm 0.1 \text{ \AA}$, respectively (Fig. 2 (e)). The observed lattice distances match well with the
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25 standard lattice distances of the cubic-LZTO structure [15]. Figure 1(f) shows a typical SAED
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27 pattern, which can be readily indexed to the LZTO lattice configuration [22]. The images of the
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29 moire fringes are shown in Fig. S1 (Supporting Information). The presence of mixed moire
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31 fringes, including translation and rotation, indicates the layered features of the prepared LZTO
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33 material [23].
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39 40 41 42 43 **3.2. Cyclic voltammetry**

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45 Figure 3(a) shows the first three CV curves of the LZTO electrode in the half-cell
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47 configuration at room temperature. The electrochemical behavior of the first cycle is different
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49 from that of the subsequent cycles, and this is because of the polarization of either the cell or the
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51 local structural changes [24]. The CV curves show a pair of cathodic ($1.22 \text{ V vs. Li/Li}^+$) and
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53 anodic ($1.83 \text{ V vs. Li/Li}^+$) peaks that are associated with the phase transition between the spinel
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55 and the rock salt [14]. The anodic peak shifts toward a higher positive potential with an
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4 increasing number of cycles, while the cathodic peak remains unchanged. An additional
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6 reduction peak around 0.5 V (vs. Li/Li⁺) corresponds to the multiple restorations of the Ti⁴⁺ ions
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8 [24-26]. During the anodic sweep, the peak around 2.5 V (vs. Li/Li⁺) is likely due to the
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10 decomposition of the amorphous lithium oxide (Li₂O) [22].
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12 13 14 15 16 **3.3 Galvanostatic charge-discharge properties**

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18 A comprehensive understanding of battery performance characteristics at different
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20 operating temperatures is important because the LZTO material exhibits different kinetics under
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22 different environments. Here, the galvanostatic charge-discharge properties of the LZTO
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24 electrode were investigated at different temperatures ranging from -5 to 55 °C. Figure 3(b)
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26 shows the first galvanostatic charge-discharge curves that were measured at a current density of
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28 0.1 Ag⁻¹ and at various temperatures. The charge-discharge characteristics at different
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30 temperatures are similar in shape, suggesting the similarity of the electrochemical reactions.
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32 They show voltage plateaus in the range of 0.2 to 0.7 V versus the Li/Li⁺ during the lithiation and
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34 in the range of 1.4 to 1.7 V versus the Li/Li⁺ during delithiation. The voltage plateaus were
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36 widened at high temperatures. The difference between the lithiation and delithiation plateaus
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38 becomes smaller with increasing temperatures. This voltage plateau temperature-dependent
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40 behavior is a result of the kinetic effect of the material. The reduced voltage difference between
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42 the lithiation-delithiation plateaus at 55 °C is due to the faster kinetics, and the direct evidence of
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44 this is obtained from the temperature-dependent electrochemical impedance-spectroscopy (EIS)
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46 data (Fig. S2 in the Supporting Information). The reduced charge-transfer resistance values at
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48 higher temperatures indicate the kinetic effect of the material.
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4 The initial discharge-capacity values of the LZTO electrode are 131.2, 131.1, 183.3, 227.3
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6 and 233.1 mAhg⁻¹ at -5, 10, 25, 40 and 55 °C, respectively. A similar trend is evident in terms
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8 of the charge capacity, as shown in Fig. S3 (Supporting Information). The charge-discharge
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10 curves for the first five cycles measured at 25 °C and at 0.1 Ag⁻¹ are shown in Fig. S4
11
12 (Supporting Information). The initial discharge capacity of 183.3 mAhg⁻¹ decreases to 147.1
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14 mAhg⁻¹ at the fifth cycle. The comparative temperature-dependent capacity retention of the
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16 LZTO electrode is shown in Fig. 3(c). The maximum capacity values are obtained at 40 °C for
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18 the charge process and at 55 °C for the discharge process. The capacity variation in the given
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20 operating temperature range is within 30%.
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29 **3.4. Rate capability and long-cycle electrochemical stability**

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31 The LZTO electrode was cycled at various charge-discharge current densities for five
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33 cycles to investigate the rate performance. Figure 3(d) shows the cycling-rate performances
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35 measured at 25 and 40 °C. The cycling performances measured at the other temperatures of -5,
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37 10, and 55 °C are shown in Fig. S5 (Supporting Information). The initial charge capacity at 0.1
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39 Ag⁻¹ is 183.3 mAhg⁻¹ at 25 °C and 227.3 mAhg⁻¹ at 40 °C, but at 5 Ag⁻¹, it decreases to 23.5 and
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41 16.7 mAhg⁻¹, respectively. The initial capacity loss (irreversible capacity) between the first and
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43 second discharges of the electrode is likely due to the irreversible decomposition of the
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45 electrolyte and the formation of a solid electrolyte interface (SEI) [24, 27]. As the applied current
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47 was set back to 1 Ag⁻¹, the specific capacity of the LZTO electrode was recovered to 105% at 25
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49 °C and 111% at 40 °C, and this increased specific capacity might be due to the activation of the
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51 electrode after the initial cycling. The LZTO electrode at 25 °C shows an improved rate
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4 capability at various rates compared with the 40 °C test. On the other hand, the LZTO electrode
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6 tested at -5, 10, and 55 °C exhibits unstable performances (Fig. S5) at each rate of the applied
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8 current density.
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11 The rate performance and the long-cycle electrochemical stability at 25 °C was further
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13 tested for up to 500 charge-discharge cycles at a high rate of 1 Ag⁻¹. Figure 4(a) shows the
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15 cycling stability and the Coulombic efficiency at 1 Ag⁻¹ for 500 charge-discharge cycles. The
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17 specific capacity and Coulombic efficiency of the first cycle is 56.83 mAhg⁻¹ and 99%,
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19 respectively. The overall Coulombic efficiency of the electrode is larger than 98% over the 500
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21 charge-discharge cycles, demonstrating that the sample has good cycling performance and
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23 reversibility. The obtained Coulombic efficiency of the LZTO electrode is comparable to that of
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25 commercial anodes and is much higher than that of the carbon anode (60%) [28-30]. After the
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27 first few cycles, the capacity increases quickly up to 100 charge-discharge cycles, and this is
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29 presumably because of the activation of the electrode, the electrolyte decomposition, or the SEI
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31 formation [24, 31]. The capacity decreases up to 250 cycles, and it then becomes stable over 500
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33 charge-discharge cycles. The samples have a capacity retention of ~ 64% after the 500 charge-
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35 discharge cycles with a capacity fading of only 0.072% per cycle. The observed rolling-cycling
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37 performance at a high rate could be due to the formation of a polymeric/gel-like layer during the
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39 fast-charging/discharging processes [32].
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49 EIS was performed to quantitatively evaluate the electrochemical behavior of the LZTO
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51 electrode before and after the cycling. Figure 4(b) shows the Nyquist plot and the fitting curves
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53 (lines). The inset shows the equivalent circuit diagram used for the fitting. The Nyquist plot
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55 consists of a semi-circle in the high-frequency region and a straight line in the low-frequency
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57 region. The straight line portion is associated with the diffusion of the Li⁺ to the electrode. The
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4 Warburg impedance is referred to as W_{0t} , R_s is the solution resistance, R_{ct} is the charge-transfer
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7 resistance, and the CPE is the constant phase element. The fitted impedance parameters are listed
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9 in Table I. The pre-cycling initial R_{ct} of the electrode is 135 Ω , but it decreases to 57 Ω after
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11 cycling. The considerably improved post-cycling R_{ct} is mainly due to the increase in the
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13 electrical conductivity during the lithiation/delithiation and the enhanced electrode-material
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15 contact area. The origin of this activation step is the delayed wetting of the electrolyte into the
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17 composite electrode [33].
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24 **3.5. Fast-charge/slow-discharge characteristics**

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26 The LZTO electrode was tested at the fast charging rates of 1.0 and 10.0 Ag^{-1} , and it was
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28 discharged at 0.1 Ag^{-1} for 100 consecutive charge-discharge cycles. The typical charge-discharge
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30 profile of the LZTO electrode that was charged at 1.0 Ag^{-1} and discharged at 0.1 Ag^{-1} is shown
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32 in Fig. 5(a). The shape of the charge profile is similar to that of the voltage profile during the
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34 slow-charging process (Fig. 3(b)). Figure 5(b) shows the charging curves of the LZTO electrode
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36 at the current densities of 1.0 and 10.0 Ag^{-1} , and Figure 5(c) shows the discharging curves when
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38 the electrodes are discharged at 0.1 Ag^{-1} . The shapes of the discharge curves (Fig. 5 (c) charged
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40 at 1.0 and 10.0 Ag^{-1}) are very similar to those of the curves that are charged at 0.1 Ag^{-1} , as
41
42 shown in Fig. 3(b). The results obtained from the fast-charging and slow-discharging
43
44 experiments are summarized in Table-II. The electrode that is charged at 1.0 Ag^{-1} exhibits the
45
46 maximum specific capacity of 149.88 mAhg^{-1} , but it decreases to 106.97 mAhg^{-1} at 10.0 Ag^{-1} .
47
48 Figure 5(d) shows the long-term specific discharge capacity and the capacity retention as a
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50 function of the number of cycles when the electrode is charged at 1.0 and 10.0 Ag^{-1} . At an ultra-
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52 high-charging rate of 10.0 Ag^{-1} , the specific capacity and the capacity retention increases
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4 gradually during the first 50 charge-discharge cycles, and then they decrease over the next 100
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7 charge-discharge cycles. A similar trend is observed when the electrode is charged at 1.0 Ag^{-1} .
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9 The maximum capacity of 106.97 mAhg^{-1} at 10.0 Ag^{-1} is achieved with a very short charging
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11 time of 44 s (Table-II). The electrode that is charged at 1.0 and 10.0 Ag^{-1} shows excellent
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13 capacity-retention values of 96.98 and 106.28%, respectively, demonstrating an excellent
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15 electrode sustainability, even at ultra-high-charging rates.
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22 **3.6. Capacitive and diffusion-limited contributions**

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24 To understand the electrochemical performance, the reaction kinetics of the LZTO electrode
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26 was studied using CV at various scan rates ranging from 0.2 to 5.0 mVs^{-1} , as seen in Fig. 6 (a).
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28 The observed total capacity is the sum of the capacitive and diffusion-limited contributions. The
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30 stronger and broader scan-rate-related cathodic and anodic peaks are characteristic features of the
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32 large polarization that occurs at high scan rates [34]. The anodic and cathodic currents (i) obey
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34 the power-law relationship with the scan rate (v) as follows [35]
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$$37 \quad i = a \times v^b \quad (1)$$

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39 where a and b are the fitting parameters. The kinetics of the Li^+ intercalation during during the
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41 cathodic and anodic are analyzed by plotting the $\log(i)$ - $\log(v)$ curves. Figure 6(b) shows the
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43 $\log(i)$ - $\log(v)$ characteristics. The estimated b (slope) values for the cathodic and anodic currents
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45 are 0.68 and 0.71, respectively, indicating that the reaction current is obtained from two
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47 phenomena, the intercalation and the surface capacitance. (If the slope is less than 0.5 it is
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49 diffusion controlled and if the slope is more than 1 it is capacitive-type storage mechanism). To
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51 quantitatively estimate the capacitive and diffusion-controlled contributions, the following
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53 equation can be used [34, 35].
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$$i = k_1 \times v + k_2 \times v^{1/2} \quad (2)$$

where k_1 and k_2 are the fitting parameters. The “ $k_1 \times v$ ” is the capacitive contribution and “ $k_2 \times v^{1/2}$ ” represents the diffusion-controlled contribution. The obtained k_1 and k_2 values are 0.8417 and 0.1823, respectively (Fig. S6 in Supplementary Information). Figure 6(c) shows the capacitive ($k_1 \times v$) and diffusion-controlled ($k_2 \times v^{1/2}$) contributions in the CV curve measured at 0.2 mV/s. Figure 6(d) shows the calculated contribution ratio between the capacitive and diffusion-controlled portions, as a function of scan rate v . As anticipated, the capacitive contribution increases linearly with an increasing scan rate, but the opposite is true for the diffusion-controlled contribution.

4. Conclusion

We successfully synthesized LZTO via a solid-state-reaction method and investigated the material as an anode electrode for LIB applications. The LZTO electrode exhibited high reversible-capacity values of 181.3 mAhg⁻¹ at 25 °C and 227.3 mAhg⁻¹ at 40 °C, rate performance, and sound kinetic characteristics at different operating temperatures. The electrode exhibited good sustainable electrochemical behavior at different operating temperatures. The LZTO electrode had a good capacity retention of 64% after 500 charge-discharge cycles with a capacity fading of only 0.072% per cycle. An excellent Coulombic efficiency larger than 98% was obtained; this value is comparable to those of the commercially available anodes and much higher than those of carbon-based anodes such as graphite (60%). The LZTO anode delivered a 106.97 mAhg⁻¹ capacity when it was charged at an ultra-fast rate of 10.0 Ag⁻¹ with a very short charging time of 44 s.

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Acknowledgments

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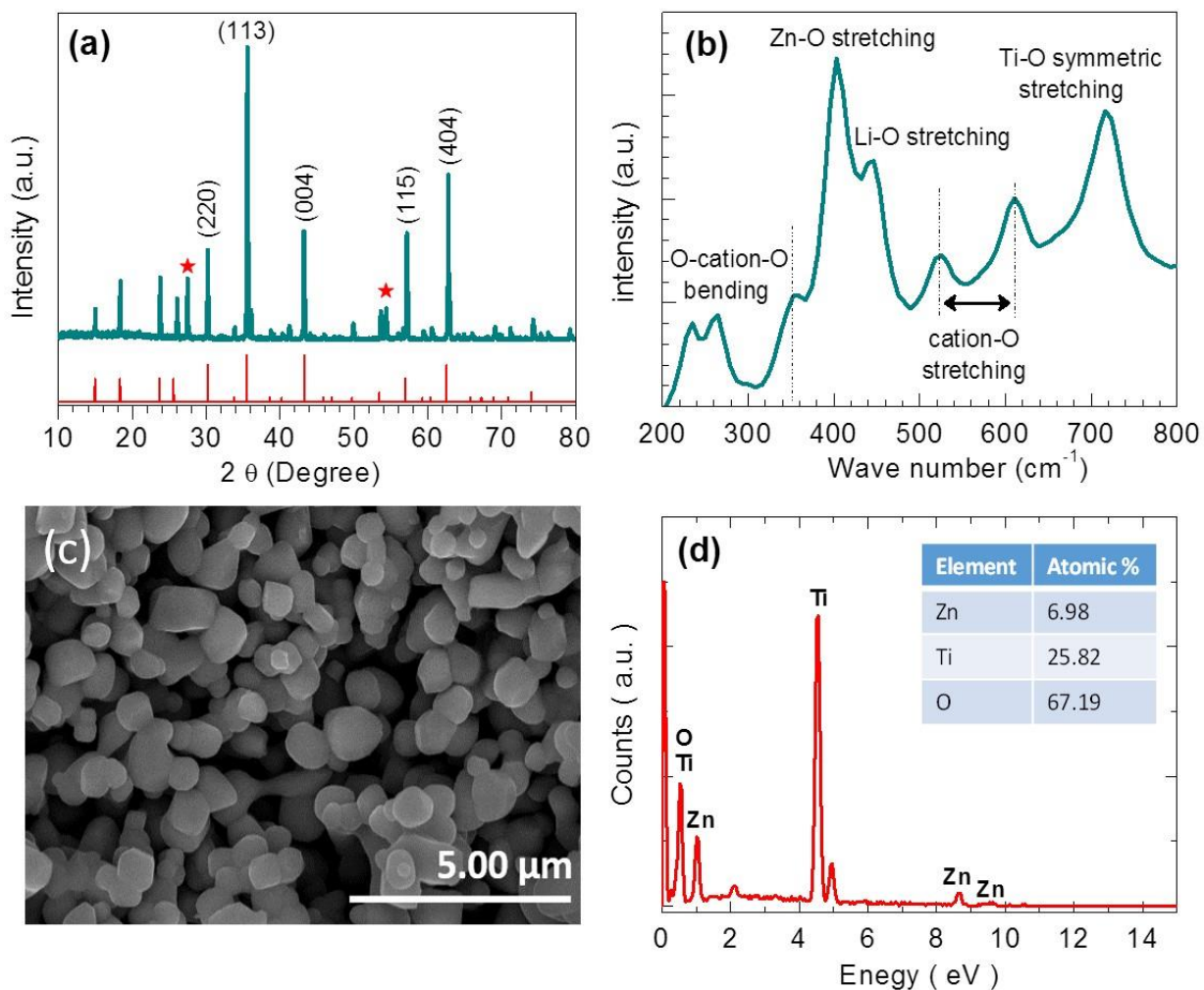


Fig. 1. (a) X-ray-diffraction (XRD) pattern of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) sample synthesized using a solid-state-reaction method, confirming the formation of the cubic-spinel LZTO structure JCPDS 44-1037. (b) Raman spectrum, (c) SEM image showing that the LZTO has a granular morphology. (d) Energy dispersive X-ray analysis spectra of the LZTO.

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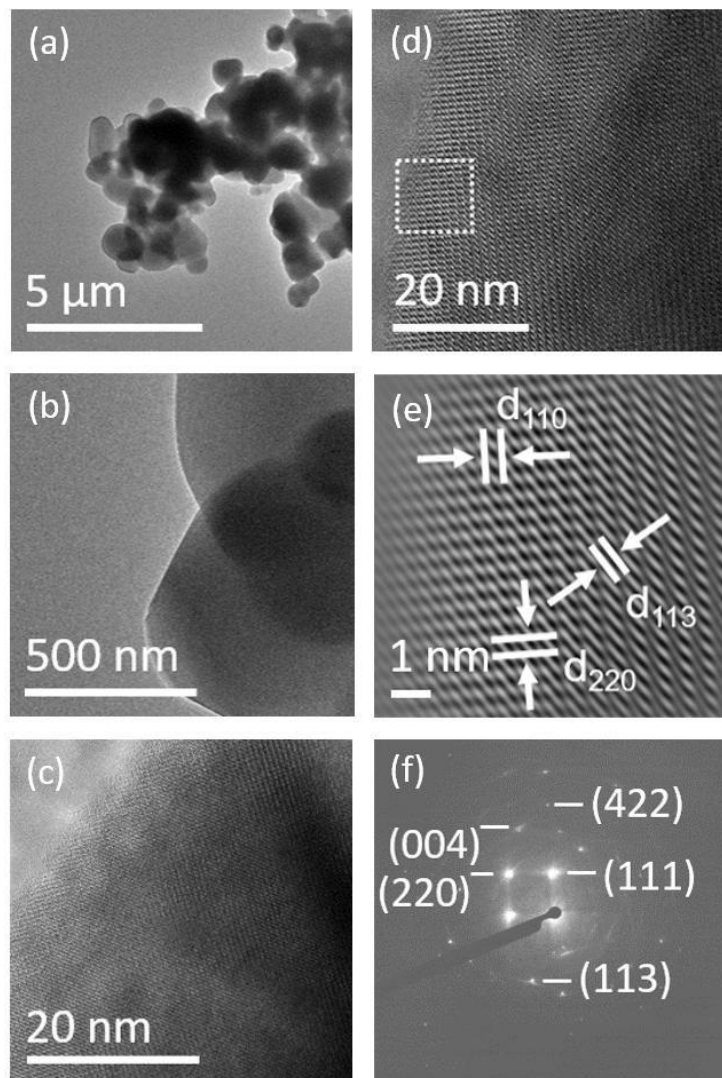


Fig. 2. (a and b) Transmission-electron-microscopy (TEM) and (c) high-resolution transmission-electron-microscopy (HRTEM) images of the LZTO powder. These images reveal that the particles are homogenous and are micro-sized, and the continuous lattice fringes that were detected in the HRTEM image confirmed that the product is in a highly crystalline state; The lattice distances for the selected area in (d) and that are shown the d_{113} , d_{220} , and d_{110} planes in (e) are 2.50 ± 0.1 Å, 2.92 ± 0.1 Å, and 5.9 ± 0.1 Å for the (113), (220), and (110) planes, respectively, (f) The crystallographic planes were obtained from the selected-area-electron-diffraction (SAED) patterns and are associated with the JCPDS 44-1037.

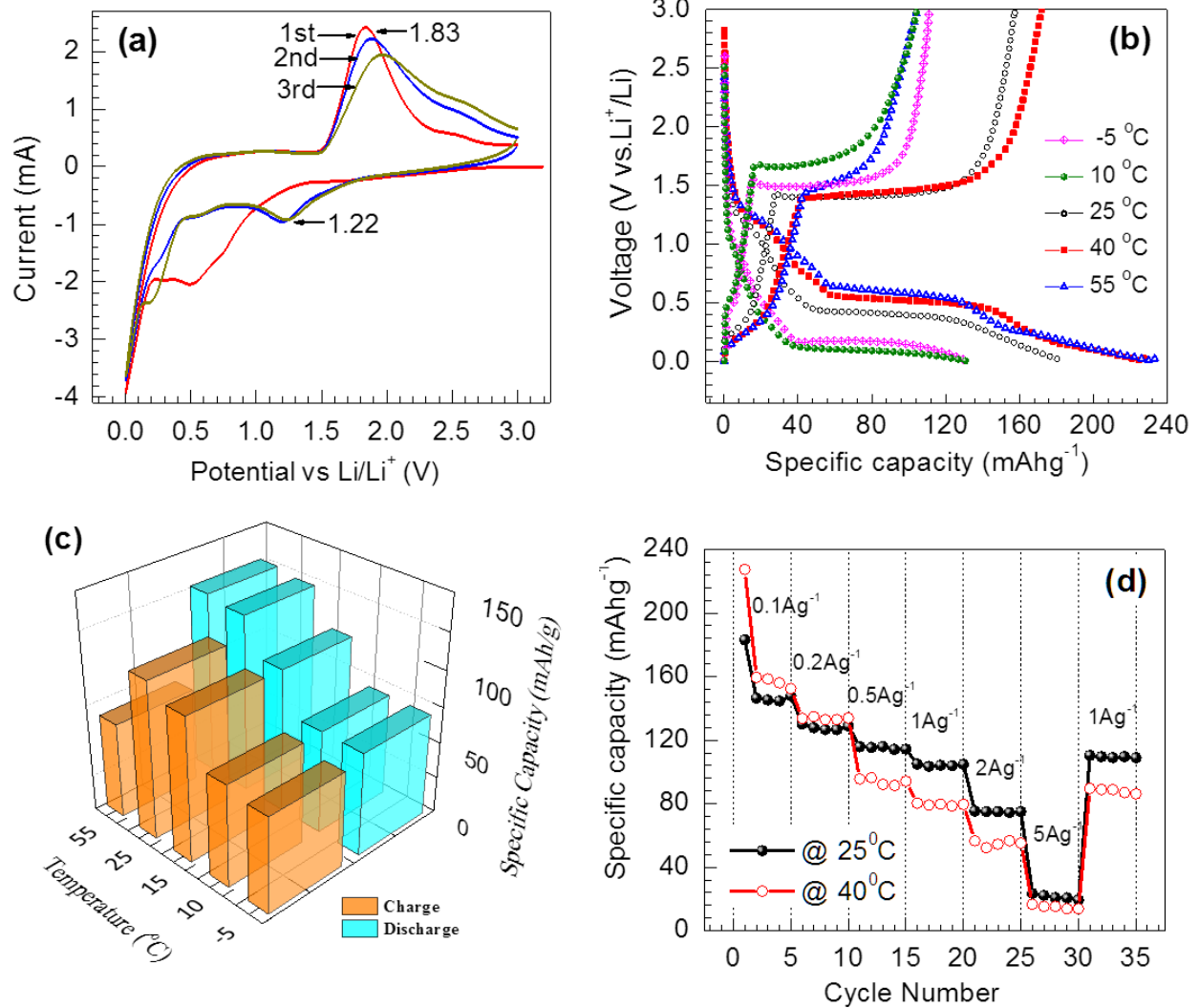


Fig. 3. (a) First three cyclic-voltammety (CV) curves of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) electrode in the half-cell configuration measured at an operating temperature of 25 °C. (b) First galvanostatic charge-discharge characteristics of the LZTO measured at different temperatures from -5 to 55 °C. (c) temperature-dependent retention of the charge-discharge capacity of the LZTO electrode. (d) Rate performances of the LZTO electrode.

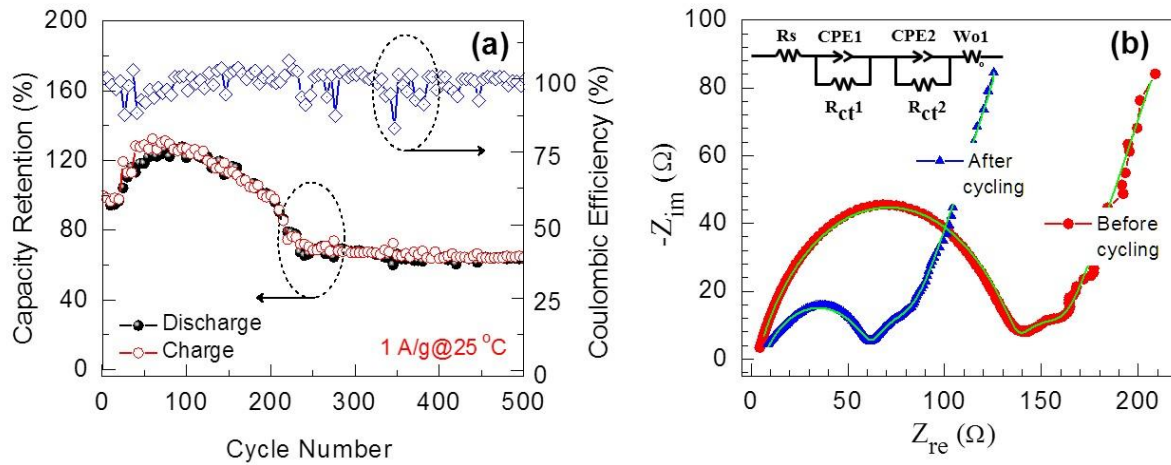


Fig. 4. (a) High-rate long-life-cycling performance and Coulombic efficiency of the LZTO electrode at 25 °C for up to 500 charge-discharge cycles at 1 Ag⁻¹. (b) Nyquist plots before and after the 500th charge-discharge cycling test. The lines represent the fitting curves using the equivalent-circuit diagram (inset).

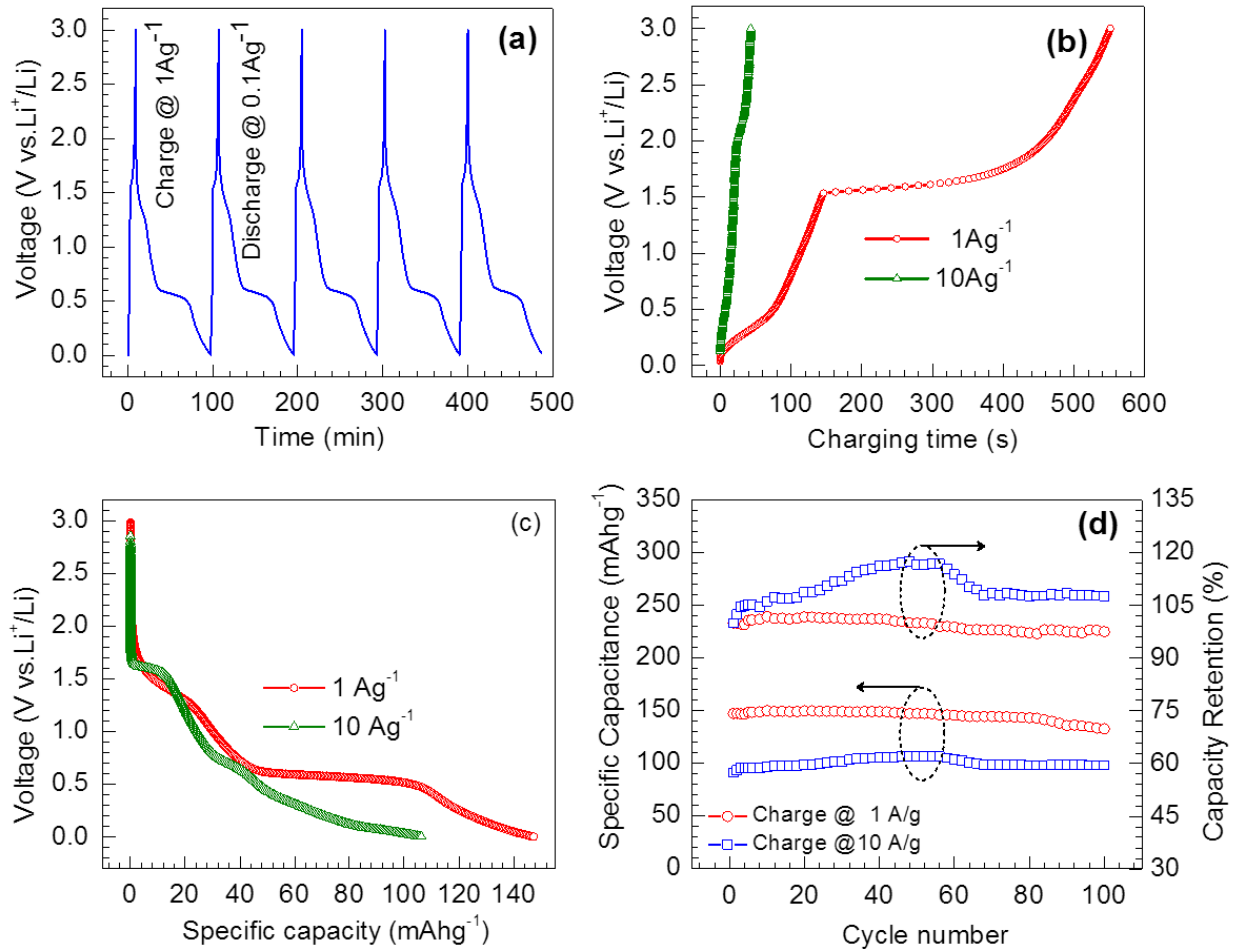


Fig. 5. (a) The typical charge-discharge profile of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) electrode that was charged at a fast rate of 1.0Ag^{-1} and discharged at a slow rate of 0.1Ag^{-1} . (b) Galvanostatic-charge profile of the LZTO electrode at current densities of 1.0, and 10.0Ag^{-1} . (c) Galvanostatic-discharge (at the rate of 0.1Ag^{-1}) profile of the LZTO electrode those were charged at 1.0 and 10.0Ag^{-1} . (d) Specific discharge capacity and the capacity retention as a function of the number of cycles for 100 charge-discharge cycles when the electrodes were charged at the fast rates of 1.0 and 10.0Ag^{-1} .

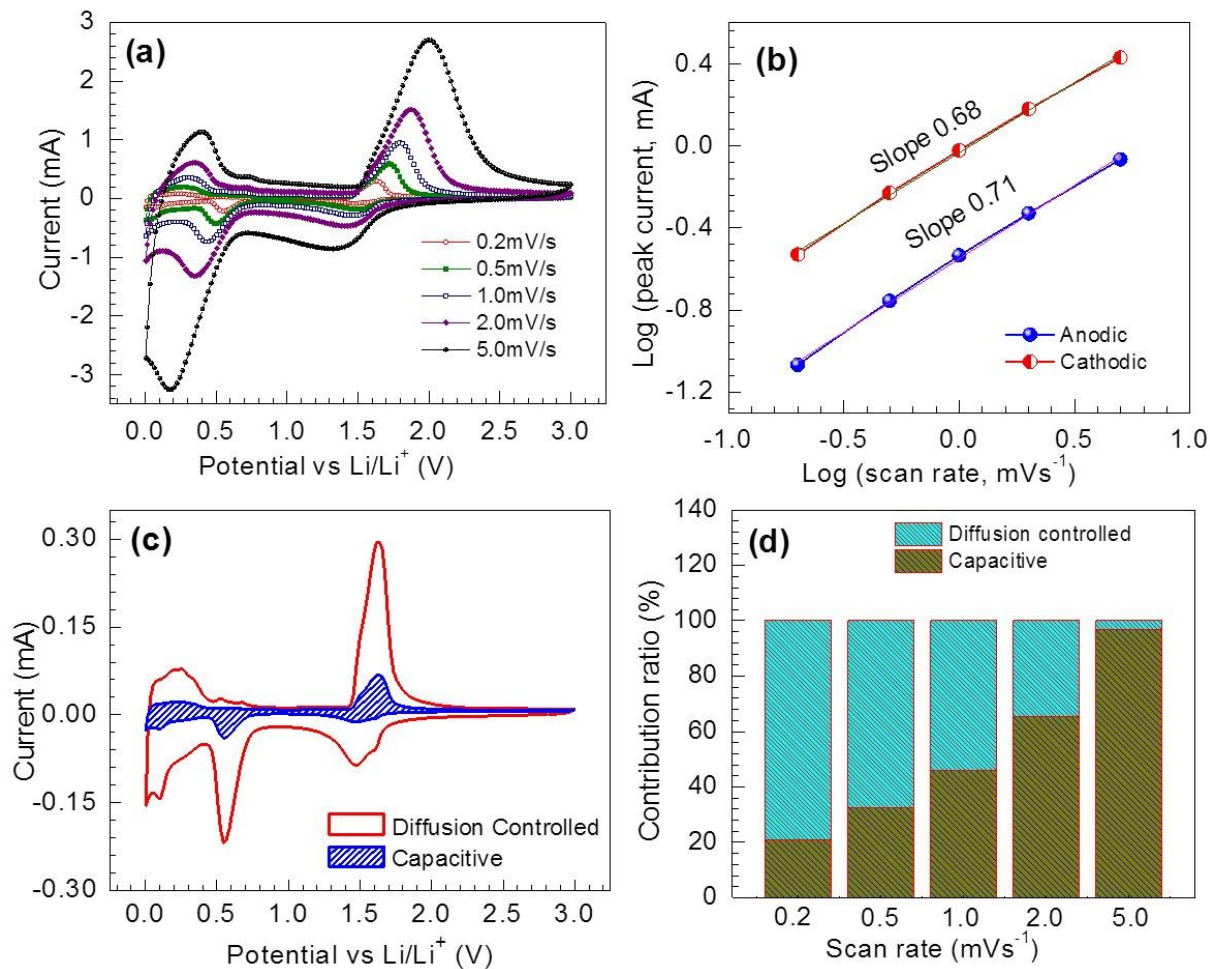


Fig. 6. (a) Cyclic-voltammetry (CV) curves at different scan rates 0.2, 0.5, 1.0, 2.0, and 5.0 mVs⁻¹. (b) The slope of log (*i*) vs log (*v*) curves gives the information about the mechanism exhibiting into the electrode. (If the slope is less than 0.5 it is diffusion controlled and if the slope is more than 1 it is controlled by the capacitive-type storage mechanism) (c) Capacitive and diffusion-controlled currents as a function of potential (vs. Li/Li⁺) at the scan rate of 0.2 mVs⁻¹. (d) Comparison of the capacitive-charge storage and the diffusion-controlled charge storage at different scan rates.

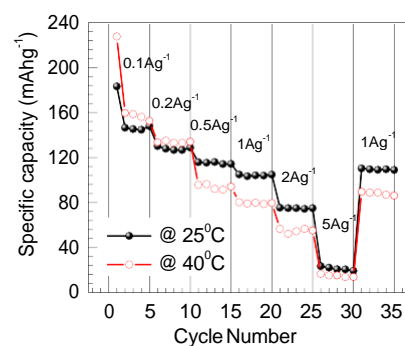
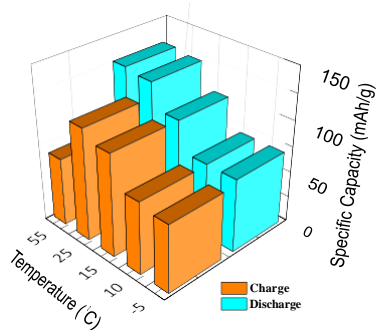
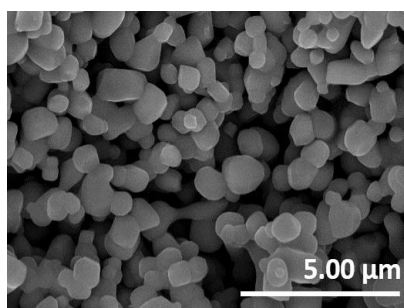
	Before test	After 500 cycles
$R_s (\Omega)$	3.25	6.03
$R_{ct1} (\Omega)$	135	57
$R_{ct2} (\Omega)$	22	13.76
$CPE1 (\mu F)$	0.743	0.621
$CPE1 (\mu F)$	0.725	0.910

Table I. Impedance parameters of the $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) electrode before and after the 500th charge-discharge cycle.

Current density A cm^{-2}	Charging time (sec)	Discharge capacity mAhg^{-1}	Capacity retention after 100 cycles (%)
1.0	591	149.88	97.54
10.0	44	106.97	106.28

Table II. Galvanostatic charge-discharge results and capacity retention that were obtained from the fast-charging and slow-discharging experiments.

Table of content



We developed an ultrafast rechargeable $\text{Li}_2\text{ZnTi}_3\text{O}_8$ (LZTO) anode for lithium ion battery application. The half-cell LZTO battery delivers the highest reversible first discharge capacity of 181.3 mAhg⁻¹ at a current rate of 0.1 Ag⁻¹ (0.1C). The maximum capacity of 106.97 mAhg⁻¹ was obtained within 44 seconds when the LZTO battery was charged at an ultrafast charging rate of 10.0 Ag⁻¹ (10 C). It showed excellent capacity-retention of 106.28%, suggesting an excellent electrode sustainability, even at ultra-high-charging rates.