



Improved ionic conductivity of lithium-zinc-tellurite glass-ceramic electrolytes



W. Widanarto^{a,*}, A.M. Ramdhan^a, S.K. Ghoshal^b, M. Effendi^a, W.T. Cahyanto^a, Warsito^c

^a Department of Physics, FMIPA, Universitas Jenderal Soedirman, Jl. dr. Soeparno 61, Purwokerto 53123, Indonesia

^b Department of Physics, AMORG, Faculty of Science, Universiti Teknologi Malaysia, Johor Bahru, Skudai 81310, Malaysia

^c Department of Physics, FMIPA, Universitas Lampung, Jl. Prof. Dr. Soemantri Brodjonegoro 1, Bandar Lampung 35145, Indonesia

ARTICLE INFO

Article history:

Received 13 April 2017

Received in revised form 13 June 2017

Accepted 1 July 2017

Available online 4 July 2017

Keywords:

Zinc-tellurite

Glass-ceramics

X-ray diffraction

Ionic conductivity

Lithium oxide

ABSTRACT

An enhancement in the secondary battery safety demands the optimum synthesis of glass-ceramics electrolytes with modified ionic conductivity. To achieve improved ionic conductivity and safer operation of the battery, we synthesized Li_2O included zinc-tellurite glass-ceramics based electrolytes of chemical composition $(85-x)\text{TeO}_2 \cdot x\text{Li}_2\text{O} \cdot 15\text{ZnO}$, where $x = 0, 5, 10, 15$ mol%. Samples were prepared using the melt quenching method at 800°C followed by thermal annealing at 320°C for 3 h and characterized. The effects of varying temperature, alternating current (AC) frequency and Li_2O concentration on the structure and ionic conductivity of such glass-ceramics were determined. The SEM images of the annealed glass-ceramic electrolytes displayed rough surface with a uniform distribution of nucleated crystal flakes with sizes less than $1\ \mu\text{m}$. X-ray diffraction analysis confirmed the well crystalline nature of achieved electrolytes. Incorporation of Li_2O in the electrolytes was found to generate some new crystalline phases including hexagonal $\text{Li}_6(\text{TeO}_6)$, monoclinic $\text{Zn}_2\text{Te}_3\text{O}_8$ and monoclinic $\text{Li}_2\text{Te}_2\text{O}_5$. The estimated crystallite size of the electrolyte was ranged from ≈ 40 to $80\ \text{nm}$. AC impedance measurement revealed that the variation in the temperatures, Li_2O contents, and high AC frequencies have a significant influence on the ionic conductivity of the electrolytes. Furthermore, electrolyte doped with 15 mol% of Li_2O exhibited the optimum performance with an ionic conductivity $\approx 2.4 \times 10^{-7}\ \text{S cm}^{-1}$ at the frequency of 54 Hz and in the temperature range of 323–473 K. This enhancement in the conductivity was attributed to the sizable alteration in the ions vibration and ruptures of covalent bonds in the electrolytes network structures.

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Introduction

The discharge capacity of a rechargeable lithium ion (Li-ion) battery owing to its very high power density makes it much better than conventional one [1–3]. It is not only safe and durable but the used electrolytes in the battery can withstand high temperatures and applied voltage, offering high mobility for Li-ions. However, the presence of liquid electrolytes in the Li-ion batteries which are in organic solutions form are flammable, thereby generate high risk of fire [4]. To surmount this limitation, conductive inorganic solid electrolyte based Li-ion batteries are proposed. Inorganic solid electrolyte due to their fire safety and great stability against Li-ions leaching has emerged as potential candidate for developing high performing Li-ion batteries [5–7]. Moreover, such solid electrolytes must be highly conductive and easily prepared at low temperatures [8], compatible with the electrode material (such as

lithium metal) as well as physically and chemically stable in the air atmosphere. Much research efforts are not directed towards the development of solid electrolytes having such abovementioned attributes.

The availability of easy synthesis methods of zinc-tellurite ($\text{ZnO}-\text{TeO}_2$) glass-ceramics, its low melting temperature and extreme stability due to the formation of ZnTeO_3 structural units in the complex networks make them advantageous for the realisation of base material towards conductive electrolytes [9,10]. In this view, we prepared a series of lithium-zinc-tellurite glass-ceramics by varying the concentration of Li_2O and subsequently characterised them to examine the feasibility of achieving a new type of solid electrolyte useful for lithium ion secondary batteries. Compositions and growth conditions of the studied glass-ceramics were optimized in terms of annealing temperature, nature of modifiers, and lithium ion contents to achieve their optimum ionic conductivity and durability. The results for surface morphology, structure, and ionic conductivity were analysed and discussed.

* Corresponding author.

E-mail address: wahyu.widanarto@unsoed.ac.id (W. Widanarto).

Experimental

Glass-ceramic electrolytes of chemical composition $(85-x)\text{TeO}_2 \cdot x\text{Li}_2\text{O} \cdot 15\text{ZnO}$ with $x = 0, 5, 10, 15$ mol% were prepared using melt quenching route. To achieve efficient solid glass electrolytes, analytical grade commercial powders of TeO_2 (99+ %, Acros), ZnO_2 (99.5+, Acros) and Li_2O (99%, Sigma-Aldrich) were used as starting materials which were manually mixed in a ceramic crucible and melted in an electrical furnace (WiseTherm) at 800°C for 20 min. Then, the melt was immediately poured into the pre-heated bronze mould (Heidolph MR 3001 K) and pressed using another heated metal plate. The quenched melt was annealed at 300°C for 3 h and naturally cooled down to room temperature [4]. The obtained glass electrolytes were milled and manually pressed to form pellets with the diameter of 10 mm and thickness of 2 mm. Later, these electrolyte pellets of glass were transformed to glass-ceramics via thermal annealing at 320°C for 3 h. This selected annealing temperature was positioned in the middle of glass transition temperature (T_g) and crystallization temperature (T_c) [11]. Referring to the Li_2O contents of 0, 5, 10, and 15 mol% the synthesized four glass-ceramic electrolyte samples were designated as C-ZT, C-LZT1, C-LZT2, and C-LZT3, respectively.

The values of T_g and T_c were measured using differential scanning calorimeter (DSC – Parkin Elmer) in the temperature range of $240\text{--}447^\circ\text{C}$ [4]. To ensure the crystalline nature of the electrolytes, X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-610 diffractometer which used $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Surface morphology of the samples was imaged using scanning electron microscopy (SEM – JEOL JSM-6510) with magnification of 10,000 times. The ionic conductivity of the electrolytes as the function of frequency was measured using the AC impedance method using (LCR meter from HIOKI 3522-50), wherein the data was acquired at a voltage of 1.5 V in the frequency range of 1–100 kHz. Meanwhile, temperature dependent (in the range of 300–473 K) ionic conductivity of the synthesized glass-ceramic electrolytes was measured.

Results and discussion

Fig. 1 shows the SEM images of the thermally annealed electrolytes. The glass-ceramic surface morphology revealed considerable roughness due to the random nucleation of crystals of varying sizes mostly less than $1 \mu\text{m}$. The surface of sample C-ZT displayed the presence of uniform and compact granular particulate (crystalline) morphology. Conversely, all other samples surface exhibited nearly same patterns with the mixture of crystalline flakes, plates and chunks of altering sizes. Furthermore, the surface appeared more uniform and homogeneous in the presence of larger crystallite sizes as the contents of Li_2O was increased.

Fig. 2 illustrates the XRD patterns of the prepared glass-ceramic electrolytes. The presence of sharp Bragg diffraction peaks clearly confirmed the crystalline nature of all samples. The diffraction peaks for glass-ceramic without containing Li_2O showed several peaks which were allocated to the crystalline structures of predominant tetragonal $\gamma\text{-TeO}_2$ and subsidiary cubic ZnO_2 . Addition 5 mol% of Li_2O produced new phases of hexagonal $\text{Li}_6(\text{TeO}_6)$ and monoclinic $\text{Zn}_2\text{Te}_3\text{O}_8$ crystal lattice. However, diffraction peaks were still dominated by Te_2O crystalline phases. At 10 mol% of Li_2O , the diffraction peaks of $\text{Zn}_2\text{Te}_3\text{O}_8$ crystal structure were enhanced and two new diffraction peaks corresponding to monoclinic $\text{Li}_2\text{Te}_2\text{O}_5$ crystal were emerged. Finally, sample containing 15 mol% of Li_2O displayed the dominance of $\text{Zn}_2\text{Te}_3\text{O}_8$ and Te_2O crystalline phases with enhanced peak intensities. The observation of a new peak of weak intensity for C-LZT3 sample indicated the occurrence of Li_2O crystalline phase.

Based on the SEM images and XRD analysis, it is affirmed that the incorporation of Li_2O in the proposed glass-ceramic electrolytes has affected significantly the surface morphology and crystalline structures where many new crystalline phases with varying crystallite shapes and sizes were found to emerge. Debye-Scherrer equation was used to estimate the size of electrolyte crystallites, where the intense XRD peaks were selected to obtain their full width at half maximum (FWHM). The size of crystals formed in

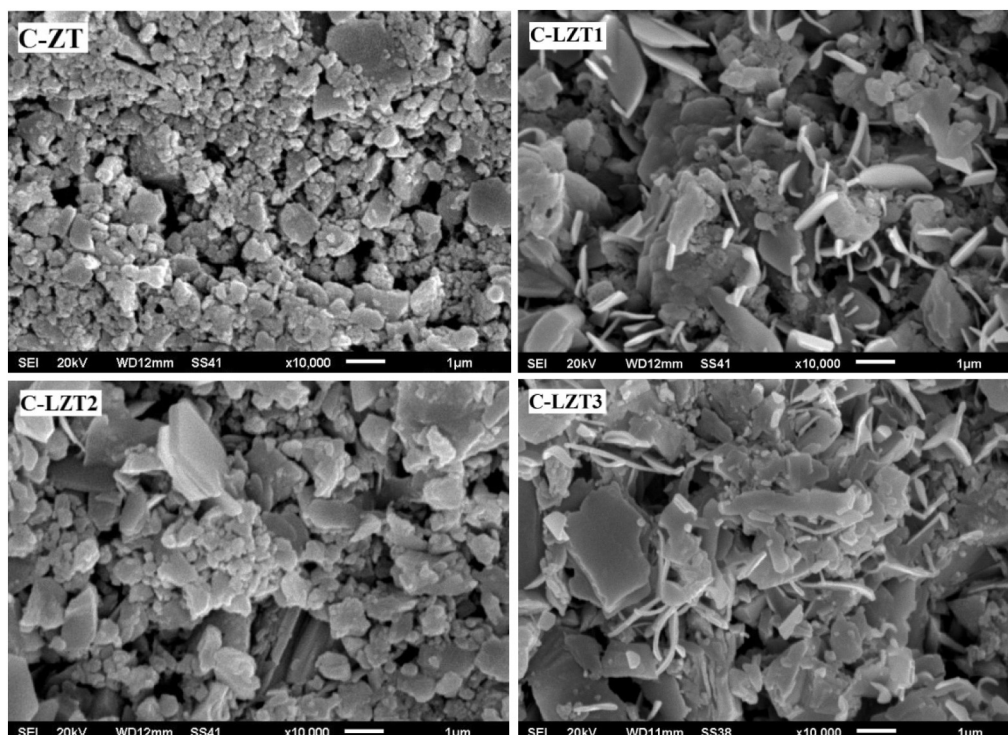


Fig. 1. SEM images of the prepared glass-ceramics electrolytes.

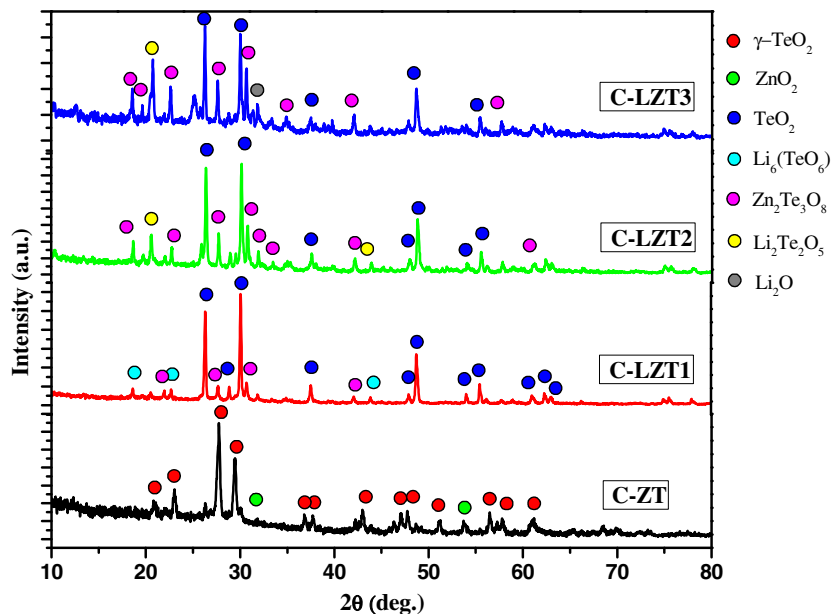


Fig. 2. Li_2O content dependent XRD patterns of synthesized electrolytes.

the synthesized glass-ceramic electrolyte was discerned to be in the range of $\approx 40\text{--}80$ nm.

Fig. 3 depicts the frequency dependent ionic conductivity of synthesized glass-ceramic electrolytes at temperature of 300 K. The ionic conductivity of all samples was found to be stable in the low frequency range up to 3 kHz. However, in the high frequency range (above 3 kHz) the ionic conductivity of all electrolytes displayed very rapid fluctuations from 10^{-8} to $20 \times 10^{-8} \text{ S cm}^{-1}$. Sample containing 15 mol% of Li_2O (C-LZT3) revealed the highest ionic conductivity at a frequency of 3.73 kHz. This enhancement in the ionic conductivity at higher frequencies was attributed to the vigorous ionic vibrations and subsequent rupture of the covalent bonds in the electrolytes that created large number of non-bridging oxygen (NBO) ions. Consequently, these high energetic ions could move through defective crystalline

structures of the glass-ceramics under the influence of an external electric field (applied voltage).

Fig. 4 displays the temperature dependent ionic conductivity of the glass electrolytes at the frequency of 54 Hz. At room temperature (300 K), the conductivity of all electrolytes remained the same. However, the ionic conductivity of all electrolytes was significantly affected with increasing temperature, which was augmented by order of magnitude ($\approx 10^{-8}$ to $10^{-7} \text{ S cm}^{-1}$) up to 323 K and dropped thereafter. This observation was majorly ascribed to the high temperature mediated enhancement in the thermal vibration of the ions and the breakage of network bonds. It is known that under thermal equilibrium at low temperature, the Li-ions are held by a weak covalent bond to zinc-tellurite lattice. Thus, the thermally agitated ions became easily mobile in the electrolyte and accelerated along the field even at tiny applied

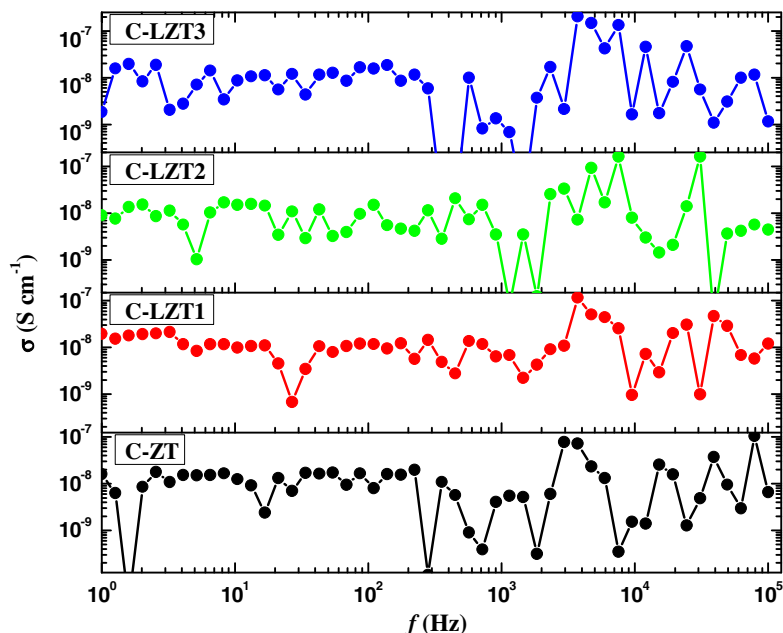


Fig. 3. Frequency dependent ionic conductivity of synthesized glass-ceramic electrolytes at 300 K.

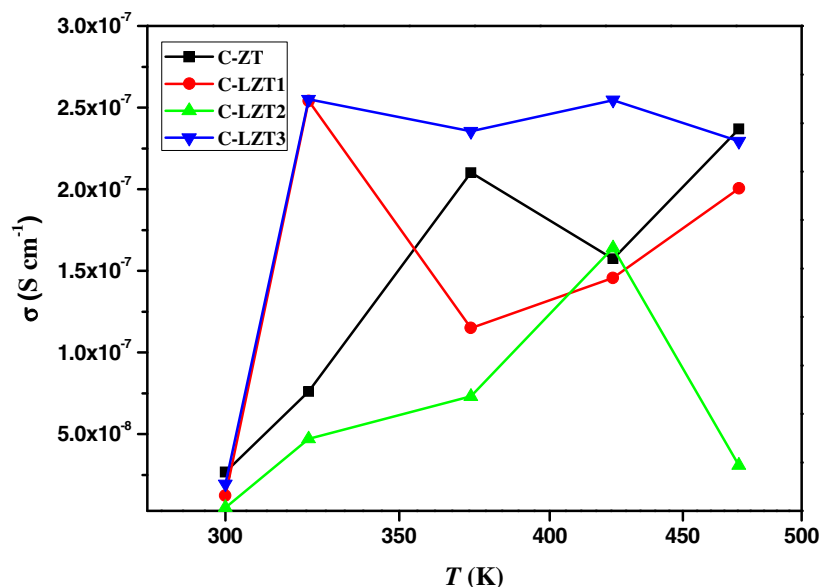


Fig. 4. Temperature dependence of the ionic conductivity for the zinc-tellurite glass electrolytes at 54 Hz.

electric field (AC voltage). This in turn enhanced the ionic mobility and thereby caused conductivity enhancement [12,13]. Conversely, the observed reduction in the conductivity at higher temperature was primarily credited to randomizations of the carriers (non Ohmic regime), leading to enhanced resistivity, decreased mobility and the diminished conductivity [4]. On the top, the presence of frequent crystal grain boundaries also notably influenced the ionic conductivity by hindering the free movement of ions in the electrolyte.

Conclusion

A new type of the lithium-zinc-tellurite glass-ceramic electrolytes was prepared with controlled concentrations of Li_2O . The obtained electrolytes revealed good crystalline phases with homogeneous surface morphology. The ionic conductivity of the electrolytes displayed significant dependence on AC frequency. Application of AC signal generated vigorous ionic vibrations and ruptured the covalent bonds between Li-ion and neighbouring atoms. Generation of large number of highly mobile ionic carriers improved the ionic conductivity appreciably. Furthermore, the ionic conductivity of the electrolytes was augmented with increasing temperature up to 323 K and then dropped. The electrolyte containing 15 mol% of Li_2O exhibited the optimum performance in terms of stable ionic conductivity of $2.4 \times 10^{-7} \text{ S cm}^{-1}$ in the temperature range of 323–473 K at 54 Hz. It was established that by suitably controlling the temperature, AC frequency, and Li_2O concentrations, a good quality zinc-tellurite glass-ceramic based solid electrolytes with improved ionic conductivity can be achieved. Our findings may be useful for overcoming the limitations associated with the conventional organic materials based liquid electrolytes.

Acknowledgements

This work was supported by Universitas Jenderal Soedirman, KEMENRISTEKDIKTI through Stranas Grand (No. 2046/UN23.14/PN/2015), and GUP 13H50/17H19 (UTM, Malaysia).

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