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Performance of $\text{LiCo}_{0.6}\text{Zn}_{0.4}\text{O}_2$ as a potential cathode material candidate for intermediate solid oxide fuel cell application

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Abstract. Li-based materials, previously used in lithium batteries, are now actively applied in solid-oxide fuel cells (SOFCs). The synthesis and characterisation of $\text{LiCo}_{0.6}\text{Zn}_{0.4}\text{O}_2$ (LCZO) cathode powder calcined at 600 °C for SOFC application has been reported. In the present work, LCZO powder was calcined at 700 °C and its properties were investigated. Results showed that the impure phases recorded through X-ray diffraction (XRD) in a previous work decreased with the ZnO phase at approximately 37.4%, and 62.6% of LCZO remained. Transmission electron microscopy was used to study the morphology of the calcined powder, wherein the crystallite size obtained from XRD well agreed with the XRD analysis result. The LCZO particle size calcined at 700 °C was examined with a particle-size analyser. The electrical conductivity of bulk pellet was tested at 400–700 °C, and the highest conductivity of 9.90 Scm^{-1} was recorded at 700 °C. Overall, this material exhibited excellent potential for proton-conducting SOFCs application.

1. Introduction

The demand for a brand-new energy sources obligates a thorough review of renewable sources along with the ability of the devices to exhibit a certain potential or comparable with the performance of fossil fuel combustion. Solid-oxide fuel cells (SOFCs), a device that utilises the chemical reactions to produce electricity between an oxidant and a fuel gas, are another potential device to fulfil the demand [1]. Moreover, SOFCs are the currently leading optional energy resource candidate because of their fuel versatility, high versatility and environmental compatibility [2]. However, reducing the operating temperature at the same time maintaining a top cell performance is mandatory for the commercialisation of SOFC technologies [3]. Thus, one of the ideas to reduce the working temperature is by replacing the electrolyte materials from oxide conducting to proton conducting. This application met another circumstance, wherein less amount of materials was discovered and able to exhibit good performance at low operating temperature similar to that of the high-temperature operating system. In addition, operating the devices under low temperature caused polarisation



resistance of the cathode and electrolyte interface to increase [4]. Thus, cathode material field becomes an important issue in deciding the cell overall performance.

In the present work, Li-based materials from lithium batteries were studied and introduced to SOFC application as a candidate of cathode materials. This well-known type of cathode or lithiated cathode materials that are normally used in lithium batteries belongs to the mixed conducting type of cathode that usually possessed high electronic conductivity. This class of cathode material utilises all triple $\text{H}^+/\text{O}^{2-}/\text{e}^-$, wherein the mechanism is visualised [5]. A few studies have been conducted utilising lithium oxide-containing cathode and revealed a significant result. For example, Chen et al. investigated the commercial $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ as a cathode material and sol-gel-synthesised $\text{Ce}_{0.9}\text{Co}_{0.15}\text{Al}_{0.05}\text{LiO}_2$ material as the electrolyte, wherein the measured peak power densities were recorded at 93.6 and 159.7 mW cm^{-2} [6]. Fan et al. fabricated a single cell consisting of $\text{LiNi}_{0.8}\text{CoO}_{0.2}\text{O}_2$ as cathode, $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.2}\text{O}_3$ (BCZY) as the electrolyte and NiO-BCZY as the anode, disclosing a splendid result with performance revealing a peak power density of 410 mW cm^{-2} at the operating temperature of 650 °C [7].

As an extension of research into the cathode material by using the lithiated materials, $\text{LiCo}_{0.6}\text{Zn}_{0.4}\text{O}_2$ that was calcined at 700 °C was chosen as the candidate, which will denote as LCZO in the subsequent discussion. Such dopant (Zn) was selected as the co-doped at the B site by considering this metal potential, wherein Zn can assist the progress of lattice volume expansion, formation of crystal structure and production of extra space for lithium ion intercalation/de-intercalation in the material [8]. By adopting Zn onto B sites of LiCoO_2 , the electrochemical performance of the cell is expected to be good. The preliminary characterisation studies on the cathode material is very before determining the electrochemical performance of the material. Considering the outmost performance of lithiated material from recent study, it is significant to fully understand the characteristic of the material itself as only a few articles reported the preliminary study of this material especially for SOFC application.

2. Methodology

2.1. Powder preparation

LNCZ cathode powder with the approximate composition of $\text{LiCo}_{0.6}\text{Zn}_{0.4}\text{O}_2$ was synthesised by glycine-nitrate combustion method, wherein lithium nitrate (LiNO_3), zinc nitrate hexahydrate ($\text{N}_2\text{O}_6\text{Zn} \cdot 6\text{H}_2\text{O}$) and cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were employed as the main chemicals. All these chemicals were purchased from Sigma Aldrich Company. The amount of the mixed chemical was calculated stoichiometrically and dissolved in deionised water for approximately 40 min. The precursor mixture was then added with the glycine, ($\text{C}_2\text{H}_5\text{NO}_2$), supplied by GeneMark, Taiwan, that acts as the combustion agent. The mixture was left for approximately 12 h for stirring continuously at room temperature. The temperature was increased to 250–300 °C to trigger and eventually start the combustion. The residue which is in a form of ash look-alike black powder was dried for one more time to remove excess water for approximately 12 h in a drying oven. Lastly, the powder was calcined at 700 °C at a heating and cooling rate of 10 °C min^{-1} by using a furnace (Berkeley Scientific, USA), for 5 h.

2.2. Powder characterisation

X-ray powder diffraction (XRD) pattern was recorded at room temperature on a Bruker AXS D8 Advance made in Germany along with radiation of CuK_α ($\lambda = 1.5406 \text{ \AA}$) to study the phase as well as the detail structure of the calcined powder. Operated at 40 kV along with 40 mA source of current and fitted with a 1-D fast detector (Lynx-Eye), the XRD analysis was inspected for 2θ from 20° to 80° with a step size of 0.025°. After calcination, manually crushed LNZO black powder was further analysed for their particle size distribution by using the Nano-ZS Analyser (PSA) by Malvern by

employing deionised water as a dispersant. For the physical morphology, LCZO powder was analysed via typical transmission electron microscopy (TEM) (FEI Talos L120C).

2.3. Electrical conductivity

A bulk pellet was pressed at 4 ton by using a stainless-steel die with a diameter of 13 mm. The pellet was further treated at 800 °C for 2 h. The electrical conductivity analysed by utilising the four probes was set up using Van Der Pauw technique under compressed air environment at a flow rate of 100 mL/min, current supply of 0.001 A and temperature ranging from 400–700 °C.

3. Result and discussion

3.1. Powder characterization

To confirm the crystal structure of the synthesised LCZO powder, XRD was performed. The obtained result showed almost similar peak to the reference LiCoO_2 , consistent with JCPDS file no. 000-050-0653 despite the minor differences in few peaks suspected to be the secondary phases of ZnO and ZnCo_2O_4 . The peaks attributed to LiCoO_2 were indexed to their miller indices (hkl) of (101), (012), (014), (015), (107), (018) and (110). As the inset in Figure 1 shows, LCZO peaks shifted to the right mainly because of the radius differences, whereas in this report, Zn was used as a dopant. Secondly, the LCZO peak showed a broader peak compared with the LiCoO_2 -referred peak because of the formation of small crystal size [9]. Refinement was conducted, obtaining 62.6% concentration of LCZO peaks as shown in Figure 1 while the rest of the peaks belong to the as stated secondary phases. All diffraction peaks for LCZO can be well indexed in a LiCoO_2 rhombohedral structure, which belongs to the R-3m space group. The average crystallite size was in the range of 21.24 nm as retrieved from XRD analysis by using Debye–Scherrer method based on the best resolved diffraction peak as shown in Equation (1) below.

$$D = \frac{0.9\lambda}{d \cos\theta} \quad (1)$$

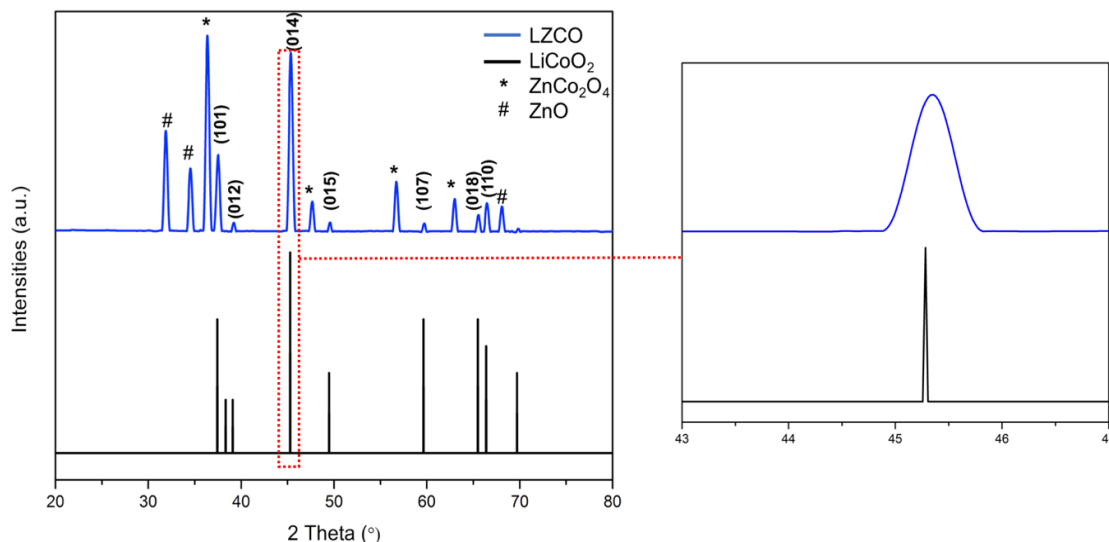


Figure 1. XRD spectra of LCZO powders calcined at 700 °C

This calculated crystallite size strongly agreed with further analysis from TEM, wherein the obtained crystallite size was approximately 20–30 nm, as shown in Figure 2 below. TEM images revealed quasi-spherical grain shape present in the deposit as well as evidenced a homogenous shape. The result of both XRD and TEM analyses were in agreement with the LCZO powder produced in nanoparticle size.

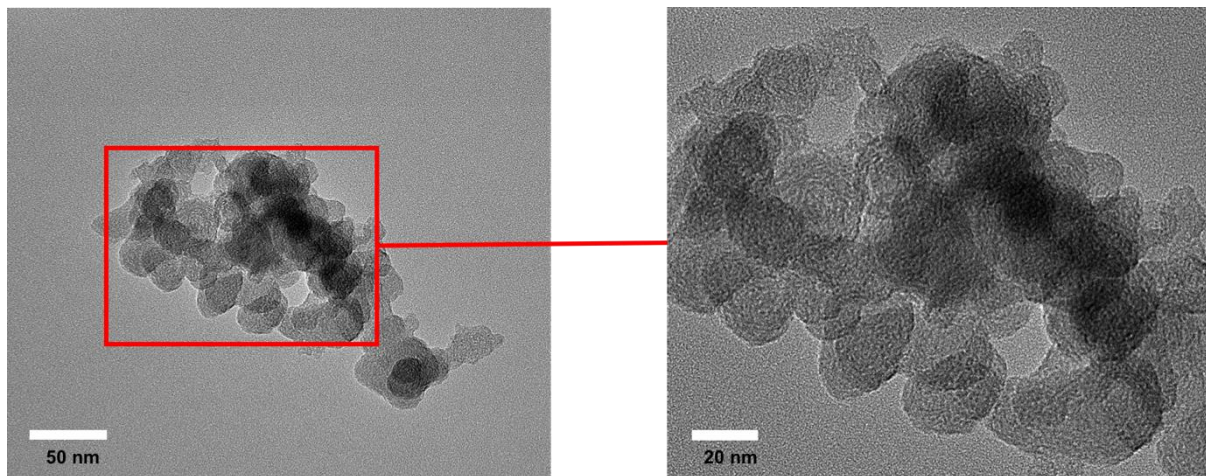


Figure 2. TEM images of LCZO powders calcined at 700 °C

Figure 3 below exhibits the bimodal particle size distribution of LCZO powders. From the well visualised figure, a total of two distinct groups of particle size distribution were identified for LCZO powders. Approximately 96.5% of the particles presenting a particle size distribution were identified in the range of 200–1200 nm, wherein the rest of 3.5% of the particle size was recorded in the range of 3000–7000 nm.

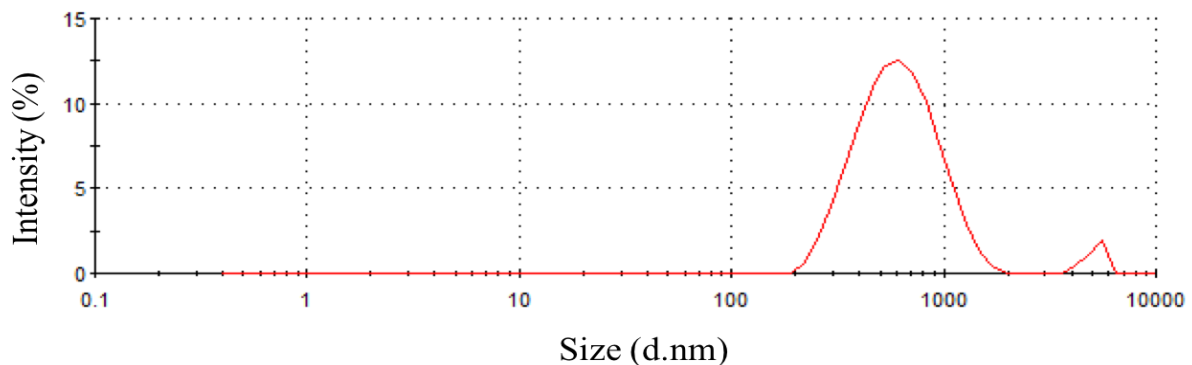


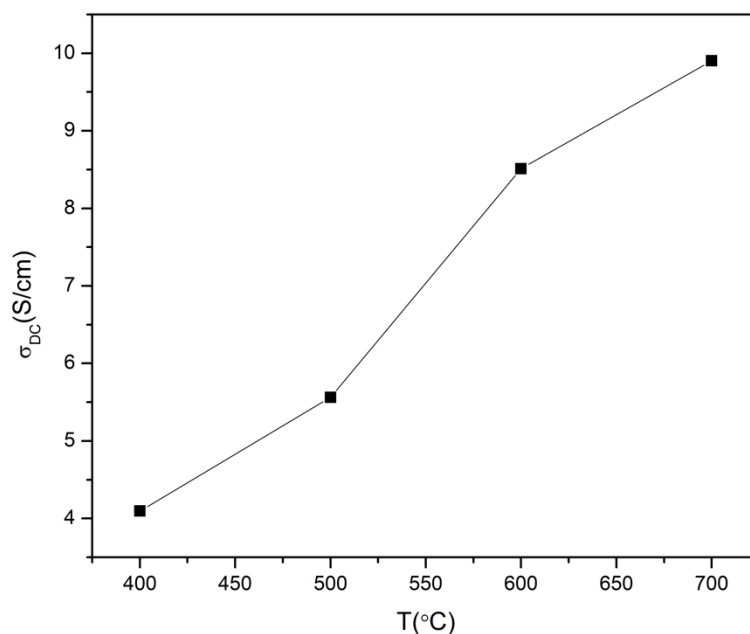
Figure 3. Particle size distribution by intensity of LCZO powders calcined at 700 °C

3.2. Electrical conductivity

An electrical conductivity of $>100 \text{ Scm}^{-1}$ is favoured to produce an electrode in SOFCs particularly for cathode material. However, by optimising the electrode microstructure, an electrical conductivity of as low as 1 Scm^{-1} is still conductive [10]. Table 1 illustrates a collection of novel materials, reporting the electrical conductivities as a comparison for LCZO performance. The electrical conductivities of LCZO bulk pellet were measured within the temperature range of 400–700 °C by using the four probe DC techniques, and the result is shown in figure 4. The values of electrical conductivities were 4.10, 5.56, 8.51 and 9.90 Scm^{-1} at 400 °C, 500 °C, 600 °C and 700 °C, respectively. As shown in the graph in figure 4, LCZO possessed semiconductor properties as electrical conductivity increased with increased temperature because conductivity is closely related to small-polaron mobility as previously reported [11][12]. Small-polaron concentration highly depends and varies with Li concentration, which is directly related to the lithiation/delithiation state [13].

Table 1. List of electrical conductivities for various novel cathode material for SOFC application

Materials	Temperature (°C)	Electrical Conductivity (S cm^{-1})	Ref
$\text{La}_{0.8}\text{Sr}_{0.2}\text{Zn}_x\text{Fe}_{1-x}\text{O}_{3-\delta}$	550	13.63	[14]
$\text{SrFe}_{0.5}\text{Ti}_{0.5}\text{O}_{3-\delta}$	800	6.32	[15]
$\text{LiCo}_{0.6}\text{Zn}_{0.4}\text{O}_2$	700	9.90	This work
$\text{LiCo}_{0.5}\text{Al}_{0.5}\text{O}_2$	500	1.0×10^{-3}	[16]

**Figure 4.** Electrical conductivity of LCZO bulk pellet at 400- 700°C.

4. Conclusions

LCZO cathode material has been successfully synthesised by using glycine–nitrate combustion technique. The produced powder was composed of single crystalline nanoparticle as visualised in TEM. The theoretical crystallite size calculated using XRD patterns showing crystallite size in range of 20- 30nm. The electrical conductivity of the LCZO increased with an increase in temperature due to its semiconductor behaviour. None the less, LCZO shows excellent promise for SOFCs operating at reduced temperatures (<700 °C) due to the fact LCZO exhibited a stable electrical conductivity reading as well as revealing electrical conductivity performance that is comparable with other reported novel materials. To make LCZO as a viable cathode material for the SOFC application, further investigation such as electrochemical performance in dry and wet air, thermal stability and chemical stability need to be conducted at various temperatures are being considered as the next plan.

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