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PRELIMINARY INVESTIGATION INTO THE FORMATION OF $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = Zr, Ca) AS TRIPLE-CONDUCTING OXIDE CATHODES FOR SOLID OXIDE FUEL CELLS

UVODNE RAZISKAVE NASTANKA TROJNIH PREVODNIH OKSIDNIH KATOD $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = Zr, Ca) ZA GORIVNE CELICE NA OSNOVI TRDNEGA OKSIDA

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A solid oxide fuel cell (SOFC) is an efficient electrochemical energy conversion device with low emissions. The cathode is one of the principal components of an SOFC, responsible for the reduction reaction. Triple conducting ($H^+/O^{2-}/e^-$) cathodes are promising due to their enhanced performance, but existing materials like $LiCoO_2$ (LCO) face stability issues at high temperatures caused by a high cobalt content. Hence, the study focused on synthesizing $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = dopant) using a glycine-nitrate process and introducing dopants (Zr/Ca) to the cobalt site of LCO to improve stability. Synthesized cathode powders were analyzed using a thermal gravimetric analysis (TGA), X-ray diffractometry (XRD), and field emission scanning electron microscopy/energy dispersive X-ray spectrometry (FESEM/EDX) to assess the thermal decomposition behavior, phase and structure formation, and microstructure, respectively. The XRD analysis confirmed a successful synthesis of homogeneous $LiCo_{0.8}M_{0.2}O_{2-\delta}$ cathode powders (M = Zr, Ca) at a calcination temperature of 800 °C. The FESEM/EDX analysis indicated homogenous elemental distribution within the powders, with final experimental molar ratios of $LiCo_{0.79}Ca_{0.21}O_{2-\delta}$ and $LiCo_{0.78}Zr_{0.22}O_{2-\delta}$ for the Ca- and Zr-doped cathodes, respectively. This successful synthesis paves the way for further research on the stability and performance of these doped cathodes in SOFC applications.

Keywords: solid oxide fuel cell, triple-conducting oxide cathode, glycine-nitrate process

Gorivna celica na osnovi trdnega oksida (SOFC; angl.: Solid Oxide Fuel Cell) je učinkovita elektro-kemijska naprava za pretvorbo energije z majhno emisijo. Katodna komponenta je ena od glavnih komponent SOFC za redukcijsko reakcijo. Trojne prevodne katode ($H^+/O^{2-}/e^-$) so obetavne za uporabo zaradi nekaterih dobrih lastnosti. Obstoječi materiali, kot je naprimer $LiCoO_2$ (LCO), imajo slabo stabilnost pri povišanih temperaturah zaradi visoke vsebnosti kobalta (Co). Zato so se avtorji tega članka osredotočili na študij sinteze oksida tipa $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = dopant) z uporabo glicin-nitratnega procesa. Pri tem so uporabili dva dopanta (Zr in Ca) kot delno nadometilo za Mo v LCO in s tem poizkušali izboljšati njegovo stabilnost. Sintetizirane katodne prahove so avtorji, da bi ocenili njihovo termično obnašanje, fazno in strukturno formiranje in nastalo mikrostrukturo, analizirali s termo-gravimetrično analizo (TGA), rentgensko difraktometrijo (XRD) in vrstično elektronsko mikroskopijo na osnovi emisije polja (FESEM/EDX). XRD analize so potrdile uspešno izvedbo sinteze homogenih katodnih prahov tipa $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = Zr, Ca) pri temperaturi kalcinacije 800 °C. FESEM/EDX analize so potrdile homogeno porazdelitev kemijskih elementov v prahovih s končnima eksperimentalnima molskima razmerjema $LiCo_{0.79}Ca_{0.21}O_{2-\delta}$ in $LiCo_{0.78}Zr_{0.22}O_{2-\delta}$ za s Ca oziroma Zr dopirano katodo. Ta uspešna sinteza bo avtorjem tega članka v prihodnosti omogočila nadaljnje raziskave stabilnosti in lastnosti te vrste katod za SOFC aplikacije.

Ključne besede: gorivne celice na osnovi trdnih oksidov, trojna prevodna oksidna katoda, glicinsko-nitratni proces

1 INTRODUCTION

A solid oxide fuel cell (SOFC) is an energy-generating device. An SOFC provides high energy efficiency in addition to being an environmentally friendly device.[1] An SOFC is made up of a dense electrolyte with two porous electrodes (i.e., cathode and anode). The main challenge of the SOFC technology is to reduce the high operating temperature, which exceeds 800 °C, so that it can be more acceptable in the market.[2] There are two types of SOFC operations: an oxide-conducting (O^{2-}) SOFC and a proton-conducting (H^+) SOFC. In an oxide-conducting SOFC, the oxide ion diffuses from the cathode to the anode through the ion-conducting solid electrolyte layer, thus forming water at the anode site. Meanwhile, in a proton-conducting SOFC, protons diffuse from the anode to the cathode, and water is formed at the cathode as a result of the oxygen reduction reaction.[1] The application of a proton-conducting electrolyte material can reduce the fuel cell operating temperature compared to ion-conducting electrolyte materials. In addition, proton-conducting electrolytes have higher ionic conductivity and theoretical electric efficiency at intermediate temperatures.[2]

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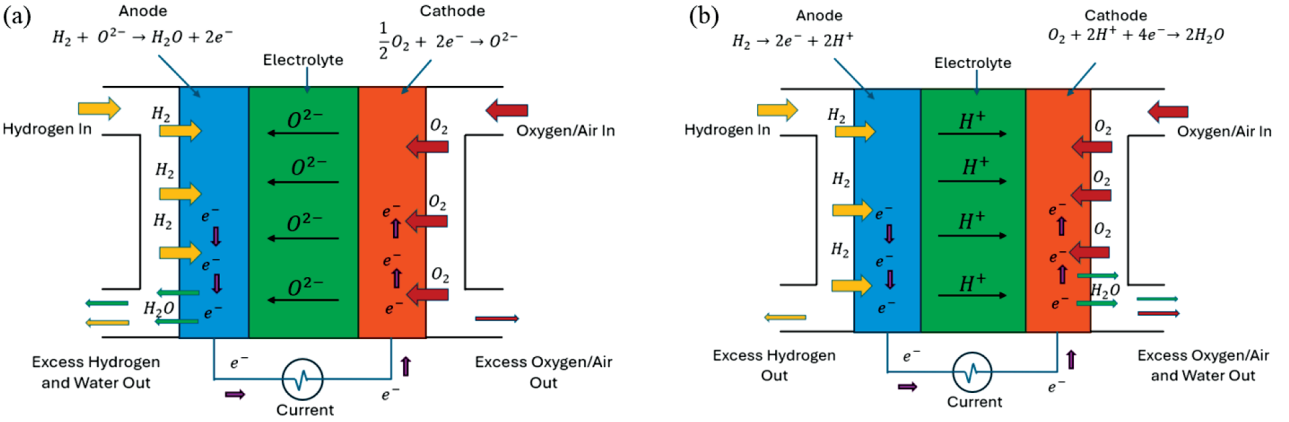

Figure 1: SOFC mechanisms: a) oxide-conducting, b) proton-conducting mechanism

Practical application of a proton-conducting SOFC faces major challenges in selecting a suitable cathode material for better electrode reaction efficiency. For good performance of an SOFC, cathode materials should have high electrical conductivity, exceptional chemical stability, adequate material porosity for oxygen diffusion at the interface, high catalytic activity, and a low cost.[3] As of now, cathode materials for H^+-SOFC can be categorized into four types: pure electronic conductor (PEC), mixed ionic and electronic conductor (MIEC), mixed protonic and electronic conductor (MPEC), and triple-conducting oxide (TCO). Pure electronic conductor cathodes, such as Pt, are a suitable choice for catalytic electrode materials, but they are expensive and have poor thermal stability. This type of cathode has a limited triple-phase boundary (TPB). The oxide ions can only diffuse on the cathode surface to react with protons to produce water, resulting in a high polarization resistance value. MIEC cathodes such as $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) show promising performance in oxide-conducting (O^{2-}) SOFCs (O-SOFCs), but they are unable to provide satisfactory power densities in H^+-SOFCs. This is because of the formation of water is limited only to the cathode/electrolyte interface. The water formed at the interface must be flowed out through the cathode bulk. MPEC cathodes provide better compatibility with the electrolyte, increasing the TPB for the water generation reaction. However, poor catalytic activity towards the oxygen reduction reaction (ORR), due to the low amount of transition metal in the solid solution and the trade-off between electronic and proton conduction following doping, results in worse performance compared to PEC and MIEC cathodes.[2,5]

The triple-conducting ($O^{2-}/H^+/e$) oxides (TCOs) are currently being developed as an alternative cathode material to replace the MIECs and cathode composites for intermediate temperature H^+-SOFC applications. TCO cathodes have a larger TPB, allowing migration of oxygen ions, hydrogen ions, and electrons through the cathode bulk and surface. Li et al. reported that the TCO cathode composed of $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) infiltrated with $PrBaCo_2O_{5-\delta}$-$BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3-\delta}$ (PBC-BZCY) exhibits a lower area-specific resistance (ASR) compared to the composite cathode of PBC-BZCY alone.[4] The ASR values measured at 600 °C in air with 3 % H_2O are 0.48 Ω cm² and 2.53 Ω cm² for GDC-PBC-BZCY and PBC-BZCY, respectively. Another work by Zhu et al. reported that the ASR value of the $SrSc_{0.175}Nb_{0.025}Co_{0.8}O_{3-\delta}$ (SSNC) TCO cathode measured on the BZCY electrolyte at 600 °C in air with 10 % H_2O is 0.26 Ω cm².[5] An SSNC is stable in a humidified condition since no additional phases are formed after it has been exposed to air with 3 % H_2O for 2 h. However, the phase stability of the SSNC is decreased due to the formation of additional phases including $SrCO_3$ and $Sr(OH)_2$ after a 10-h exposure in a humidified condition.

More complex TCO cathodes are developed as reported by Zhang et al.[6] They developed infiltrated TCO cathodes containing BZCY, $Ba(Zr_{0.4}Ce_{0.4}Y_{0.2})_{1-x}Co_xO_{3-\delta}$, $(Ce,Zr,Y)O_2$, and Co_3O_4. The ASR values of this cathode in air and wet air at 650 °C are 0.961 Ω cm² and 0.560 Ω cm², respectively. A fabricated symmetrical cell using the designed cathode exhibited operational stability of 70 h at 650 °C. Apart from the above TCO cathodes, lithium-based materials have also been recently proposed as TCO cathodes for IT-H^+-SOFC applications because these materials can increase the concentration of oxygen at grain boundaries and promote higher ionic conductivity.[7,8] The ASR and conductivity values of an $LiFeO_2$-$LiAlO_2$ cathode at 650 °C are 0.16 Ω cm² and 0.50 S cm^{-1}, respectively.[9] The ASR value of an $LiNiCuZnO_x$ (LNCZ) cathode working with a $Ce_{0.8}Sm_{0.2}O_2$-$(Li/Na)_2CO_3$ electrolyte at 600 °C is 1.63 Ω cm².[10] Both Li-based cathodes were tested in air/H_2 atmosphere. The Li-based cathode is also compatible with the BZCY electrolyte, with no formation of secondary phases. An $LiCo_{0.6}Sr_{0.4}O2$ (LCSO) cathode in a symmetrical cell shows an ASR value of 0.75 Ω cm² in dry air at 800 °C.[11]

Doping alkali metals such as lithium into a transition metal oxide increases the electrode conductivity and activity. Moreover, the doping of alkali metals is beneficial, as it can increase the ORR with an increase in the electron conductivity and oxygen vacancy density.[2] $LiCoO_2$

(LCO) exhibits a sufficient capacity rate, energy, and power density. However, one of the drawbacks of this material is its unstable structure during charging, particularly at the cobalt site. The structural stability of the $LiCoO_2$ compound can be improved by doping it with metal.[12] Besides, the high Co content in LCO causes it to become unstable at high temperatures, increasing the cost of the material.[13] Many dopants have been tested to replace the amount of Co in LCO. $LiCo_{0.5}Al_{0.5}O_2$ (LCAO) with a layered structure has proved to have high proton conductivity, which is 0.1 S/cm at 500 °C.[14] $LiNi_{0.8}Co_{0.2}O_2$ (LNCO) with a layered structure can conduct oxide ions, protons, and electrons. LNCO showed a good ORR with a low activation energy at 0.88 eV.[2] An $LiNi_{0.79}Co_{0.2}Zn_{0.01}O_2$ (LNCZO) cathode gives a peak power density of 1.32 W/cm^2 at 650 °C in SOFC applications with H_2 as the fuel.[7] Doping Sr into LCO increases the cathode electronic and ionic conductivity, as well as enhancing its thermal stability.[15]

In the context of SOFCs, the study of doped lithium cobalt oxide (LCO) materials goes beyond simply evaluating their electrochemical properties. It includes a fundamental understanding of their synthesis and stability in SOFCs' harsh operating conditions, particularly the types of dopants used. The dopants selected for this study are calcium (Ca) and zirconium (Zr). Ca, an alkaline earth metal with a fixed oxidation number, can increase proton conductivity.[14] Meanwhile Zr is selected to increase the LCO thermal stability and increase proton conductivity.[16] This study focuses on the synthesis of $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (with M representing the dopant; alkaline earth metal: calcium, Ca; and transition metal: zirconium, Zr) using the glycine-nitrate process. This method provides precise control over the composition and morphology of the doped material, which is critical for achieving the desired properties. Our primary goal is to confirm the feasibility of producing a doped LCO and investigate its stability under SOFC operating conditions. The stability of doped LCO materials in SOFC environments is critical due to the high temperatures and corrosive atmospheres involved. Understanding the structural changes, phase stability, and chemical interactions that occur within a doped LCO electrode during an extended operation is crucial for ensuring long-term SOFC performance and durability. Our findings will not only shed light on the fundamentals of doped LCO synthesis but also highlight its potential application in next-generation energy conversion technologies.

2 EXPERIMENTAL PART

Cathode powders $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (LCMO) were synthesized with the glycine-nitrate combustion method. Detailed steps were as follows: $Li(NO_3)$, $Co(NO_3)_3$, and $Zr(NO_3)_4$ were mixed together at stoichiometric ratios and dissolved in deionized water to form a solution, and then glycine (Biotech grade; GeneMark, Taiwan) was added. The mixture was stirred for 18 hours to form a homogeneous solution. Then, the solution was continuously stirred and heated up to 320 °C to promote combustion and form precursor powders. The same technique was repeated with $Ca(NO_3)_2$. The resultant as-prepared powders were then subjected to further heat treatment. The thermal decomposition of the precursor powders was characterized with simultaneous thermal analysis equipment (TGA, Perkin Elmer Pyris Diamond, USA) in a temperature range of 30–900 °C at a heating/cooling rate of 5 °C/min in compressed air conditions, with a flow rate of 100 mL/min. All the synthesized powders were then calcined at temperatures of 750 °C and 800 °C for 5 h using a vertical furnace (Berkeley Scientific BSK-1000X-S, USA) to remove impurities. The calcined powders were then analyzed using an X-ray diffractometer (XRD, Bruker DS-Advance, Germany) to determine changes in terms of phase and structure formation.

The determination of phase and structure of crystals of the LCMO precursor powder after calcination was performed using X-ray diffraction. The powder was analyzed using an XRD instrument (BRUKER D8-ADVANCE, Germany). This analysis was carried out at room temperature with a voltage of 40 kV and a current of 30 mA. The diffraction process using copper monochromatic radiation (Cu-Kα) with a wavelength of 0.15406 nm was carried out at a diffraction angle of 20° to 80°, at a scan step of 0.02°. The analysis of the raw data obtained was performed using PANalytical Xpert Highscore Plus software. D-spacing calculation was performed using the following equation:

$$\text{d spacing} = \frac{\lambda}{2 \sin \theta}$$

where λ is the X-ray wavelength and θ is the diffraction angle in XRD expressed in radians. Lattice parameter a is calculated with:

$$a = \text{d spacing} \cdot \sqrt{h^2 + k^2 + l^2}$$

The particle morphology of the cathode powder was observed through a field emission scanning electron microscope (FESEM) (Zeiss, Germany). The FESEM was used at room temperature, with a voltage and working distance of 15 kV and 0.8 nm, respectively. An elemental distribution analysis was performed using an energy-dispersive X-ray instrument (EDX) (EVO MA 10, Germany) matched with the FESEM. The SEM voltage used during the element distribution analysis was 15 kV. Mapping analysis techniques were used to detect the presence and distribution of cobalt, calcium, and zirconium.

3 RESULTS AND DISCUSSION

The characterization of the thermal behavior of the $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = Zr or Ca) (LCMO) precursor powder via a thermogravimetric (TG) analysis was evaluated

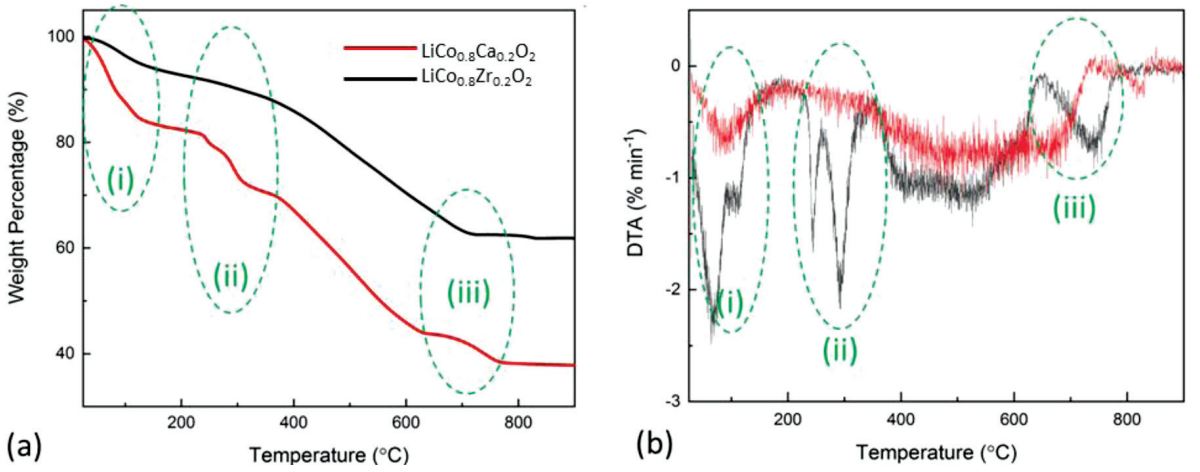

Figure 2: a) TGA and b) DTA curves for precursor powder LCMO

through the percentage of weight loss recorded with increasing heating temperature. **Figure 2** shows the TG signal graph for the prepared LCMO cathode precursor powder. In general, there are three stages of weight loss, each represented by a peak in the thermogravimetric differential signal (derivative thermogravimetry, DTG). The gradual weight loss of the precursor powder is due to the decomposition or removal of different impurities remaining in the precursor powder after the glycine-nitrate combustion.

In **Figure 2**, three stages of the thermal decomposition behavior of the cathode precursor powders can be observed. During Stage 1 (30–180 °C), there is decomposition of organic and inorganic compounds that have low boiling points such as nitrate compounds (boiling point = 160 °C). At Stage 2 (180 – 600 °C), there is decomposition of complex organic and inorganic compounds formed as a result of reactions between metal nitrate salts. During Stage 3 (> 600 °C), the weight loss is attributed to the decomposition of excess trapped carbon waste. The weight loss at this stage also marks the beginning of the crystallization and structural changes needed for the formation of metal oxides.[17] The total weight loss of the cathode powder was 38.14 % for $LiCo_{0.8}Zr_{0.2}O_{2-\delta}$ (LCZO) and 62.18 % for $LiCo_{0.8}Ca_{0.2}O_{2-\delta}$ (LCCO). Based on the results of this TG analysis, the recommended calcination temperatures for all cathode precursor powders for XRD tests are 750 °C or 800 °C, as these temperatures were recorded as the lowest ones required for completely removing impurities from the provided cathode precursor powders.

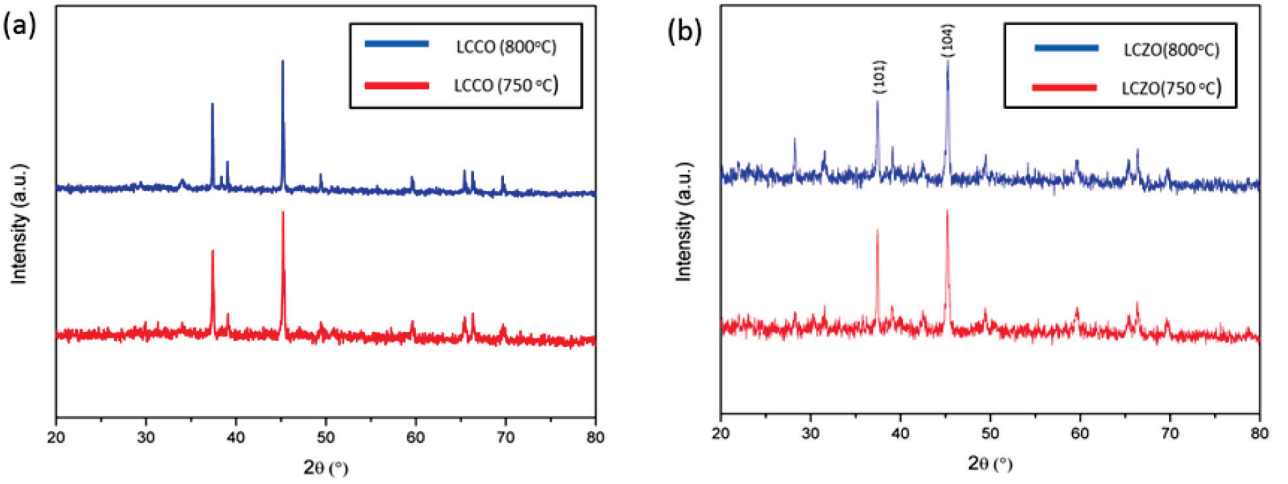

Figure 3: XRD spectra of cathode precursor powders: a) LCCO and b) LCZO after calcination at 750 °C and 800 °C for 5 h

Table 1: XRD analysis summary

Material	Space group	Secondary phase	Lattice parameter			Crystal size (nm)
			a	b	c	
LCCO	R-3m	–	2.81611	2.81611	14.06295	43.74
LCZO	R-3m	–	2.8106	2.8106	14.07405	35.45

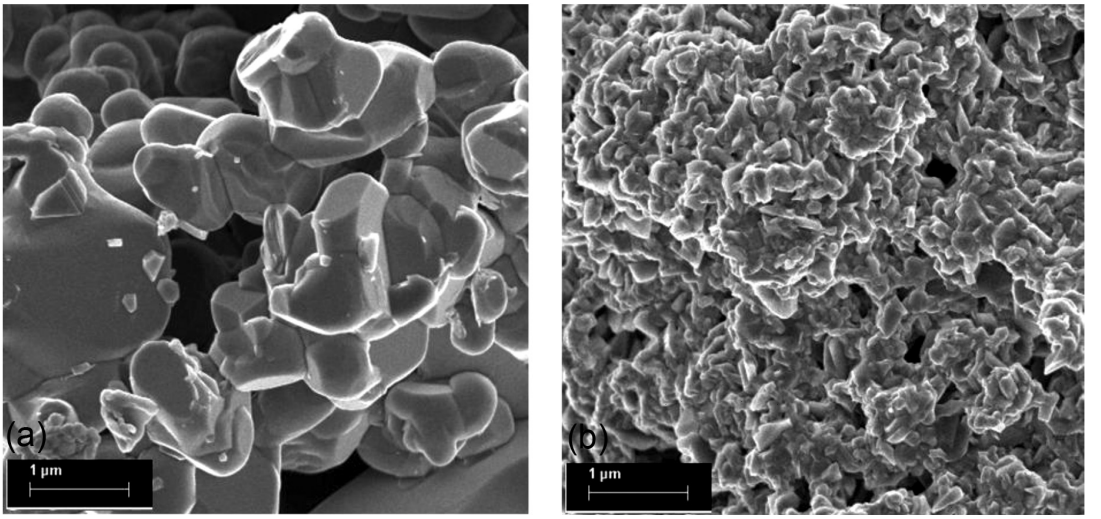

Figure 4: FESEM micrograph images of cathode precursor powders: a) LCCO and b) LCZO after calcination at 800 °C for 5 h

Figure 3 shows the X-ray diffraction (XRD) spectra of all LCMO cathode precursor powders prepared after being calcined for 5 h at 750 °C and 800 °C. Based on the figure, all the calcined powders were found to contain the main perovskite phase, the $LiCoO_2$ phase, which corresponds to the International Centre for Diffraction Data (ICDD) reference code 96-450-5483. The peaks in the XRD spectrum are assigned to their corresponding Miller indices (hkl): (101), (104), (110), and (113). The peak intensity for the perovskite phase of the LCMO increases, while the peak intensity for the secondary phase decreases as the temperature increases. **Table 1** shows the data retrieved with the XRD analysis.

Figure 4 shows FESEM micrograph images of the two LCMO cathode powders. These particles interact with each other and form agglomerated particles. The particle size values of the LCMO powder obtained with direct measurement from the micrograph image are shown in **Table 2**.

Table 2: Particle size values of LCMO powder obtained with direct measurement

Cathode	LCCO	LCZO
Particle size(mm)	0.49	0.25

Overall, EDX spectral patterns, along with the mapping of all LCMO cathode powders produced, were homogeneous. **Figures 5a** and **5b** show the EDX spectra along with the mapping of the LCMO powder to study the homogeneity and elemental composition in the powder. The peaks of Co, O, Ca and Zr can be clearly seen from the EDX spectra. There is no other peak related to impurities. Elemental mapping confirms homogeneous distributions of the elements.

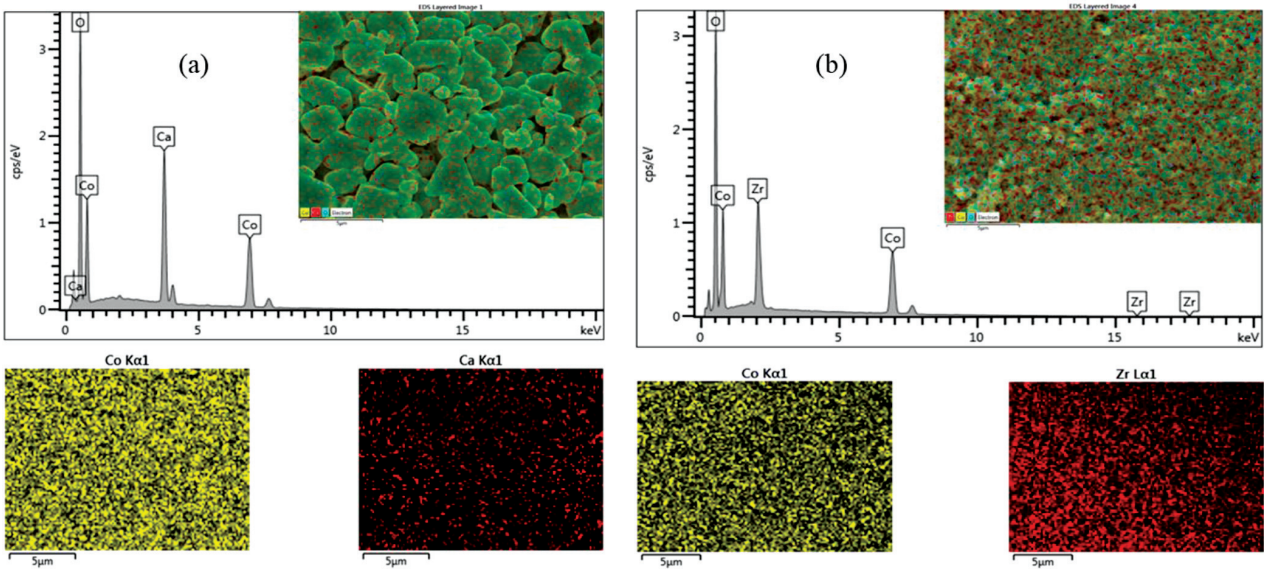

Figure 5: EDX spectra with element mapping of a) Co and b) Ca or Zr. Each element is represented by a different color: green for cobalt, yellow for oxygen, and red for either calcium or zirconium

Lithium cannot be identified using the EDX method because it is too light to be detected.[18,19] Additionally, cobalt also underwent a slight reduction, but it was not fully determined as the EDX analysis was only performed on certain areas (a larger mapping area would give more accurate values).[20,21]

Table 3 shows the elemental composition of the precursor powder

Table 3: Elemental composition of LCMO cathode powder including Co, M (Ca,Zr) and O

Element	Theoretical molar ratio (mol)	Experimental molar ratio (mol)	
		LCCO	LCZO
Co	0.8	0.79	0.78
M	0.2	0.21	0.22
O	$2-\delta$	2.34	2.05

4 CONCLUSIONS

In conclusion, homogeneous cathode powder $LiCo_{0.8}M_{0.2}O_{2-\delta}$ (M = Ca or Zr) was synthesized. XRD analysis confirmed the successful synthesis of homogeneous LCMO cathode powders (M = Zr, Ca) at a calcination temperature of 800 °C. FESEM/EDX analysis indicated homogeneous elemental distributions within the powders, resulting in final experimental molar ratios of $LiCo_{0.79}Ca_{0.21}O_{2-\delta}$ and $LiCo_{0.78}Zr_{0.22}O_{2-\delta}$ for the Ca- and Zr-doped cathodes, respectively. The successful synthesis of these materials sets a solid foundation for future investigations into their electrochemical performance, essential for a full assessment of their potential in SOFC applications.

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Declarations

Muhammad Amirul Mamsor and Nurul Akidah Baharuddin are the main contributors. The authors declare that they have no competing interests.

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