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## Comparative Characterization on Structural Properties of Calcined $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ Carbonate as Potential Composite Cathode for SOFC

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# Comparative Characterization on Structural Properties of Calcined $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$ - $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ Carbonate as Potential Composite Cathode for SOFC

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**Abstract.** In this research work, Samarium Strontium Cobalt Oxide,  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC) and Samarium Doped Ceria,  $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$  (SDC) carbonate or (SDCc) were used as the new composite cathode powder materials. This composite cathode powder was prepared via high energy ball milling (HEBM) method for SOFC application. The composition of 50 wt.% of SSC was chosen to be added with 50 wt.% of SDCc powder. The prepared powders of composite cathode SSC:SDCc were then undergone calcination process at different operating temperatures which has been varied from 600 °C, 650 °C, 700 °C and 750 °C. Characterizations of the SSC-SDCc composite cathode powders were performed through X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). However from the XRD analysis, there was an appearance of new secondary peaks which corresponded to strontium carbonate (strontianite),  $\text{SrCO}_3$  of SSC-SDCc composite cathode powders. The result obtained from FTIR analysis verified the existence of carbonates elements in all SSC-SDCc composite cathodes. Based on FTIR studies, the selection for operating temperatures of calcination did not give significant impact on the thermal and structural properties of calcined SSC-SDCc carbonate composite cathodes. Additionally, the presence of secondary phase revealed from the XRD study might result in different microstructural that could influence the electrochemical behavior.

Keywords: component; Calcination, SOFC, carbonate, SSC.

## 1. Introduction

The increasing of energy consumption in the world has been more important than the past ten years. Recent technologies of SOFC as energy are not yet fully developed to accomplish all demands that has brought many researches in improving the SOFC components. These includes cathode, anode, interconnector, electrolyte and the technology of manufacturing [1, 2]. This research is conducted for the purpose on elucidation new potential cathode materials that can be operated at low temperature of solid oxide fuel cell, in order to ensure SOFC will operate in optimum operation, without any limitation such as high polarization resistance and chemical instability. Temperature within the range of 400 °C to 600 °C for operating SOFC has gained more concern and interest for research compared to high operating temperature solid oxide fuel cell [3, 4].



In recent years, numerous researchers of SOFCs are more engrossed on the issues associated with operational temperature and presents significant solutions regarding cathode material selection, synthesis, and processing. Therefore, it is expected that high performance can be achieved by using mixed ionic electronic ceramic (MIEC) material electro-catalyst in a composite of electrolyte material [5, 6]. Besides that, the performance can be improved if the operating temperature of cathode composite SOFC was lowered to approximately 400 °C. Nowadays, samarium strontium cobaltite (cobalt oxide),  $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  (SSC) perovskite oxide has been revealed as a potential cathode material because of its higher ionic conductivity properties. It also, exhibits extraordinary electronic conductivity compared to barium strontium cobalt ferrite (BSCF) that reveals a good catalysis for oxygen reduction and is particularly compatible with the ceria carbonate based electrolytes [7-9]. According to previous researchers, SSC based composite cathode was normally used with other ionic conducting electrolyte such as gadolinia doped ceria (GDC) and samarium doped ceria (SDC) [10, 11]. Unfortunately, SSC shows high thermal expansion coefficient (TEC) mismatch and high reactivity with some electrolytes when operating at high temperature. Prior researcher have proved that this weakness might be reduced by adding SDC electrolyte with pure SSC [12, 13]. The modification on SDC has been made by adding SDC with alkaline binary carbonate. This modification was scrutinized in order to develop new SDC-carbonate (SDCc) that can overcome the thermal mismatch and chemical instability issues of SOFC [14, 15]. Enlargement of path and transportation for ionic conduction to occurs are predictable can be provide by the carbonates addition on SDC. This remarkable will further improve the performance of composite cathode [16]. However, the composite cathodic reaction mechanism with corresponding SSC itself are not well understood and need to evaluate in details.

SSC perovskite oxides with alkaline-earth metal ions can interact easily with  $\text{CO}_2$  from air atmosphere in order to form a carbonate phase at outer SSC layer. SSC has lack of phase stability under processing and cell fabrication in static air atmosphere that is due to the presence of carbon dioxide ( $\text{CO}_2$ ) [17]. This situation can lead to formation of secondary phase such as strontium carbonate,  $\text{SrCO}_3$  and strontium cobalt oxide,  $\text{SrCoO}_3$  that may disrupt the electrochemical behavior of SSC. Previous work revealed the presence of impurities or secondary phases from SSC based composite cathode has to be clearly investigated. One of the crucial requirements of composite cathode is the chemical compatibility that should be maintain up to cell operation. Chemical compatibility issues remain critical for composite cathode which is strongly determined by the phase stability of the composite cathode [18-20].

Method on the process of starting SSC-SDCC composite cathode powder with high energy ball milling (HEBM) technique is very crucial and still new. By using HEBM technique, hypothetically powders with homogeneous, finest and well distributed will be obtained. Enhancement of TPB area will be occurred [21, 22]. Influences of calcination as heat treatment process on the composite cathode powder notable significance impact on cathode powder and the microstructure. Consequently, the correlation of method of powder preparation with calcination towards SSC is still new, particularly SDCc as the electrolyte. Currently, there is no research study on the influence of calcination temperature on SSC-SDCC composite cathode powder properties. In this work, the their phase, chemical and structural properties were effects of temperature on the composite cathode powder microstructure regarding investigated in detail by several characterization technologies.

## 2. Materials and Experimental Method

### A. Materials Preparation

In this study, four groups of samples were prepared. Initially, composite electrolyte which was prepared by employing suitable amounts of 20 wt. % from the binary carbonates and 80 wt. % from the SDC powders was produced. In order to prepare SSC-SDCC composite cathode powders, commercial SSC raw powder (Kceracell, Korea) was mixed with SDCC via high energy ball

milling (HEBM), (Fritsch Pulveristte, Germany) method at 550 rpm. Combination of SSC-SDCC was carried out in ethanol as the solvent media for 24 hours. The composite cathode powder obtained were differentiated as presented in Table 1. However, to eliminate an excess ethanol in this sample powders, the powders were further dried in an oven for several hours with operating temperature at 100 °C. Furthermore, the composite cathode powder produced was grounded using agate mortar and followed by calcination process in a furnace with operating temperature at 680 °C for 1 hour. Finally, the same procedure was employed until the composite cathode powder was completely grounded. Then, the prepared powders were subjected to calcination temperatures of 600, 650, 700 and 750 °C, before it will be used for further characterization as mentioned in the next section.

### B. Characterizations

Table 1 below is the list with sample recognition of all SSC-SDCC sample powders which had been prepared in this research work to investigate the characteristic of the starting composite cathode powders, X-ray diffractometer from Bruker D8 Advanced was used in order to observe the crystallinity and purity of the SSC-SDCC composite cathode powder. In this instrument, X-rays of 1.5406 Å wavelength was generated by Cu K sources. The X-ray diffraction data were taken at 2 angles ranging from 20° to 80°. Finally, Fourier Transform Infrared (FTIR) was carried out using Perkin Elmer Spectrum 100 FTIR spectrometer. The analysis for existence of carbonate and chemical bonding can be done by employing the FTIR that was ranged from 3000 to 600 cm<sup>-1</sup>. The spectra obtained were recorded in the transmittance mode with a resolution of 4 cm<sup>-1</sup>.

Table 1. List of SSC-SDCC Composite Cathode Powders

Sample recognition	SSC (wt. %)	SDCc (wt. %)	Temperature (°C)
As prepared	50	50	-
SSCB60	50	50	600
SSCB65	50	50	650
SSCB70	50	50	700
SSCB75	50	50	750

## 3. Results and Discussion

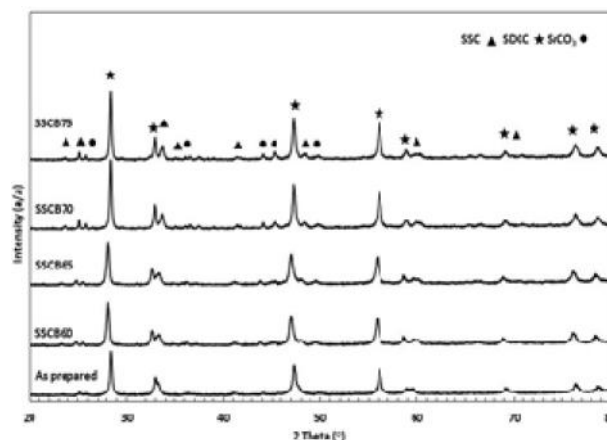
### A. Phase and Chemical Analysis

From the XRD spectra depicted in Fig. 1, XRD spectrum for uncalcined powder of AU sample exhibited an equivalent characteristic with commercial and orthorhombic lattice structure of Sm<sub>0.5</sub>Sr<sub>0.5</sub>CoO<sub>3-δ</sub>, SSC uncalcined powder (No. JCPDS 53-0112), and a face-centred cubic lattice of Sm<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>1.9</sub>, SDC (No. JCPDS75-0158) [19, 20]. The carbonate phase from binary carbonate displayed the crystallite peak of the SDC phase pure fluorite crystal structure where the face-centred cubic lattice was similar to the crystal structure from commercial SDC.

However, a secondary phase of strontium carbonate or strontianite (SrCO<sub>3</sub>) was emerged at 2θ 25.18°, 44.07°, 45.85°, and 49.85° for calcined powder of SSC-SDCc composite cathode. These new secondary peaks appeared after the mixing process of SSC-SDCc via HEBM method. These peaks did not change the phase structure. However, Haider et al., (2011) acknowledged that the appearance of secondary peak SrCO<sub>3</sub> in the cathode cells has always been phenomenal. The increase in the calcination temperature had caused the intensities of all secondary peaks to be free from the calcination temperatures. It was caused by the instability of SSC perovskite during the calcination process [18]. The A-site cations from pure SSC tend to interact with the ambient carbon dioxide, CO<sub>2</sub> in air atmosphere.

This interaction was then produced a surface carbonate layer on SSC which can be defined as secondary phase of strontium carbonate [20, 23]. This phase of  $\text{SrCO}_3$  was resulted from elements of Sr contained in SSC and the present of carbonate ( $\text{CO}_3$ ) contained in  $(\text{Li/Na})_2\text{CO}_3$ . The impurities from  $\text{SrCO}_3$  in nanoscale materials might be remarkable for the dissimilarity between crystallite surface and volume ratio. This dissimilarity might occur between large bulk crystallites and nanoparticles consisted in SSC-SDCc composite cathode powders [24].

According to prior researcher, the presence of an impurity phase came from the formation of  $\text{SrCO}_3$  secondary phase in the combustion synthesis of SSC composite nanopowders [18]. The evolution of crystalline phase from as-synthesized SSC powders had also been studied in an open-air area for 2 hours at various calcination operating temperatures from 600 to 1200 °C. The as-prepared powder and the powder calcined at 600 °C contained the corresponding oxides such as  $\text{SrCO}_3$  and cobalt oxide  $\text{Co}_3\text{O}_4$ . The completely single perovskite phase of SSC was reported to be formed at the calcination temperature of 1100°C above for 2 hours [14].



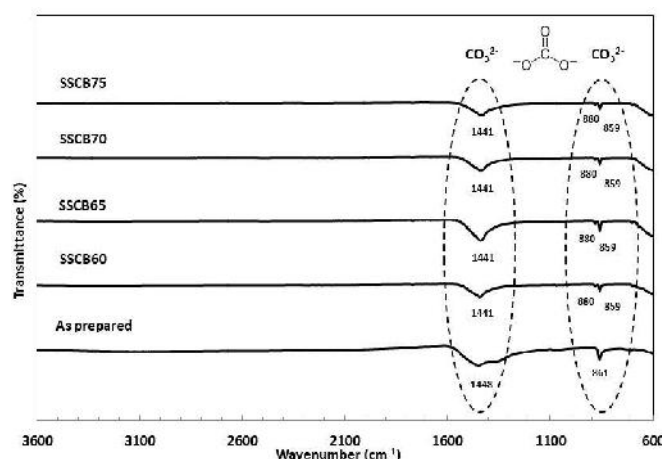
**Figure 1.** XRD patterns for all composite cathode powder

### B. Bonding Structural Analysis

The presence of ions carbonate ( $\text{CO}_3$ ) after powder preparations and calcination process had become an issue in ensuring the existence of carbonate after the heat treatment process. The characteristic transmittance lines of the SSC- SDCc composite cathode infrared rays were taken and analyzed to examine the presence of functional groups and carbonates after calcination process. A broad band ranging from 3000 to 3600  $\text{cm}^{-1}$  has the feature that corresponds to hydrogen (H O–H) [25]. It can also be attributed to adsorbed water because of the connection of the sample and the environment.

FTIR spectra of as-prepared and calcined composite cathode powders at various temperatures are depicted in Fig. 2. FTIR analysis revealed that the  $\text{CO}_3^{2-}$ , carbonate (the carboxylate salt group) was situated at wavenumbers of 1428-1449  $\text{cm}^{-1}$  and 855-859  $\text{cm}^{-1}$  [19]. Previous findings had stated that the  $\text{CO}_3$  bonding was observed at 1430-1436  $\text{cm}^{-1}$  and 861-862  $\text{cm}^{-1}$  from all SSC-SDCc composite cathode powders. From this figure, it can be detected that  $\text{CO}_3^{2-}$  was slightly shifted from higher wavenumbers of 1449 and 859  $\text{cm}^{-1}$  to lower wavenumbers of 1428 and 855  $\text{cm}^{-1}$ .

These bands became narrow with the increasing of calcination temperatures from 600-750 °C. In order to ensure the ionic and electronic conduction were done in good means, the existence of carbonate layers was very crucial. This dramatic effect might enlarge the electrochemical cell performance properties of SSC-SDCc for SOFC application [25, 26].



**Figure 2.** FTIR spectrum for all composite cathode powder

#### 4. Conclusion

In the present work, the effect of calcination temperature on powder properties of SSC-SDCc composite cathode was investigated systematically. Secondary peaks of  $\text{SrCO}_3$  and  $\text{SrCoO}_3$  were appeared from the XRD spectra analysis which obtained from the mixing process of SSC and SDCc. While FTIR study showed the existence of carbonate after calcination process on SSC-SDCc composite cathode powder. Based on FTIR studies, the existence of carbonate after 750 °C of calcination temperature has been remarkable that the selection operating temperatures of calcination between 600 °C until 750 °C in this study did not give significant impact on the thermal and structural properties of calcined SSC-SDCc carbonate composite cathode. However, more detailed investigation will be performed in future to determine the effects of secondary phase,  $\text{SrCO}_3$  based on the porosity, thermal expansion coefficients and electrochemical impedance spectroscopy performance testing.

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