Structural and Electrical Properties of Na$_x$COO$_2$
Thermoelectric Synthesized via Citric-Nitrate Auto-Combustion Reaction

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Abstract. A series of Na$_x$CoO$_2$ thermoelectric has been successfully prepared from nanoparticles powder synthesized via citric-nitrate auto combustion reaction. In this work, the aqueous Co nitrate was mixed with a controlled concentration of aqueous Na nitrate to obtain the mixture solution with Na molar concentration, $x$ from 0.1 to 0.9. A calculated amount of citric acid and ammonia solutions were added to the mixture as a fuel and ignition agent for the combustion reaction respectively. The drying process at 300 °C on the hotplate with an infrared lamp at the top has turned the mixture solution into precursor gels which yielded fine ashes throughout the auto combustion reaction. The ashes are calcined at 700 °C for 1 h, pelletized by 14.2 MPa of compressive force and sintered at 900 °C for 1 h. The TG/DT analysis of the gel samples show that the decomposition reaction of the Na and Co nitrates occurred in a highly exothermic single-step reaction at around 250 °C to 280 °C and left the desirable mass. The XRD analysis revealed that the calcination process has transformed the mass into pure Na$_x$CoO$_2$ phase. The atomic percentage obtained from the EDX indicated that the Na in Na$_x$CoO$_2$ yielded with expected $x$ in each sample. The FESEM images of the calcined samples depicted two distinct microstructures appeared in samples with $x$ ≤ 0.3 which was recognized as Na$_x$CoO$_2$ and CoO$_2$ phases. Whereas for the Na$_x$CoO$_2$ samples with $x$ ≥ 0.5 a single, dense and plate-like microstructure is developed during the calcination process. The pellet sample with $x = 0.7$ exhibits the highest temperature dependence electrical conductivity around 690 S·cm$^{-1}$ at 330 K compared to other samples due to effective phonon scattering center provided by Na ions by this concentration.

1. Introduction

In the last 20 years, thermoelectric materials have become significant interest driven by the need for more efficient materials for electronic refrigeration and power generations via direct conversion of waste heat into useful electric energy [1]. Performance of thermoelectric materials indicated by the figure of merit ZT was greatly depended on thermopower or Seebeck effect S, total thermal conductivity $\kappa$, and electrical conductivity $\sigma$ [2]. Active efforts are focusing on increasing the ZT either by lowering the lattice thermal conductivity or most fundamentally by developing new materials with large temperature dependence electrical conductivity. For all known bulk thermoelectric material such as skutterudites, clathrates, half-Heusler alloys, and complex chalcogenides have considerably high thermopower [3, 4]. However many of these compounds involved un-stable and toxic elements such as tellurium, antimony,
and germanium. Since the call to develop new thermoelectric materials is strong and will remain so as the technology improves and becomes less expensive, the discovery of ceramic oxide thermoelectric has brought excitement. Ceramic oxide materials have shown promising potential as high temperature thermoelectric materials with better stability, less toxicity and negative environmental effect compared to conventional thermoelectric compounds. The Na$_x$CoO$_2$ which consist of two layers; CoO$_2$ layer and Na layer is one important ceramic oxide thermoelectric material with high electrical conductivity [5, 6]. However, the thermoelectric properties of this oxide are largely varied by its Na concentration because of its roles in adjusting the concentration of electron in CoO$_2$ layer and acting as phonon scattering centre. It has been reported that the ZT of Na$_x$CoO$_2$ with concentration ratio Na/Co = 0.5 and Na/Co = 0.8 at 650 K is 0.02 and 0.4 respectively [7]. Moreover cracking and exfoliation during conventional sintering method are also serious [8]. Therefore the synthesizing method is crucial in order to achieve the accurate concentration of Na in Na$_x$CoO$_2$ compound with increased thermoelectric properties.

Among the methods, citric-nitrate auto-combustion reaction attracted much attention because of it has successfully been used in synthesizing various ceramic oxides with well-controlled of the concentration includes Al$_2$O$_3$, YBa$_2$Cu$_3$O$_{7-δ}$, ZrO$_2$ and TiO$_2$ [9-11]. This method is capable to vaporize the impurities hence producing highly pure samples through high exothermic combustion reaction. Thus in this work, Na$_x$CoO$_2$ is synthesized using citric-nitrate auto-combustion reaction to yield highly pure samples with controlled Na molar concentrations as formulated, homogeneous and nanostructure powder, and have increased electrical conductivity.

2. Methodology

The aqueous solution of Na nitrate (0.5 M), and Co nitrate (0.5 M) was prepared by dissolving analytical grade and 99.9 % pure of respective reagent powders into distilled water. The determined amount of aqueous NaNO$_3$ was added into aqueous Co(NO$_3$)$_2$ to obtain the solutions with the mole ratio of Na:Co = $x$:1 where the $x$ was varied from 0.5 to 0.9. Subsequently, the calculated amount of citric acid was added to the mixture and the pH was adjusted to around 7 by adding ammonia solution. The as-prepared solution was heated on the plate heater at 300 °C with an infrared lamp on top of it to provide a uniform heating. The continuous heating process turned this solution into a gel before combusted and yielded fine ashes. Most of the combustion process involved flame which turned the gel into very fine, spongy and black ashes. The ashes were calcined inside a furnace at 700 °C for 1 h under normal atmosphere and self-cooled to room temperature in the furnace. Calcination process has transformed these highly reactive ashes into a more stable, black and dense powder. Calcined powders were pelletized to the diameter of 10 mm and 2 mm thickness pellet by applying 50 MPa load. The pellets were sintered at 900 °C for 1 h under normal atmosphere. Thermal stability and decomposition characteristic of the precursor gels were determined by thermogravimetric (TG) and differential thermal analysis (DTA). These studies were performed under Argon atmosphere from room temperature to 700 °C by a heating rate of 5 °C min$^{-1}$ in a NETZSCH thermal analyser unit (409C) and using α-alumina as a reference for DTA. The structure of the samples was characterized using X-ray diffraction (XRD) technique using Ni-filtered Co Kα radiation (Bruker D8-advanced machine). The peak position and intensities were obtained in between 20° and 80° with a velocity of 0.02° s$^{-1}$. Particles sizes were calculated from the line broadening of the XRD peaks by using the Scherer formula. Lattice structure and parameters of the sample was determined using Rietfeld analysis. Field emission scanning electron microscope (FESEM: Zeiss Ultra 40XB) was used to observe microstructure and particle size of the samples. Elemental identification of the samples was determined by EDX technique. The temperature dependence electrical conductivity ($σ$) of the pellet samples was measured using four-point probe method by cooling the samples from 900 to 300 K.
3. Results and discussion

The TG-DTA curves of the precursor gels are shown in Figure 1. It can be seen that each gel lost its mass with relatively same pattern started with minor lost at the temperature 100 °C - 200 °C, followed by a major drop at temperature 250 – 280 °C and finally constant plateau from 300 °C to 700 °C. As for \( x = 0.1 \) sample, there is an additional drop of mass occurred at around 400 °C. Figure 1 also showed the DTA curves where the occurrence of an intense exothermic peak at temperatures ranged from 250 °C to 280 °C indicates the main decomposition of precursor gels.

![Figure 1. TGA curves of the gel samples with different concentration, \( x \) of Na. Inset shows the DTA patterns of the gel samples.](image)

The minor loss of mass at around 100 °C to 200 °C is due to the removal of excesses water and decomposition of citric acid. As the temperature increases, citric acid (\( \text{C}_6\text{H}_8\text{O}_7 \)) began to decompose to aconitic acid (\( \text{C}_6\text{H}_6\text{O}_6 \)) at the temperature 183 °C. Upon heating, aconitic acid is further decomposed to itaconic acid (\( \text{C}_5\text{H}_6\text{O}_4 \)). Polymerization reaction for itaconic acid has occurred when reached its melting temperature of 166 °C which produced itaconic anhydride (\( \text{C}_5\text{H}_4\text{O}_3 \)) with byproduct water and carbon dioxide. Iaconic acid is acted as a fuel once ignited. The combustion reaction of the gel is triggered by the decomposition of ammonia solution and zinc nitrate. Ammonium nitrate, cobalt hydroxide and sodium hydroxide are formed after the combustion reaction. Ammonium nitrate further pyrolysis has ignited the itaconic acid hence triggered the combustion reaction of the gel to yield nascent oxygen, \( \text{N}_2 \), water, amount of heat energy. The heat energy that released from the reaction is sufficient to remove the water in the sodium hydroxide and cobalt hydroxide and produced \( \text{Na}_x\text{CoO}_2 \).

In the combustion reaction, the citrate ion is acted as the reducing agent while nitrate ion acted as the oxidizing agent. The combustion process is done within a few seconds and emitted a large amount of carbon dioxide and \( \text{N}_2 \) gases. This kind of combustion mode is known as the rapid deconcentration which occurred for gel samples with \( x = 0.3, 0.5, 0.7 \) and 0.9. Whereas for the gel with \( x = 0.1 \), the additional mass loss at 400 °C can be attributed to the deconcentration of itaconic anhydrate at around 390 °C [12] which was formed during the low intensity combustion reaction.
Figure 2. XRD pattern of Na$_x$CoO$_2$ calcined powders samples with different concentration, $x$ of Na ions. Bars at bottom indicated Bragg diffraction pattern for Na$_{0.74}$CoO$_2$.

Figure 3. FESEM images of Na$_x$CoO$_2$ powders samples with different with different concentration, $x$ of Na ions; (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, and (e) $x = 0.9$. 
Figure 2 shows the XRD pattern of Na$_x$CoO$_2$ samples with different $x$ after calcination at 700 °C. It can be seen that the XRD peaks of samples with $x > 0.1$ existed at the same Bragg diffraction angles of Na$_{0.7}$CoO$_2$ peaks indicated by red bars at the bottom of the figure. The most significant peaks for NaCoO$_2$ were attributed from (004), (100), (102), (103) and (104) planes which are in agreement as reported by Ding et al. [13]. Crystallite size of the samples that calculated from the Scherer’s equation is in the range from 48.8 nm to 85.2 nm. It can be observed that a strong and narrow peak is due to the excellent crystallinity of Na$_x$CoO$_2$. As for the sample with $x = 0.1$, most of the peaks are assigned for CoO$_2$ phase particularly at 20 31.7°, 34.4°, 59.2° and 65.6°. It can be seen from the figure that the significant peaks of CoO$_2$ and NaCoO$_2$ phases were decreased and increased respectively with the increase in Na concentration. There is no additional peak presence in the patterns other than CoO$_2$ and Na$_x$CoO$_2$ phases indicated that there is high possibility of no impurities existing in the sample. High purity of the samples is attributed to the effectiveness of combustion reaction in burning and vaporizing the un-wanted masses hence the latter was able to yield pure Na$_x$CoO$_2$ phase.

Figure 3 shows FESEM images of the calcined Na$_x$CoO$_2$ powder samples. It can be observed in Figures 3 (a) and (b) that there are two significant microstructures existed in samples with $x = 0.1$ and 0.3 respectively. The particle-shaped structure is recognized to be Na$_x$CoO$_2$ while the bar structure is representing Co oxide. The increase of Na concentration in the Na$_x$CoO$_2$ samples with $x = 0.5$, 0.7 and 0.9 has yielded a single type microstructure as shown in Figures 3 (c), (d) and (e) respectively which is in agreement with the XRD findings. Detail observation on the figure revealed that the Na$_x$CoO$_2$ microstructures have been transformed from individual particles into dense, melted, and plate-like microstructure by increased of Na concentrations as described by Baster et al. [14]. The concentrations of Na in the samples is confirmed by the EDX results as listed in Table 1. It is shown that the atomic percent, at. % of Na detected within the samples is almost the same as the expected at. %. The expected atomic mass of Na was calculated based on the concentration of Na in the samples. Thus the resultant atomic mass provides evidence that the Na has merged with CoO$_2$ structure with suggested formula listed in Table 1.

| Na concentrations (x) | EDX analysis (Atomic %) | Formula |
|-----------------------|-------------------------|---------|
|                       | Co     | Expected Na | Achieved Na | Expected | Achieved |
| 0.1                   | 28.54  | 2.86       | 1.78        | Na$_{0.00}$CoO$_2$ |
| 0.3                   | 28.44  | 8.52       | 6.58        | Na$_{0.23}$CoO$_2$ |
| 0.5                   | 28.24  | 14.18      | 13.94       | Na$_{0.49}$CoO$_2$ |
| 0.7                   | 28.34  | 19.84      | 19.26       | Na$_{0.68}$CoO$_2$ |
| 0.9                   | 28.4   | 25.56      | 25.06       | Na$_{0.88}$CoO$_2$ |

Figure 4 shows the temperature dependence electrical conductivity of Na$_x$CoO$_2$ samples. Generally, the electrical conductivity is found to be enhanced with increases of Na molar concentration where the highest value of 690 S·cm$^{-1}$ is achieved in the sample with $x = 0.7$ at 330 °C. The electrical conductivity achieved in this work is in the range of the value for the same Na$_x$CoO$_2$ concentration reported by Liu et al. [15]. It can be clearly seen that the electrical conductivity in Na$_{0.1}$CoO$_2$ and Na$_{0.3}$CoO$_2$ samples are significantly low compared to other samples. This occurrence can be attributed to the small percentage of the yielded Na$_x$CoO$_2$ phase in the samples. Once the Na concentration is increased up to $x \geq 0.5$, single phase of Na$_x$CoO$_2$ is completely developed hence increase the amount and movement of conducting electron. On top of that, the role of Na as phonon scattering center is the primary mechanism contributed to the increase of electrical conductivity in Na$_x$CoO$_2$ samples. The increase of Na ions has lower the lattice vibrations which occurred at higher temperature hence allowed the electrons pass through the lattice structure.
Figure 4. Temperature dependence electrical conductivity of Na$_x$CoO$_2$ samples varied by Na concentration, $x$.

It also can be seen in Figure 4 that the electrical conductivity in the sample with $x = 0.9$ has been reduced. This phenomenon is highly due to the lattice distortion by the Na ions which have increased the travel distance of electron between CoO$_2$ layers. The increment of phonon scattering center offered by Na ions in this sample resulted in a nearly constant value of the electrical conductivity at increased temperatures.

4. Conclusion

The citric-nitrate auto-combustion reaction is an effective method for synthesizing Na$_x$CoO$_2$ compound with well-controlled Na molar concentration. A single step and high exothermic reaction during auto-combustion have evaporated out the impurities which the latter yielded pure Na$_x$CoO$_2$ during calcination. The temperature dependence electrical conductivity of Na$_x$CoO$_2$ is maximized in the sample with $x = 0.7$ attributed Na as effective phonon scattering center.

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References

[1] Koumoto K, Funahashi R, Guilmeau E, Miyazaki Y, Weidenauff A, and Wan C 2013 Journal of the American Ceramic Society, 96 1.
[2] Chen Z, Han G, Yang L, and Zou J 2012 Progress in Natural Science: Materials International, 22 535.
[3] Tritt T M, and Subramanian M A 2006 MRS Bulletin 31.
[4] Shiab X, Chenab L and Uberc C International Materials Reviews 2016 61 379.
[5] Liu W, Yan X, Chen G, and Ren Z. 2012 Nano Energy, 1 42.
[6] Krasutskaya N S, Klyndyuk A I, Evseeva L E, and Tanaeva S Inorganic Materials 2016 52 393.
[7] Ito M and Furutomo D 2008 Journal of Alloys and Compounds 450 517.
[8] Schneider C, Schichtel P, Mogwitz B, Beyer A, and Rohnke M 2016 Physica Stat. Soli (a) 213 1284.
[9] Suan M S M and Johan M R 2014 Materials Research and Innovations 18 73.
[10] Singh K A, Pathak L C, and Roy S K, 2007 Ceramics International 33 1463.
[11] Chandradass J and Kim K H 2009 Met. Mater. Int. 15 1039.
[12] Suan M S M and Johan M R 2013 Physica C 492 49.
[13] Ding J J, Zhou Y N, Sun Q, and Fu Z W 2013 Electrochemical Acta, 87 388.
[14] Baster D, Dybko K, Szot M, Świerczek K, and Molenda J 2014 Solid State Ionics 262 206.
[15] Liu P, Chen G, Cui Y, Zhang H, Xiao F, Wang L and Nakano H 2008 Solid State Ionics 179 2308.