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High temperature electrical conductivity and thermoelectric power of Na_xCoO_2

Pusheng Liu [a], Gang Chen [a,*], Ying Cui [a], Hongjie Zhang [a], Feng Xiao [a], Lin Wang [a], Hiromi Nakano [b]

[a] Department of Applied Chemistry, Harbin Institute of Technology, Harbin 150001, People's Republic of China
[b] Electron Microscope Laboratory and High-Tech Research Center, Ryukoku University, Seta, Otsu, 520-2194, Japan

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ABSTRACT

Layered cobalt oxides, Na_xCoO_2, with the density of sodium ions, x, ranging from 0.65 to 0.85, were prepared by rapid heat-up method. The determination by X-ray diffraction pattern of crystal structure and the grain morphology studied by scanning electron microscopy were reported. The measurements of electrical conductivity and thermoelectric power were carried out between 300 K and 1100 K. It has been found that the concentration of sodium ions sandwiched between two neighboring CoO_2 layers plays a crucial role in transport properties.

1. Introduction

Layered cobalt oxides, Na_xCoO_2, display several interesting properties with the variation of the concentration of sodium ions x. These properties include a superconducting phase of $Na_{0.35}CoO_2$ when it is intercalated by water molecules around 5 K [1], a charge-ordered insulating phase of $Na_{0.5}CoO_2$ [2] and potential applications of the composition($x \sim 0.70$)in thermoelectric energy conversion field [3]. Since the discovery of moderately large thermoelectric power (Seebeck coefficient) together with high electrical conductivity in Na_xCoO_2($x \sim 0.70$), tremendous experiments were done to search new phases for thermoelectric conversion applications. Although they simultaneously possess large thermoelectric power, high electrical conductivity and low thermal conductivity, the figure of merit was found to be too small to utilize in the practical thermoelectric conversion devices in this x range($x \sim 0.7$). While in the x range of 0.7–0.85, high temperature electrical conductivity and thermoelectric power are poorly reported [4,5].

These layered oxides consist of two layers: CoO_2 layer and Na ions layer. CoO_2 layers acting as an electron reservoir are responsible for the electrical conductivity and large thermoelectric power, while Na ions layer sandwiched between two neighboring CoO_2 layers working as a structural unit directly adjust the concentration of electron in CoO_2 layers and decrease the thermal conductivity along the stacking direction c [6,7]. Recently, neutron diffraction and electron diffraction measurements have shown that the crystal structure of the oxides is strongly dependent on sodium content [8–10]. Here we use X-ray diffraction pattern supported by Rietveld refinement to study the crystal structure at ambient temperature, the electrical conductivity and thermoelectric power have been systematically studied for the composition (x=0.65–0.85) between 300 K and 1100 K.

2. Experimental method

Polycrystalline samples of Na_xCoO_2 with various sodium content were prepared from Na_2CO_3 (99.99%) and Co_3O_4 (99.98%) by rapid heat-up method. The detailed procedure can be found elsewhere [11]. Due to the volatility of sodium element at high temperature, an extra amount of Na_2CO_3 was added. Taking the preparation of $Na_{0.78}CoO_2$ as a sample, Na_2CO_3 and Co_3O_4 in amounts according to $Na_{0.80}CoO_2$ were mixed together by ball milling for 24 h, and then the samples were directly put into the furnace at 1023 K for 12 h in air. After grinding, the powders were pressed into the pellet with the diameter of 15 mm and fired again in the furnace at 1023 K for another 12 h in the O_2 flow.

X-ray diffraction data were collected at ambient temperature from 5° to 100° with a step of 0.05° on Rigaku D/max diffractometer working with Cu Kα radiation. The sodium content was determined by means of inductively coupled plasma optical emission spectrometers (ICP-OES, Perkin Elmer, Optima 5300DV). Energy dispersive X-ray (EDX) spectroscopy implemented in a transmission electron microscope (TEM, JEM-2000EX) was used to analyze the chemical composition of some of the prepared samples. The particles morphology was studied by scanning electron microscopy (SEM, Hitachi S4800). The electrical conductivity and thermoelectric power were measured using a laboratory-designed apparatus in the temperature range of 300 K to 1100 K in air. The

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* Corresponding author. Tel./fax: +86 451 86 413753.
E-mail address: gchen@hit.edu.cn (G. Chen).

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electrical conductivity of the bar-shaped sample ($20\times4.5\times2$ mm^3) was measured by the four probe method. For the measurement of the thermoelectric power, Thermo-electromotive force measured as a function of temperature gives a straight line and its slope is thermoelectric power. The detailed procedure is described below. The sample with a pair of Pt/Rh thermocouples attached to two ends (bar-like samples) was first heated to a certain temperature, and then one of the ends was heated by an extra source to produce the temperature gradient. The temperature and voltage signals were collected by a commercial data acquisition system (Keithley 2700, Keithley Instruments Inc., America).

3. Results and discussion

Fig. 1 shows X-ray diffraction patterns of the as-synthesized Na_xCoO_2 ($x=0.65–0.85$). All the patterns are in good agreement with hexagonal γ-Na_xCoO_2 phase when x ranging from 0.65 to 0.80. For $x=0.85$ composition, a slight trace of the unreacted Na_2CO_3 was detected in X-ray diffraction pattern (marked by the small up-triangle symbol in Fig. 1). The refined crystallographic cell parameters for each sample are calculated on the basis of the X-ray diffraction patterns, as listed in Table 1. The lattice parameters a and c are found to exhibit a reverse behavior with increasing sodium content, while the cell volumes almost stay the same. The increase of crystallographic a, varying in a manner consistent with sodium content, may be caused by gradually increasing coulomb repulsion of sodium ions in the same layer. The shrinkage of lattice parameter c may result from an increasing coulomb attraction between CoO_2 layers and sandwiched Na ions layer.

X-ray diffraction patterns were fitted by least square method employing the software GSAS&EXPGUI [12,13]. Fig. 2 gives a fitting pattern for $Na_{0.78}CoO_2$ sample. Since the grain is easily oriented for this synthesis method, some of the reflections, such as (002), are refined in the process of the fitting. To demonstrate the preferred orientation of the grains, SEM was used to study the micromorphology of the composition ($x=0.78$), as illustrated in Fig. 2. It can be seen from the panel on the left hand that the grains show hexagonal architecture and the panel on the right hand shows the sheet-like transect configuration. For the refinement of sodium fractional occupancy (occ.), the summed occupancy value should be made consistent with the known composition of Na ions, i.e. $\text{occ.}_{Na(1)}+\text{occ.}_{Na(2)}=x$, and then the occupancy for each position was allow to refine. The crystal parameters of $Na_{0.78}CoO_2$ at ambient temperature are given in Table 2.

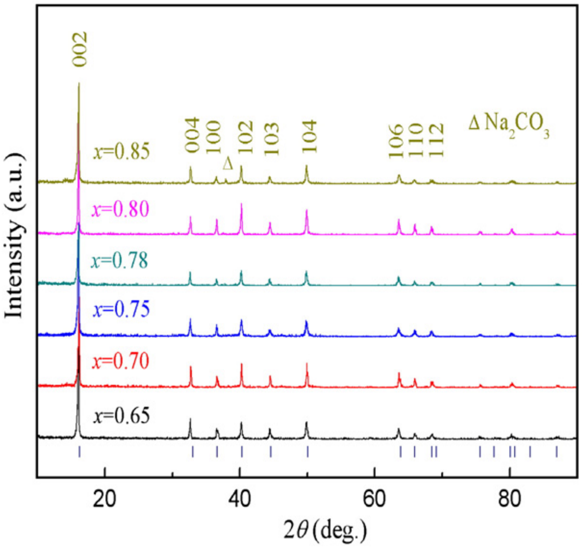

Fig. 1. Powder X-ray diffraction patterns of the as-synthesized Na_xCoO_2 ($x=0.65–0.85$). The small up-triangle symbol denotes the unreacted Na_2CO_3. We have used rapid heat-up method to prepare $x=0.60$ or below, but single phase cannot be obtained.

Table 1
Crystallographic cell parameters of Na_xCoO_2 ($x=0.65–0.85$)

x	a (Å)	b (Å)	c (Å)	V (Å^3)
0.65	2.828 (1)	2.828 (1)	10.953 (3)	75.88 (4)
0.70	2.830 (3)	2.830 (3)	10.950 (2)	75.96 (2)
0.75	2.831 (1)	2.831 (1)	10.946 (4)	76.00 (1)
0.78	2.831 (2)	2.831 (2)	10.944 (1)	76.00 (5)
0.80	2.833 (3)	2.833 (3)	10.935 (1)	76.01 (6)
0.85	2.835 (5)	2.835 (5)	10.933 (2)	76.03 (3)

The sodium content was determined using ICP-OES method by several batches of samples. It is found that the volatility of sodium element cannot be ignored when samples fired at 1023 K. In the present study, an extra amount of Na_2CoO_3 was added to complement the sodium loss. The measured results of ICP-OES method are shown in Table 3.

Fig. 3 presents curves of the electrical conductivity vs. temperature for the as-synthesized composition ($x=0.65–0.85$). We note that all the samples show metallic conduction behavior in the range measured. The magnitude of the electrical conductivity at ambient temperature is between 300–650 S/cm. It is found that the electrical conductivity is strongly dependent on the concentration of sodium ions x. In the x region of 0.65–0.78, the electrical conductivity undergoes a monotonic enhancement with increasing sodium content, when x reaches 0.78, the sample displays the best electrical conductive behavior. But for the samples with high sodium content, i.e. x ranging from 0.80 to 0.85, the electrical conductivity shows a reverse behavior, dropping to 300 S/cm for the composition ($x=0.85$).

The electrical conductivity initially increases as the amount of sodium increase up to 0.78. The same behaviors have been reported for the composition (0.55–0.75) by Motohashi et al. in the low temperature range [11]. As discussed in the introduction part, the density of electron in the CoO_2 layer, which is critical to the electrical conductivity, can be altered by the sandwiched sodium content. It can be concluded that the ratio of Co^{3+} against Co^{4+} increase with increasing sodium content, via the simple calculation of chemical valence. Meanwhile the distortion of CoO_2 layer is severe with the shrinkage of c axis. So the density of electron in the reservoir layer together with the distortion of CoO_2 plays a crucial role in electrical conductivity. Fig. 4 gives transmission electron microscope (TEM) and X-ray spectroscopy (EDS) of the composition ($x=0.80$). For the samples with the high concentration of the sodium content, TEM and EDS were performed to analyze the morphology and chemical composition of $Na_{0.80}CoO_2$. A lot of fiber-like grains were found in Fig. 4 and they were assigned to the non-magnetic insulating Na-rich phase H3 [4,5,14,15]. Meanwhile with increasing sodium, a slight trace of unreacted Na_2CoO_3 was detected in the X-ray diffraction pattern, as shown in Fig. 1. So the decrease of the electrical conductivity of the compositions ($x>0.78$) may be attributed to the introduction of secondary phase, H3 or unreacted Na_2CoO_3.

Fig. 5 displays the temperature dependence of the electrical conductivity for $Na_{0.75}CoO_2$ sample fired in different atmospheres. The response of electrical conductivity on atmosphere is prominent. It can be observed distinctly from Fig. 5 that the electrical conductivity increases with increasing PO2 partial pressure. For the sample fired under hydrogen atmosphere, the electrical conductivity differs much from the samples fired in pure oxygen and air. The introduction of reductive atmosphere obviously affects the transport properties of the sample. The hall coefficient measurement reveals that this kind of