

Transport properties of $\text{Na}_x\text{CoO}_{2-y}$

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April 6, 2007

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Abstract

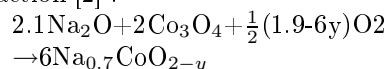
The study of the electrochemical intercalation of sodium in the cobalt bronze $\text{Na}_x\text{CoO}_{2-y}$ has shown a strong dependence of the discharge curves on the conditions of preparation (temperature and oxygen pressure) of the starting phase...

1 Introduction

Some of us have recently reported a study of the intercalation (deintercalation) of sodium in sheet $\text{Na}_x\text{CoO}_{2-y}$ bronzes[1]. Cells constituted by a sodium anode, a solution of NaClO_4 in propylene carbonate and a $\text{Na}_x\text{CoO}_{2-y}$ phase used as cathode, have been cycled under various current densities. Resulting voltage versus sodium content curves are strongly dependent on the oxygen content of the starting material.

To explain this behavior a general study of the intercalation in these materials in connection with oxygen content and transport properties has been carried out. In relation with the oxygen stacking on the layer phase, structural transitions can be observed during the electrochemical process. In order to have a simple model the P2 type bronze, which does not show a structural transition, has been selected for this study.

The starting phase have been obtained by direct synthesis according to the reaction [2] :



It requires two overnight thermal treatments at 700°C . From this starting material different oxygen contents can be obtained by thermal treatments (seven

days) under various conditions of temperature (400-700° C) and oxygen pressure (0.1-1 atm). Under such conditions, materials are well homogenized and can be kept at room temperature by quenching.

A perspective view of the structure of this material is given in fig. 1. It consists of CoO_2 sheets made of edge-sharing CoO_6 octahedra. The Na^+ ions are intercalated in a trigonal prismatic environment between adjacent slabs[2].

For the sodium stoichiometric phase NaCoO_2 the trivalent cobalt ions are in the low-spin t_{2g}^6 state. The resulting band is completely filled. When sodium ions are removed from the intersheet space an equivalent number of cobalt ions are formally tetravalent. For the composition $\text{Na}_{0.70}\text{CoO}_2$, holes resulting from the sodium non-stoichiometry are present in the t_{2g} band.

The purpose of this work is to study the relations between the oxygen departure from stoichiometry, the transport properties and the electrochemical behavior of $\text{Na}_{0.70}\text{CoO}_{2-y}$.

2 Thermogravimetric study

A thermogravimetric study has been carried out to determine the deviation from stoichiometry (y).

TGA has been realized on sintered parallelepipedic samples ($15 \times 7 \times 1 \text{ mm}^3$) with a spiral spring quartz balance. The apparatus, which has been previously described, has a sensitivity of about 10 mg/cm [3]. The sample has been maintained under 10^{-3}Torr at room temperature and then heated at 973 K under oxygen for 50 h.

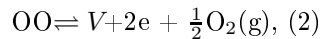
The experiments have been carried out at constant temperature, under various oxygen partial pressures. To corroborate the obtained data, a complementary study has been done in function of temperature at constant oxygen pressure (0.21 atm). Equilibration was carried out until constant weight was obtained. Depending on the temperature (673-983 K) equilibria were attained in 30-60 h. The upper temperature limit was fixed by the stability of the material while the lower was imposed by the kinetics of the system. The oxygen pressure range was 0.1-1 atm. As the material contains tetravalent cobalt ions, decomposition may occur for oxygen pressure smaller than 0.1 atm.

In the temperature range 903-988 K the weight variation of the sample ($m - m_0$) versus oxygen pressure obeys the relation :

$$m - m_0 = y(P_{O_2})^{-1/6}, \quad (1)$$

where, y is a constant,

All the isothermal curves converge to the same point which corresponds to the hypothetical oxygen stoichiometric sample. In the defect theory this behavior would indicate the existence of doubly ionized oxygen vacancies resulting from the reaction :



Nevertheless, as will be discussed in the following, this material is a p-type conductor and consequently it is impossible to make the assumption $[e] = 2[V]$ which would make it possible to confirm this model. Another hypothesis would

be the presence of interstitial cobalt. Although thermogravimetric experiments do not allow the determination of the nature of the defects, they do allow the characterization of the oxygen departure from stoichiometry versus the synthesis conditions for all materials used in the transport and electrochemical studies Fig. 2 shows the variation of y versus $(P_{O_2})^{1/6}$.

3 Electrical properties

Electrical conductivity and thermoelectric power measurements have been carried out at high temperature under thermodynamic equilibrium conditions and at low temperature on quenched pellets. The conductivity was measured by the four-point method using dc. It should be noted that the ionic conductivity (Na^+ transport) of the studied material does not perturb the measurements, as it is several orders of magnitude smaller than the electronic conductivity [4]. Thermoelectric power studies have been carried out with a new apparatus described elsewhere [5].

Fig. 3 shows the variation of the electrical conductivity versus oxygen pressure at several temperatures under equilibrium conditions. The conductivity, σ , obeys the relation :

$$\sigma = K(P_{O_2})^{+1/20}. \quad (3)$$

where K is a constant.

The positive exponent of eq. (3) indicates that holes are predominant in the transport phenomena.

The nature of these charge carriers is confirmed by the thermopower data (fig. 4).

From a schematic point of view the trivalent ($3d^6$) and tetravalent ($3d^5$) presumably low-spin cobalt ions form a partially filled band for the CoO_2 sheets. Electrons resulting from the oxygen departure from stoichiometry compensate partially the original electron holes, arising from sodium nonstoichiometry, which remain the effective charge carriers.

As a result the conductivity varies linearly with $(P_{O_2})^{+1/20}$. The y decrease with increasing oxygen pressure leads to a decrease of the compensation effect. Consequently the hole concentration increases and the conductivity does the same (eq. (3)). The small value of the exponent ($+1/20$) suggests that the majority of the charge carriers (original holes resulting from sodium nonstoichiometry) remains unchanged by changes of the oxygen pressure.

The thermal variation of the conductivity is given in fig. 5 for different oxygen pressures. With increasing temperature the electron number arising from the oxygen deviation from stoichiometry increases : $y = K' \exp(-\Delta E/kT)$. Consequently the conductivity decreases simultaneously with the hole concentration due to this compensation effect.

Low-temperature measurements (figs. 6 and 7) on quenched pellets emphasize this compensation phenomena. Though the variation of the conductivity with temperature shows a metallic character, the high value observed at room

temperature for the thermoelectric power and their thermal dependence illustrate a more complex behavior.

4 Electrochemical study

Fig. 7 shows the variation of cell voltage versus sodium content for two phases having the same Na / Co atomic ratio (0.70), but different y values. These curves (open-circuit voltage) are obtained in the following way : the cell made with about 40 mg of the starting $\text{Na}_{0.70}\text{CoO}_{2-y}$ phase is discharged for 2h under $20 \mu\text{A}$, then the circuit is opened. The cell relaxes until constant voltage is obtained (the relaxation time is the range 2-8 h). This process is continuously repeated until complete discharge.

The comparison of the two curves shows that they differ essentially by a horizontal shift. The two characteristic plateaus are obtained for each sample at exactly the same voltage : 2.54 V and 2.44 V. Nevertheless these voltage values are observed for both materials for different sodium contents. Indeed as a result the assumption of a succession of sodium-ordered phases fails. For the less oxygen-deficient phase ($y = 0.004$) a given value of the voltage is obtained for a bigger intercalation amount of sodium than for the more oxygen-deficient phase. This behavior emphasizes the results obtained by electrical measurements, the electrons arising from the oxygen vacancies compensate partially the original positive charge carriers.

During the intercalation process the injected electrons raise the Fermi level by an energy which depends on the density of states in its neighborhood. When the electronic compensation resulting from the oxygen departure from stoichiometry decreases, a higher amount of sodium must be intercalated to obtain the same potential value (i.e. the same Fermi level).

We would like to thank E. Marquestaut for technical assistance.

References

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Figure 1: Layer structure of $\text{Na}_{0.70}\text{CoO}_2\text{-}y$

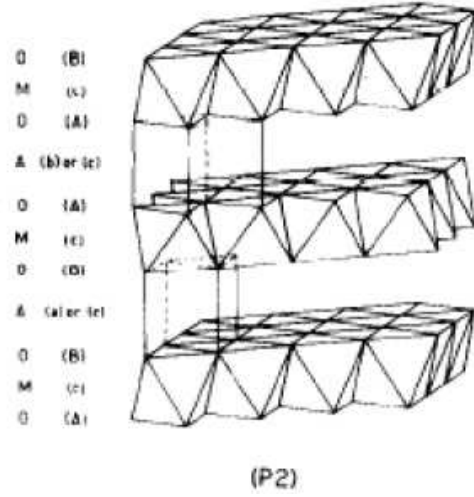


Figure 2: Pressure dependence of nonstoichiometry in $\text{Na}_{0.70}\text{CoO}_2\text{-}y$

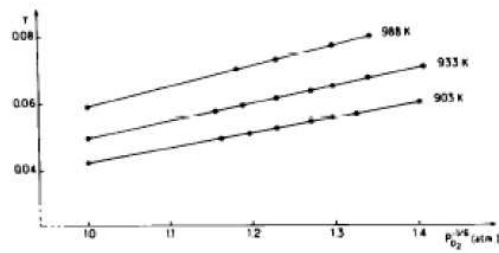


Figure 3: Electrical conductivity versus logarithm of oxygen pressure

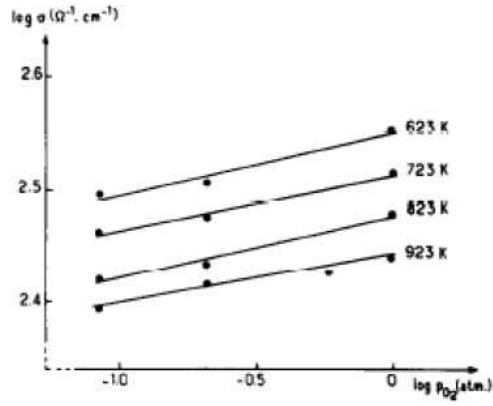


Figure 4: Temperature dependence of the electrical conductivity under equilibrium conditions

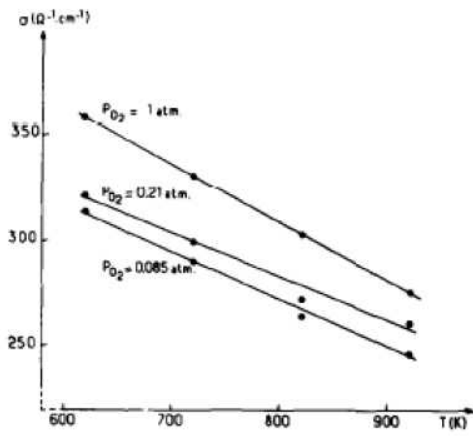


Figure 6: Temperature dependence of the thermoelectric power of quenched pellets

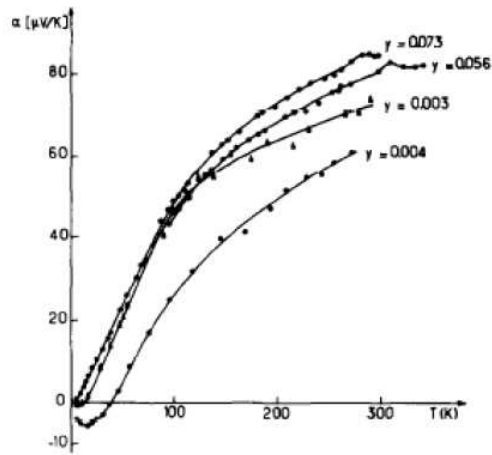
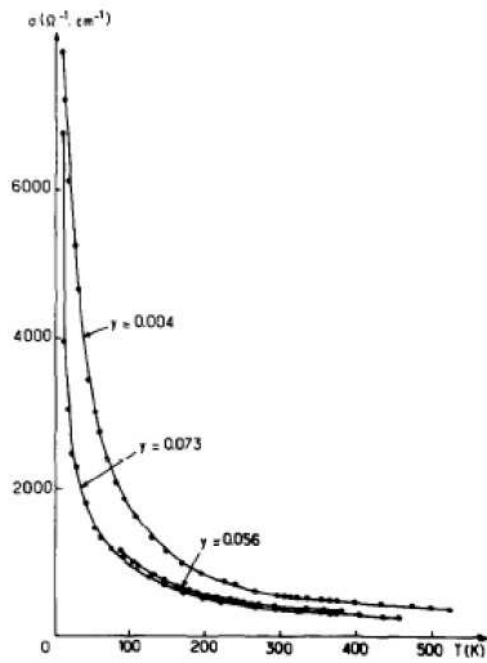


Figure 5: Temperature dependence of the electrical conductivity of quenched pellets



Surface des solides