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THERMOGRAVIMETRIC STUDIES OF Na_xMO_2-type BRONZE

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ABSTRACT

The paper presents the results of thermogravimetric studies of $Na_{0.7}CoO_2$ bronze as a function of oxygen pressure at temperatures ranging from 400 to 700 °C.
The proposed method of analysis of defect type, based on the calculation of derivative of the function $\ln(\mathrm{def}) = f(\ln p_{O_2})$, has shown the existence of cobalt ions in sodium sites.

INTRODUCTION

The Na_xMO_2-type compounds (where M - transition metal), belong to the group of materials applied as electrodes in electrochemical cells working on the basis of intercalation of alkaline ions. Owing to the layered structure of this compound, it is possible to introduce the alkaline ions between the $(MO_2)_n$ layers formed by MO_6 octahedra already at ambient temperature. These compounds exibit also appreciable electronic conduction being associated with direct overlap of 3d orbitals of transition metals in the layer built of octahedra. The thermogravimetric and electrical conductivity measurements have shown additionally that these compounds axhibit also some defects in transition metal-oxygen sublattice wich significantly influences their electrochemical properties [1, 2].
This paper proposes a method of analysis of thermogravimetric data enabling determination of defect types. It also presents the results of studies on the deviation from stoichiometry and electrical conductivity of cobalt bronze in function of temperature and oxygen pressure.

EXPERIMENTAL

The starting material has been obtained by direct synthesis from Na_2O and Co_3O_4 in air at the temperature of 970 K. For determining the deviation from stoichiometry a spiral microbalance was used [3]. The balance contained a quartz spiral with a sensitivity of 10 mg/cm up to loads of 1,5 g. The studies have been done in the temperature range 990-670 K and oxygen pressure range 100-10 kPa. At oxygen pressure lower than 10 kPa the sample has been found to undergo decomposition.
Electrical conductivity measurements have been carried out by means of a four-probe direct-current method in the annalogous temperature and oxygen pressure ranges.
Fig. 1 presents a dependence of deviation from stoichiometry, w (in mol of oxygen/mol of $Na_{0.7}CoO_2$) on oxygen pressure. The obtained results presented in such a coordinate system for different temperature can be described by two straight lines. Thus the dependence of the deviation from stoichiometry in oxygencobalt sublattice on oxygen pressure can be is described by the following eq.

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$$w = \text{const}\ p_{O_2}^{1/n} \qquad (1)$$

The values of 1/n exponents are listed in Table 1.

Fig. 2 shows the dependence of electrical conductivity on oxygen pressure at different temperatures. This dependence can be described by the following equation:

$$\sigma = \text{const}\ p_{O_2}^{1/20} \qquad (2)$$

The sodium content in Na_xCoO_2 can vary in a quite broad range 0.55-1 [4]. This compound can thus be treated as defected in sodium sublattice in relation to $NaCoO_2$. Consequently it will contain sodium vacancies in the amount of 1-x mole, and to satisfy the electroneutrality condition - the equivalent amount of Co^{+4} ions (electron holes). The thermogravimetric and electrical conductivity measurements carried out in function of oxygen pressure indicate that this compound contains also other defects. The negative value of the exponent in the dependence of the deviation from stoichiometry on oxygen pressure (Table 1) show that the predominant defects which should be considered are oxygen vacancies or interstitial cobalt ions (cobalt ions in sodium position) and electron holes. Formation of these defects can be written as follows:

$$O_O^x + 2h^{\bullet} = 1/2\ O_2 + V_O^{\bullet\bullet} \qquad (3)$$

$$Co_{Co}^x + 2O_O^x + 2V_{Na}' + 4h^{\bullet} = Co_{Na}^{\bullet\bullet} + O_2 \qquad (4)$$

The dependence of defect concentration on oxygen pressure can be determined on the basis of equilibrium constant for the reaction of defect formation and electroneutrality condition which for the reaction (3) can be written as follows:

$$K = (V_O^{\bullet\bullet})p_{O_2}^{1/2}/(h^{\bullet})^2\ ; \qquad (V_{Na}') = 2(V_O^{\bullet\bullet}) + (h^{\bullet}) \qquad (5)$$

The dependence of oxygen vacancy concentration and that of electron holes on oxygen pressure is:

$$K(1-x-2w)^2 = w\ p_{O_2}^{1/2} \qquad (6)$$

$$K(h^{\bullet})^2 = 1/2\left[1-x-(h^{\bullet})\right]p_{O_2}^{1/2} \qquad (7)$$

where $(V_O^{\bullet\bullet}) = w$, $(V_{Na}') = 1-x$, $(h^{\bullet}) = 1-x-2w$

The obtained complex relations do not allow to determine in a simple way the character of the dependence of defect concentration on oxygen pressure. It is, however, possible to determine the character of the dependence between $d\ln(def)/d(\ln p_{O_2})$ and ionic defect concentration. These derivatives have been calculated by differentiating the obtained implicit functions with the substitution $x = e^{\ln x}$.

For oxygen vacancies the following relationships have been found:

$$\frac{d \ln w}{d \ln p_{O_2}} = -\frac{1}{2}\,\frac{1-x-2w}{1-x+2w} = \frac{1}{n_w} \qquad (8)$$

$$\frac{d \ln(h^{\bullet})}{d \ln p_{O_2}} = \frac{w}{1-x+2w} = \frac{1}{n_h} \qquad (9)$$

As follows from the above calculations, the obtained derivatives, being equivalent to exponents in eqs. (1) and (2), are dependent on defect concentration (at constant x).

Fig. 3 shows the function described by eq. (8) for $x = 0.3$, together with analogous functions for Co_{Na} and defects of different ionization degree ($V_O^{\bullet}$, $Co_{Na}^{\bullet}$, $Co_{Na}^{\bullet\bullet}$, $Co_{Na}^{\bullet\bullet\bullet}$) obtained as above described.

Fig. 4 shows, in turn, the functions given by eq. (9) as well as the analogous functions for defects of different ionization degree. From the theoretical calculations presented in Fig. 4 it follows that the $d\ln(h^{\bullet})/d\ln p_{O_2}$ derivative, for both types of defects, has relatively small positive values which is consistent with the experimentally obtained value of exponent in eq. 2. For ionic defects the discussed dependences are different. The derivative values are negative. On the basis of comparison between the values of derivatives and experimentally obtained values of exponents (Table 1) in the concentration range studied it can be stated that predominant ionic defects in the cobalt bronze, except for sodium vacancies, are cobalt ions Co^{+3} substituted for sodium.

ACKNOWLEDGENT

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REFERENCES

1. J. Molenda, C. Delmas and P. Hagenmuler, Solid State Ionics 9, 10 (1983) 431
2. J. Molenda, Phys. Stat. Sol. (b) 122 (1984) 591
3. S. Mrowec and A. Stokłosa, J. Thermal Anal. 2, (1970) 73
4. J. Braconnier, C. Delmas, C. Fouassier, P. Hagenmuler, Mat. Res. Bull. 15, (1980) 1797

Table 1.

The exponents of the dependences of the deviation from stoichiometry and electrical conductivity on oxygen pressure eqs. (1) and (2).

T (K)	$-1/n_w$ I	$-1/n_w$ II	$1/n_h$
990	0.98	0.82	
935	0.96	0.65	
923			0.045
905	0.96	0.67	
823			0.055
723			0.050
623			0.056
	$\delta = \pm$ 0.02		$\delta = \pm$ 0.008

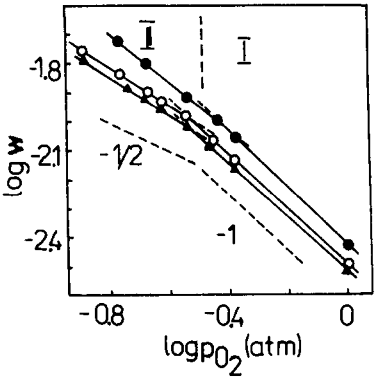

Fig. 1. The dependence of deviation from stoichiometry in $Na_{0.7}CoO_2$ on the oxygen pressure for temperatures: ●-990K, o-935K, ▲-905K

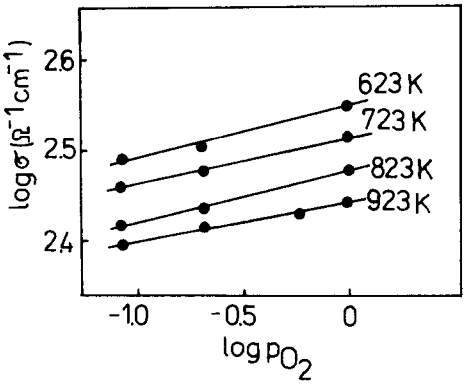

Fig. 2. The dependence of electrical conductivity in $Na_{0.7}CoO_2$ on the oxygen pressure for several temperatures

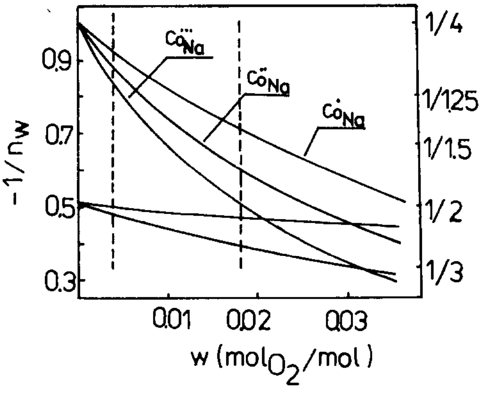

Fig. 3. The dependence of the exponent $1/n_w$ (eqs. (16) and (18)) as a function of nonstoichiometry for defects of different ionization degree

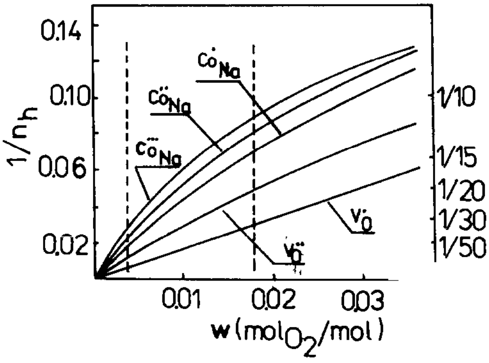

Fig. 4. The dependence of the exponent $1/n_h$ (eqs. (17) and (19)) as a function of nonstoichiometry for defects of different ionization degree