JOURNAL OF APPLIED ELECTROCHEMISTRY 21 (1991) 308–312

Calcium β''-alumina and Nasicon electrolytes in galvanic cells with solid reference electrodes for detection of sulphur oxides in gases

G. RÓG*, A. KOZŁOWSKA-RÓG, K. ZAKUŁA

Institute of Materials Engineering, Academy of Mining and Metallurgy, 30059 Kraków, Poland

W. BOGUSZ

Institute of Physics, Warsaw University of Technology, 02525 Warszawa, Poland

W. PYCIOR

Sulfur Industry Development Research Center, "Siarkopol", 39405 Tarnobrzeg, Poland

Received 27 June 1990; revised 30 September 1990

Calcium-β''-alumina and Nasicon were applied as solid electrolytes for SO_x ($x = 2$ or 3) gas detection. The following two galvanic cells with solid reference electrodes were assembled

$$Pt|O_2, CaO\,||\,Ca\text{-}\beta''\text{-}Al_2O_3\,||\,CaSO_4|SO_3, SO_2, O_2|Pt$$

$$Pt|O_2, Na_2O\,||\,Nasicon\,||\,Na_2SO_4|SO_3, SO_2, O_2|Pt$$

Calcium and sodium sulphates were used as auxiliary electrolytes to provide protection of β''-Al_2O_3 or Nasicon electrolytes from chemical reaction with SO_2. The e.m.f. was measured in the temperature range 850–1070 K for five various test gases. The measured e.m.f.s had values a little lower than the calculated ones. The results show clearly that both the cells can act as SO_x electrochemical sensors for temperatures not exceeding 1070 K.

---

1. Introduction

The continuous measurement of the concentration of sulphur oxides is required for the control of many industrial processes, as well as for the monitoring of air pollution. Numerous efforts have been made to develop SO_x ($x = 2$ or 3) sensors using galvanic cells with solid electrolytes. First, SO_2–O_2–SO_3 concentration cells with alkali metal sulphate electrolytes were studied [1–5]. Alkali metal sulphates are alkali ion conductors at elevated temperatures. These cells functioned well at small differences in the partial pressures of SO_2 between the anode and the cathode. For large differences in P_{SO_2} the e.m.f.s were, however, lower than the calculated values. This fact appears to be due to the permeation of gases through pores and cracks in the electrolyte as a result of the low sinterability of alkali metal sulphates. Then, sodium β-alumina and Nasicon were used as electrolytes for SO_x sensing [6–8]. These materials are well known as sodium ion conductors, being used in sodium–sulphur batteries. They can be easily sintered to acceptable densities. The Nasicon electrolyte was also combined with an Na_2SO_4 auxiliary electrolyte, providing protection of Nasicon from chemical reaction with SO_2 [8]. The e.m.f. of the cells with Nasicon and sodium β-alumina was found to be in close agreement with values given by the Nernst equation. It is worth mentioning that silver β-alumina was also used instead of sodium β-alumina [9]. Another type of galvanic cell for SO_x sensing is that with a solid reference electrode. The use of a solid reference electrode is important from the point of view of miniaturization of the sensor. The ($Au + Au_2Na$), ($\beta + \beta''$)-alumina [10] and a mixture of metal sulphate with metal oxide [11, 12] as such electrodes were applied.

In the present paper two galvanic cells with calcium β''-alumina and Nasicon solid electrolytes were investigated. Their arrangements can be represented as

$$Pt|O_2, CaO\,||\,Ca\text{-}\beta''\text{-}Al_2O_3\,||\,CaSO_4|SO_3, SO_2, O_2|Pt \qquad (1)$$

$$Pt|O_2, Na_2O\,||\,Nasicon\,||\,Na_2SO_4|SO_3, SO_2, O_2|Pt \qquad (2)$$

Ca-β''-alumina belongs to a family of β-alumina superionic conductors. So far it has been successfully used in a secondary calcium solid electrolyte high temperature battery [13]. The calcium and sodium solid reference electrodes consisted of an appropriate

---

* Author to whom correspondence should be addressed.

0021-891X/91 $03.00 + .12

oxide dispersed in the calcium β-alumina or Nasicon matrix, respectively [14, 15]. The β''-alumina phase is thermodynamically unstable with respect to the pure oxide phase. Therefore the temperature of the measurements was chosen to be sufficiently low to minimize the reactions between electrode and electrolyte, i.e. the oxide activity in the reference electrode was maintained equal to unity. $CaSO_4$ and Na_2SO_4 were used as auxiliary electrolytes. They protected the electrolyte phase from attack by SO_x. The sulphate phase also plays an essential role in establishing the cathode equilibrium.

2. Experimental details

2.1. *Preparation/characterization of solid electrolytes*

Ca-β''-alumina was prepared from MgO-stabilized Na-β''-alumina by ion exchange in the molten salt condition. The method of Na-β''-alumina preparation was described in [16]. The ion exchange experiments with Ca^{2+} ions were performed in an α-alumina crucible filled with a $Ca(NO_3)_2$–$CaCl_2$ eutectic mixture. The Na-β''-alumina pellets (3 mm thick and 12 mm in diameter) were dipped in the fused salt at 850 K in air and held there for over 24 h. The exchange surfaces of the samples were then cleaned from solidified eutectic salt by immersion in a molten $CaCl_2$ bath. Then the samples were treated with anhydrous ethyl alcohol to remove the residue of the salt. The extent of ion exchange, as determined by weighing the pellets before and after exchange, was greater than 96%.

The Nasicon electrolyte was prepared from Na_2CO_3, SiO_2, ZrO_2 and $NH_4H_2PO_4$ using the method described in [17]. The raw materials were wet ball-milled and calcined at 470 K and 1270 K. After each calcination the powder was remilled. Then the powder was pressed into pellets of 10 mm diameter and of 2 mm thickness. Sintering was conducted at 1520 K on platinum foil for 10 h.

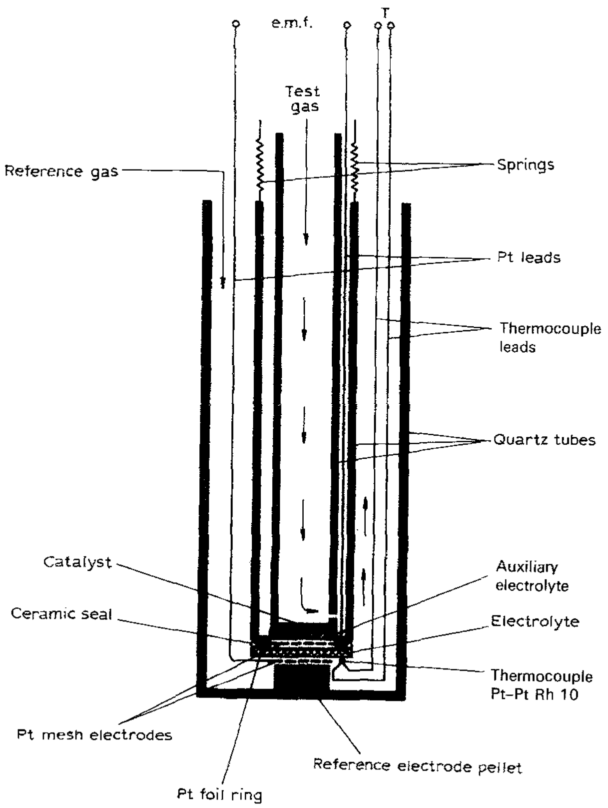

Fig. 1. Schematic diagram of the experimental apparatus.

All electrolyte samples were X-ray controlled.

2.2. *Reference electrodes and auxiliary electrolytes*

The calcium solid reference electrode was prepared in the following way: a pellet of Ca-β''-alumina was ground and milled. The powder was accurately mixed with a pure calcia powder. The mixture was then pressed into pellets. Thus each pellet contained pure calcia as a separate phase.

The sodium solid reference electrode was prepared by the method given in [14]. The appropriate amount of a Nasicon powder was impregnated by a saturated aqueous solution of sodium carbonate. The powder was dried and calcined, preliminary at 470 K overnight, and at 1170 K for 4 h. It was then milled and pressed into pellets. The X-ray analysis of the pellets indicated that a pure Na_2O phase was present in the mixture with Nasicon phase. A minute amount of free ZrO_2 was also detected.

The calcium auxiliary electrolyte was prepared from an almost equimolar mixture of Ca-β''-alumina and of anhydrous $CaSO_4$ powders. The mixture was pressed into pellets.

Similarly, the sodium auxiliary electrolyte was pelletized from a mixture of Nasicon and anhydrous Na_2SO_4 powders.

2.3. *Galvanic cell and e.m.f. measurements*

A schematic diagram of the experimental apparatus is shown in Fig. 1. The reference electrode and the auxiliary electrode pellets were spring-loaded on either side of the electrolyte pellet. Platinum mesh electrodes were placed on both surfaces of the electrolyte pellet. Additionally a platinum foil ring was put on the upper surface of the electrolyte to protect it from attack by SO_x. Platinum wires were spot-welded to the platinum electrodes. To separate the test gas from the reference electrode compartment a ceramic seal was used. This was placed between an electrolyte pellet and a quartz tube lying in the electrolyte. Gas leakage was found to be negligible under these conditions. The upper surface of the auxiliary electrolyte was painted with Pt paste containing 20 wt % of $LaCrO_3$ catalyst. The catalyst accelerates the attainment of equilibrium in the (SO_2 + O_2) mixture. The entire cell was placed in a larger quartz tube with a reference gas atmosphere. The quartz tube with the cell was placed in a vertical resistance furnace and heated to the measurement temperature. The temperature was controlled by Pt–Pt/10% Rh thermocouple, the junction of which was fixed on the electrolyte pellet surface. All the e.m.f. measurements were performed in the temperature range 850–1070 K. Gas mixtures containing different amounts of SO_2 served as test gases. After the e.m.f. had been measured, the phase composition of the reference electrode pellet was X-ray controlled. The presence of the pure oxide phase was confirmed in each e.m.f. experiment.

2.4. *Test gases*

Test gases were obtained by mixing separate metered streams of dry SO_2 and Ar containing a known amount of O_2 in a tower packed with glass beads. The oxygen content in Ar was measured by means of a solid state oxygen electrochemical sensor based on yttria-stabilized zirconia. The test gas flowed through the inner quartz tube around the auxiliary electrolyte and solid electrolyte pellets at a rate of 1.2×10^{-6}–$2.0 \times 10^{-6}\,\mathrm{m^3\,s^{-1}}$. The cell e.m.f. was independent of the flow rate. At higher temperatures SO_2 and O_2 react to form SO_3 and in this way the gas composition changes. The equilibrium composition can be calculated from the standard Gibbs energy change, ΔG_3^0, for the reaction

$$SO_{3(g)} = SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \tag{3}$$

ΔG_3^0 (in joules) is expressed as a function of temperature (in kelvin) [18]

$$\Delta G_3^0 = 97780 - 92.78\,T \qquad (\pm 300) \tag{4}$$

Assuming α moles of SO_3 are formed at equilibrium at any fixed T one can find the partial pressures of SO_2, SO_3 and O_2 at equilibrium

$$P_{SO_2} = P^*(1 - \alpha)\Big/\sum n_i$$

$$P_{SO_3} = P^*\alpha\Big/\sum n_i$$

$$P_{O_2} = P^*(n_{O_2} - \alpha/2)\Big/\sum n_i$$

where P^* is the total pressure of the mixture, n_{O_2} and n_{Ar} are the initial numbers of oxygen and argon moles in the gas mixture, respectively, and $\Sigma\, n_i = 1 + n_{O_2} + n_{Ar} - \alpha/2$. Thus, the equilibrium constant, K_3, of Reaction 3 is given by

$$K_3 = \left(P^*\Big/\sum n_i\right)^{1/2} (1/\alpha)[(1 - \alpha)(n_{O_2} - \alpha/2)^{1/2}] \tag{5}$$

K_3 is related to ΔG_3^0 by the expression

$$K_3 = \exp(-\Delta G_3^0/RT) \tag{6}$$

Then, for a given inlet gas composition, and from a knowledge of ΔG_3^0 at the specified temperature, the value of α was computed.

3. Results and discussion

The e.m.f. of the Cells 1 and 2 is a result of the difference in the activity of Me^{n+} ions ($Me^{n+} = Ca^{2+}$ and Na^+, respectively) at the electrodes. By the assumption that the cell works reversibly, the e.m.f. is related to the activity of Me^{n+} ions, a'_{Me} and a''_{Me}, by the Nernst equation

$$E = RT/(2F)\ln(a'_{Me}/a''_{Me})^q \tag{7}$$

where $q = 1$ for Me = Ca and $q = 2$ for Me = Na, respectively, F is the Faraday constant, R the gas constant, and T the absolute temperature.

The Me activity at the cathode, a''_{Me}, is fixed by the dissociation reaction

$$Me_qSO_4 \rightleftharpoons q\mathrm{Me} + SO_{3(g)} + \tfrac{1}{2}O_2(P''_{O_2}) \tag{8}$$

The equilibrium constant for Equation 8, K_8, is

$$K_8 = (a''_{Me})^q P_{SO_3}(P''_{O_2})^{1/2}(P^*)^{-3/2} \tag{9}$$

where $P^* = 1.013 \times 10^5$ Pa.

Assuming that SO_3, SO_2 and O_2 are in equilibrium at the electrode according to Equation 3, the equilibrium constant, K_3, is expressed by

$$K_3 = P_{SO_2}(P''_{O_2}/P^*)^{1/2}(P_{SO_3})^{-1} \tag{10}$$

Thus, one obtains from Equations 9 and 10

$$(a''_{Me})^q = K_3K_8(P^*)^2/(P_{SO_2}P''_{O_2}) \tag{11}$$

The Me activity at the reference electrode (anode), a''_{Me}, is fixed by the reaction

$$q\mathrm{Me} + \tfrac{1}{2}O_2(P'_{O_2}) = Me_qO \tag{12}$$

If a_{MeO} at the electrode is assumed to be unity, the equilibrium constant for Reaction 12, K_{12}, is

$$K_{12} = (a'_{Me})^{-q}(P^*/P'_{O_2})^{1/2} \tag{13}$$

Hence

$$(a'_{Me})^q = K_{12}^{-1}(P^*/P'_{O_2})^{1/2} \tag{14}$$

By combining Equations 7, 11, and 14 one obtains

$$E = RT/(2F)\ln\frac{P_{SO_2}P''_{O_2}}{K_3K_8K_{12}(P'_{O_2})^{1/2}(P^*)^{3/2}} \tag{15}$$

Taking into account

$$-RT\ln K_3 = \Delta G_3^0 = \Delta_f G^0(SO_2) - \Delta_f G^0(SO_3) \tag{16}$$

$$-RT\ln K_8 = \Delta G_8^0 = -\Delta_f G^0(Me_qSO_4) + \Delta_f G^0(SO_3) \tag{17}$$

$$-RT\ln K_{12} = \Delta G_{12}^0 = \Delta_f G^0(Me_qO) \tag{18}$$

($\Delta_f G^0(i)$ is the standard Gibbs free energy of formation of the compound (i)), the Equation 15 may be transformed into the following form

$$E = \varepsilon_1 + \varepsilon_2 + RT/(2F)\ln\frac{P_{SO_2}P''_{O_2}}{(P^*)^2} \tag{19}$$

where

$$\varepsilon_1 = \frac{1}{2F}[\Delta_f G^0(Me_qO) + \Delta_f G^0(SO_2) - \Delta_f G^0(Me_qSO_4)] \tag{20}$$

$$\varepsilon_2 = -RT/(4F)\ln(P'_{O_2}/P^*) \tag{21}$$

Table 1. Initial partial pressure of SO_2 (p_{SO_2}) *and corresponding equilibrium partial pressures of* SO_2 (P_{SO_2}) *and of oxygen* (P''_{O_2}) *in the test gases in the temperature range 850–1070 K*

Test gas no.	p_{SO_2} *(Pa)*	*T* *(K)*	P_{SO_2} *(Pa)*	P''_{O_2} *(Pa)*
1	20 360	850	4 710	29 580
		920	9 370	31 300
		980	13 270	32 620
		1070	15 900	33 630
2	15 900	850	4 430	22 790
		920	8 270	24 310
		980	11 140	25 430
		1070	12 970	26 240
3	11 040	850	4 010	14 660
		920	6 750	15 860
		980	8 520	16 630
		1070	9 570	17 090
4	5 890	850	3 000	7 940
		920	4 380	8 580
		980	5 080	8 900
		1070	5 440	9 080
5	2 680	850	1 710	5 870
		920	2 240	6 120
		980	2 460	6 220
		1070	2 560	6 270

The value of ε_1 was calculated on the basis of the $\Delta_f G^0$ values found in [19]. The value of ε_2 was calculated for a partial pressure of oxygen at the reference electrode $P'_{O_2} = 2.1 \times 10^4$ Pa, and for a total gas pressure $P^* = 1.013 \times 10^5$ Pa. In Table 1 the partial pressures of SO_2, P_{SO_2} and of O_2, P''_{O_2}, at equilibrium for temperatures at which the e.m.f. was measured, are given. The values correspond to various test gases. The equilibrium pressures were calculated from the initial composition of the test gas, in which the partial pressure of SO_2 was P_{SO_2}. Equations 19–21 served the calculations of the e.m.f. The measured e.m.f. values are compared with the calculated ones in Table 2. The measured e.m.f.s are mean values of five independent series of measurements. For both cells the response time, including the time needed for the experimental system to be flushed by the new gas mixture, was not longer than 360 s. The e.m.f. values were practically constant for 6–8 h and then decreased slowly with time. In order to visualize the relation between calculated e.m.f.s and measured ones, the e.m.f. as a function of ln $[P_{SO_2} P''_{O_2} (P^*)^{-2}]$ for a temperature of 980 K is shown for both cells in Fig. 2.

Table 2. Values of e.m.f. (mV) of the Cells 1 and 2

Test gas no.	*T* *(K)*	*E.m.f. of Cell 1*		*E.m.f. of Cell 2*	
		Calculated	*Measured*	*Calculated*	*Measured*
1	850	311	296 ± 15	542	524 ± 12
	920	317	299 ± 10	551	531 ± 16
	980	315	308 ± 9	552	536 ± 15
	1070	300	284 ± 10	540	533 ± 18
2	850	299	282 ± 12	531	505 ± 16
	920	302	286 ± 13	536	515 ± 10
	980	297	274 ± 15	534	509 ± 14
	1070	279	260 ± 8	519	502 ± 14
3	850	279	256 ± 12	511	489 ± 18
	920	277	262 ± 13	511	484 ± 15
	980	268	253 ± 10	505	480 ± 17
	1070	245	220 ± 16	485	467 ± 15
4	850	246	221 ± 8	478	460 ± 11
	920	235	219 ± 10	469	440 ± 14
	980	220	205 ± 12	456	443 ± 13
	1070	190	179 ± 16	430	412 ± 14
5	850	215	196 ± 9	446	421 ± 15
	920	195	179 ± 12	429	402 ± 12
	980	174	166 ± 10	411	397 ± 13
	1070	138	123 ± 11	378	361 ± 12

According to Equation 19 this function should be linear for given *T*. All the measurement points lie beneath the calculated curve. Similarly for other temperatures the measured values are lower than the calculated ones, as shown clearly in Table 2. The following factors may be considered as the reasons of such a lowering of the e.m.f.: (i) the permeation of gases through the electrolyte, (ii) deviations from the equilibrium state in the test gas, (iii) side reactions at the reference electrode/electrolyte interface, which can occur especially at higher temperatures, (iv) inaccuracy in the $\Delta_f G^0(i)$ determination (see Equations 19 and 20). As mentioned above, the equilibrium partial pressure of SO_2, P_{SO_2}, is related to the initial partial pressure of SO_2, p_{SO_2}. Conservation of sulphur requires that

$$p_{SO_2} = P_{SO_2} + P_{SO_3} \tag{22}$$

Inserting this into Equation 10 gives

$$K_3 = (P''_{O_2}/P^*)^{1/2} P_{SO_2}/(p_{SO_2} - P_{SO_2}) \tag{23}$$

Consequently

$$P_{SO_2} = p_{SO_2} K_3/[K_3 + (P''_{O_2}/P^*)]^{1/2} \tag{24}$$

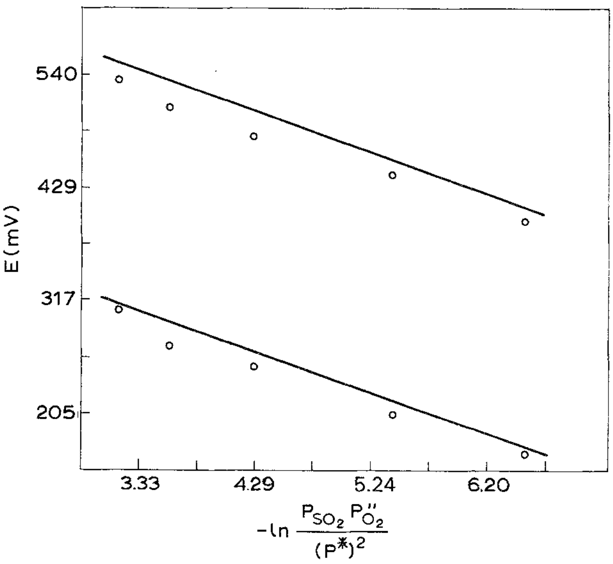

Fig. 2. Variation of the e.m.f. of the Cells 1 and 2 with test gas composition at 980 K. (——) Calculated; (○) measured.

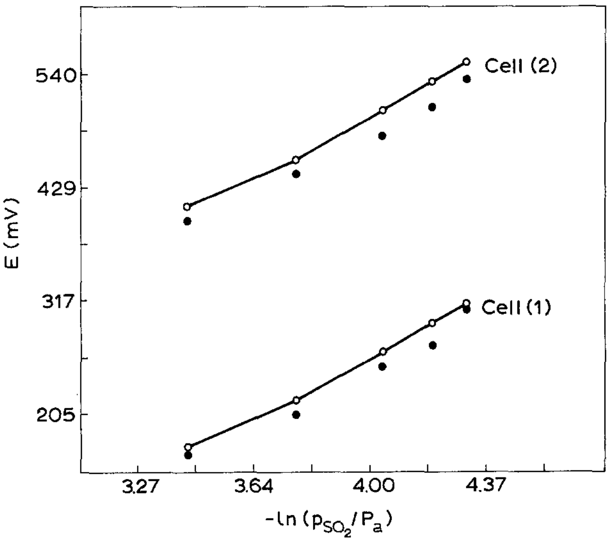

Fig. 3. E.m.f. of the Cells 1 and 2 as a function of the initial SO_2 partial pressure in a test gas at 980 K. (○) Calculated; (●) measured.

Substituting P_{SO_2} in Equation 19 by p_{SO_2}, the e.m.f. as a function of the initial partial pressure is obtained

$$E = \varepsilon_1 + \varepsilon_2 + RT/(2F) \ln Z(p_{SO_2}/P^*) \quad (25)$$

where

$$Z = \frac{K_3(P''_{O_2}/P^*)}{K_3 + (P''_{O_2}/P^*)^{1/2}}$$

As seen from Equation 25 the e.m.f. is a complicated function of initial partial pressure of SO_2 in the gas mixture. Figure 3 shows the e.m.f. of the Cells 1 and 2 as a function of the logarithm of initial partial pressure of SO_2 (in Pa) at 980 K. The points representing the measured e.m.f. are situated below the calculated curve, similarly to the diagrams shown in Fig. 2. The difference between the observed and the calculated values does not exceed 30 mV for the Cell 1, and 25 mV for the Cell 2, i.e. it is not greater than a few percent of the measured e.m.f. Since the e.m.f. of the cells is a measure of the product of two pressures ($P_{SO_2} P''_{O_2}$) (*cf.* Equation 19) the oxygen pressure should be independently measured, if absolute values for the SO_2 partial pressure are required. Because of the deviation of the measured e.m.f. from the calculated values, calibration of the cells is needed. Thus, calcium-β''-alumina and Nasicon seem to be promising electrolytes in SO_x electrochemical sensors with solid reference electrodes.

References

[1] M. Gauthier and A. Chamberland, *J. Electrochem. Soc.* **124** (1979) 1842.
[2] M. Gauthier, A. Chamberland, A. Belanger and M. Poirer, *ibid.* **124** (1977) 1584.
[3] K. T. Jacob and D. B. Rao, *ibid.* **126** (1979) 1842.
[4] W. L. Worell and Q. G. Liu, *Sensors and Actuators* **2** (1982) 385.
[5] Y. Saito, T. Maruyama, Y. Matsumoto, K. Kobayashi and Y. Yano, *Solid State Ionics* **14** (1984) 273.
[6] E. Sugimoto and Z. Kozuka, *J. Min. Met. Inst. Jpn.* **100** (1984) 603.
[7] T. Maruyama, Y. Saito, Y. Matsumoto and Y. Yano, *Solid State Ionics* **17** (1985) 281.
[8] R. Akila and K. T. Jacob, *J. Appl. Electrochem.* **18** (1988) 245.
[9] M. Itoh and Z. Kozuka, *J. Electrochem. Soc.* **133** (1986) 1512.
[10] M. Itoh, E. Sugimoto and Z. Kozuka, *Trans. JIM* **25** (1984) 504.
[11] N. Imanaka, Y. Yamaguchi, G. Adachi and J. Shiokawa, *J. Electrochem. Soc.* **132** (1985) 2519.
[12] Y. Sato, T. Maruyama and Y. Yano, *Can. Metall. Q.* **25** (1986) 51.
[13] A. F. Sammels and B. Schumacher, *J. Electrochem. Soc.* **133** (1986) 235.
[14] G. Róg and A. Kozłowska-Róg, *Solid State Ionics* **7** (1982) 291.
[15] G. Róg, S. Koziński and A. Kozłowska-Róg, *Electrochim. Acta* **28** (1983) 43.
[16] G. Róg and A. Kozłowska-Róg, *ibid.* **30** (1985) 335.
[17] W. Bogusz, *Phys. Stat. Sol.* (*a*) **66** (1981) K109.
[18] 'JANAF Thermochemical Tables', 2nd ed. (The Thermal Research Laboratory, Dow Chemical Company, Midland Michigan, 1971).
[19] I. Barin and O. Knacke, 'Thermochemical Properties of Inorganic Substances' (edited by O. Kubaschevski), Springer Verlag, Berlin (1973).