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An electrochemical investigation of the thermodynamic properties of $Na_2Mo_2O_7$ and Na_2NiO_2

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Abstract

The thermodynamic properties of the compounds $Na_2Mo_2O_7$ and Na_2NiO_2 were determined by using the high temperature galvanic cells Pt,Ar + CO_2 + O_2, Na_2CO_3 |NASICON|$Na_2Mo_2O_7$ + Na_2MoO_4, O_2 + CO_2 + Ar,Pt (I) and Pt,Ar, Ni + NiO + Na_2NiO_2 |NASICON|$Na_2Mo_2O_7$ + Na_2MoO_4 + MoO_2, Ar,Pt (II) in the temperature range 650–800 K and 673–773 K, respectively. The reversible emf of cell-I, at $P_{CO_2} = 112.6$ and 282 Pa, and cell-II can be expressed as $E'_{I}(P_{CO_2} = 112.6\ \mathrm{Pa}) = -282.7 + 1.13T$ (±2) mV, $E''_{I}(P_{CO_2} = 282\ \mathrm{Pa}) = -274.7 + 1.081T$ (±2) mV and $E_{II} = 1383 + 0.230T$ (±1.5) mV, respectively. The standard Gibbs energy of formation of $Na_2Mo_2O_7$ and Na_2NiO_2 from elements computed from the emf's of the cells and auxiliary information from the literature are expressed as $\Delta_f G_m{}^\circ\langle Na_2Mo_2O_7\rangle = -2240.0 + 0.618T$ (±2) $\mathrm{kJ\,mol^{-1}}$ and $\Delta_f G_m{}^\circ\langle Na_2NiO_2\rangle = -684.1 + 0.257T$ (±7) $\mathrm{kJ\,mol^{-1}}$, respectively. © 1997 Elsevier Science B.V.

1. Introduction

The corrosion of structural stainless steel used in coolant circuits of liquid-metal-cooled fast breeder reactors (LMFBRs) is enhanced by dissolved oxygen in liquid sodium. When dissolved oxygen is present in liquid sodium, ternary compounds of Na–M–O (M = Fe, Cr, Mo and Ni) systems are formed and involved in this corrosion process. An accurate knowledge of phase relations and thermodynamic properties of these ternary systems are important for understanding the corrosion processes. Previous work in this laboratory have established phase relations in the system Na–M–O (M = Ni, Mo and Fe) [1–3]. Thermodynamic properties of Na_4MoO_5, Na_2MoO_4 and $Na_2Mo_2O_7$ were estimated by Lindemer et al. [4]. Thermodynamic properties of Na_4MoO_5 were determined by Gnanasekaran et al. [5]. Weller and King [6] reported the enthalpy and entropy of formation of Na_2MoO_4 at 298.15 K. Enthalpy of formation of Na_2MoO_4 was determined by O'Hare et al. [7] also by using solution calorimetry. Iyer et al. [8] have measured the enthalpy increments of Na_2MoO_4 and $Na_2Mo_2O_7$ in the temperature range 335 to 760 K using the drop calorimetric technique. There are no experimental values on the Gibbs energy of formation of $Na_2Mo_2O_7$. The standard free energy of formation of Na_2NiO_2 from component oxides was measured using an emf technique based on CaF_2 solid electrolyte by Shaiu et al. [9]. However the authors themselves did not consider their data reliable. As part of a larger program of research on phase relations and thermodynamic properties of condensed phases in the Na–M–O (M = Cr, Fe, Ni & Mo) systems, the Standard Gibbs energy of formation of $Na_2Mo_2O_7$ and Na_2NiO_2 was determined using a solid state galvanic cell technique in the temperature range 650 to 800 K.

2. Experimental details

2.1. Materials

Na_2MoO_4 (99.95% E. Merck, Germany), Na_2CO_3 and MoO_3 (99.9% Aldrich Chem. Co., USA) and MoO_2 (99.5% Ventron, Germany) were used in this work. High purity Ar + CO_2 calibrated gas mixtures containing 1.4×10^4

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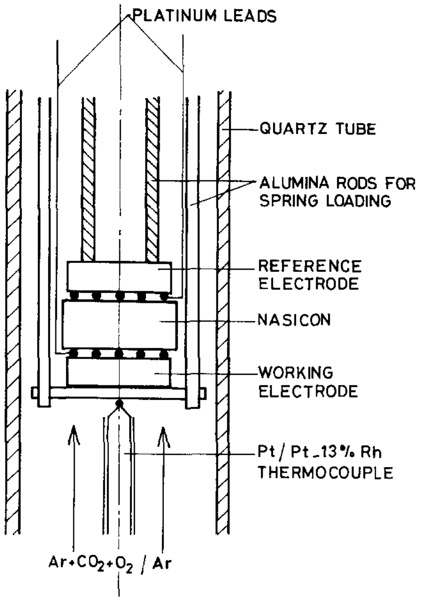

Fig. 1. Schematic representation of the cell used for emf measurements.

ppm of CO_2 and high purity Ar and O_2 gases were obtained from Bhoruka Gas, India.

Sodium oxide was prepared by reacting $NaNO_3$ (AR grade, Merck, India) with molten Na followed by distilling off the excess Na. The details of this preparation are described elsewhere [1]. $Na_2Mo_2O_7$ was prepared by mixing equimolar ratio of Na_2MoO_4 and MoO_3 and heating in a Pt boat at 800 K under a flow of dry air. Na_2NiO_2 was prepared as described in Ref. [1]. The molybdates were stored in a vacuum desiccator whereas Na_2O and Na_2NiO_2 were stored in a moisture free inert atmosphere glove box. The compounds $Na_2Mo_2O_7$ and Na_2NiO_2 were characterised by X-ray diffraction. Owing to the moisture sensitive nature of Na_2NiO_2, samples of Na_2NiO_2 were loaded and sealed in Lindemann capillaries before being taken out for X-ray diffraction analysis. The X-ray diffraction patterns obtained for Na_2NiO_2 were compared with the patterns given in Refs. [10,11], respectively. NASICON was prepared as described in Ref. [12]. $Ar + CO_2 + O_2$ gas mixtures of fixed CO_2 partial pressures (112.6 and 282 Pa) were prepared by passing high purity O_2 and $Ar + CO_2$ gas mixtures containing 1.41% CO_2 through a calibrated mass flow controller and mixing them in a stainless steel chamber. The out flowing gas mixtures were analyzed for CO_2 concentration by gas chromatography and were found to be 112.6 and 282 Pa, respectively.

2.2. Emf measurement

Emf measurements using the galvanic cells

$$\mathrm{Pt,Ar} + CO_2 + O_2\mathrm{,}Na_2CO_3|\mathrm{NASICON}|Na_2Mo_2O_7 + Na_2MoO_4\mathrm{,}O_2 + CO_2 + \mathrm{Ar,Pt} \qquad \text{(I)}$$

and

$$\mathrm{Pt,Ar,Ni} + \mathrm{NiO} + Na_2NiO_2|\mathrm{NASICON}|Na_2Mo_2O_7 + Na_2MoO_4 + MoO_2\mathrm{,Ar,Pt} \qquad \text{(II)}$$

were made as a function of temperature in the range 650 to 800 K and 673 to 773 K, respectively. The electrodes were prepared by mixing equal volume fractions of the condensed phases, pelletising them and sintering at 800 K. A stacked pellet assembly shown in Fig. 1 was used for emf measurements. The preparation of the electrodes as well as the assemblage of the cell-II were done in a moisture free inert atmosphere glove box. The cell-I was operated under fixed CO_2 partial pressures of 282 and 112.6 Pa and O_2 partial pressures of 8.0×10^4 and 9.2×10^4 Pa. Cell-II was operated under pre-purified Ar gas. Since the Na activities at each electrodes of cell-I and cell-II are extremely low, there is no danger of transport of Na from one electrode to the other via the gas phase. The cell assembly was housed inside a vertical furnace such that the electrodes were maintained at the constant temperature zone. A stainless steel foil was wrapped over the outer quartz tube surrounding the cell and was earthed to minimize induced emf on the Pt leads. The cell temperature was measured by a Pt/Pt–13% Rh thermocouple. The temperature of the cell was controlled within ± 1 K. The cell voltage was measured using a high impedance electrometer (Keithley Model 617). At each temperature the cell emf was monitored for at least 5 h. For cell-I the time required to attain constant emf (1 mV) varied from 20 to 45 min depending on the temperature of measurement, longer periods being required at lower temperature. After measurements the cell was left at the highest temperature of measurement for 48 h and the electrode/electrolyte interfaces were examined.

For cell-II the time required to attain constant emf varied from 60 to 100 min. After the initial stabilisation the emf's of cell-II were steady and reproducible for a period of 96 h and later the cell output started drifting. Interaction between the NASICON and $\mathrm{Ni} + \mathrm{NiO} + Na_2NiO_2$ electrode was observed on examination. The observed stability and reproducibility of emf values for a prolonged period of 96 h indicated that the kinetics of interaction was very slow. Experiments were therefore carried out using fresh electrodes and electrolytes and emfs were recorded within 84 h.

In each cell, steady emf's which were within ± 1 mV were recorded. The reversibility of the cells was checked by microcoulometric titration in both directions. The reproducibility of the cell was also verified by making measurements during several cycles of increasing and decreasing temperatures. Phase compositions of the electrodes were analyzed by X-ray diffraction before and after emf measurements.

3. Results and discussion

3.1. The compound $Na_2Mo_2O_7$

The X-ray diffraction pattern of the compound $Na_2Mo_2O_7$ obtained in this study matches with the reported pattern [10].

The variation of the emf of cell-I with temperature at $P_{CO_2} = 112.6$ and 282 Pa is shown in Fig. 2. The least-squares regression analysis of the emf data at $P_{CO_2} = 112.6$ and 282 Pa yields

$$E'_I = 1.13T - 282.7\ (\pm 2)\ \text{mV} \quad (1)$$

and

$$E''_I = 1.08T - 274.7\ (\pm 2)\ \text{mV}, \quad (2)$$

respectively. The overall cell reaction can be written as

$$Na_2Mo_2O_7 + Na_2CO_3 = 2Na_2MoO_4 + CO_2. \quad (3)$$

Since the overall cell reaction involve CO_2 gas, the cell emf is expected to vary with CO_2 partial pressure. The cell emf, Gibbs free energy change for Eq. (3), ΔG_3, and the standard Gibbs free energy change, $\Delta G_3°$, corresponding to Eq. (3) are related by the expression

$$\Delta G_3 = -nFE = \Delta G_3° + RT \ln P_{CO_2}, \quad (4)$$

where $n = 2$ is the number of electrons involved in the electrode reactions, F is the Faraday constant and R is the universal gas constant. It is clear from Eq. (4) that the change in emf ($\Delta E = E'_I - E''_I$) for a fixed change in P_{CO_2}($\Delta P_{CO_2} = P'_{CO_2} - P''_{CO_2}$) as a function of temperature can be expressed as

$$\Delta E = (-RT/nF) \ln P'_{CO_2}/P''_{CO_2}. \quad (5)$$

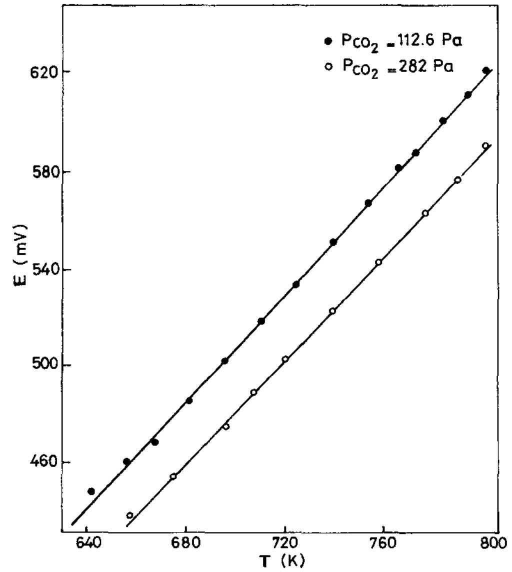

Fig. 2. Temperature dependance of the emf of cell-I at $P_{CO_2} =$ 112.6 and 282 Pa.

Table 1
Difference in emf (ΔE) between the values $P_{CO_2} = 112.6$ and 282 Pa at various temperatures

T (K)	ΔE experimental *	ΔE calculated [a]
650	24.0	25.7
675	25.0	26.6
700	26.0	27.6
725	28.0	28.6
750	29.0	29.6
775	30.0	30.6
800	31.0	31.6

* Calculated from Eqs. (1) and (2).
[a] Calculated using Eq. (5) at $P_{CO_2} = 112.6$ and 282 Pa.

This has been verified experimentally at $P_{CO_2} = 112.6$ and 282 Pa. The data are given in Table 1. This provides an additional check for the internal consistency of the emf data. The standard Gibbs energy change corresponding to Eq. (3) obtained from the emf can be represented as

$$\Delta G_3°(P_{CO_2} = 112.6\ \text{Pa}) = 54.55 - 0.161T\ (\pm 1)\ \text{kJ}, \quad (6)$$

$$\Delta G_3°(P_{CO_2} = 282\ \text{Pa}) = 53.01 - 0.160T\ (\pm 1)\ \text{kJ}. \quad (7)$$

The mean value of $\Delta G_3°$ can be given as

$$\Delta G_3° = 53.78 - 0.1605T\ (\pm 1)\ \text{kJ}. \quad (8)$$

The standard free energy of formation of $Na_2Mo_2O_7$ from elements and component oxides can be evaluated from this data on $\Delta G_3°$ and auxiliary thermodynamic data on Na_2MoO_4 and Na_2CO_3. The standard Gibbs energy of formation of Na_2MoO_4 in the temperature range 650 to 800 K was evaluated from the estimated standard enthalpy of formation of Na_2MoO_4 at 298.15 K by Lindemer et al. [4], enthalpy and entropy increments measured by Iyer et al. [8] and enthalpy and entropy increments of Na(l), Mo(s) and O_2(g) [13] and is given as

$$\Delta_f G_m°\langle Na_2MoO_4\rangle = -1458.78 + 0.3666T\ (\pm 0.2)\ \text{kJ mol}^{-1}. \quad (9)$$

Using the data on Na_2CO_3 and CO_2 from Ref. [14], the standard Gibbs energy of formation of $Na_2Mo_2O_7$ is obtained as

$$\Delta_f G_m°\langle Na_2Mo_2O_7\rangle = -2240 + 0.618T\ (\pm 2)\ \text{kJ mol}^{-1} \quad [650\text{–}800\ \text{K}]. \quad (10)$$

Table 2
Values of standard enthalpy and entropy of formation of $Na_2Mo_2O_7$ from elements and component oxides

Method	T (K)	$\Delta_f H_m$ (kJ mol^{-1})	$\Delta_f H_{ox}$ (kJ mol^{-1})	$\Delta_f S_m$ (J mol^{-1})	$\Delta_f S_{ox}$ (J mol^{-1})	Ref.
Estimated	298.15	−2245.0	−349.0	−627.0	20.04	[4]
Emf technique	298.15	−2248.5	−352.5	−635.0	12.00	this work

The standard Gibbs energy of formation of $Na_2Mo_2O_7$ from component oxides was calculated using $\Delta_f G^\circ\langle Na_2O\rangle$ and $\Delta_f G^\circ\langle MoO_3\rangle$ from Ref. [14] as

$$\Delta_f G_{ox}^\circ\langle Na_2Mo_2O_7\rangle = -344 - 0.011T\ (\pm 8)\ \text{kJ mol}^{-1}. \qquad (11)$$

The enthalpy and entropy of formation of $Na_2Mo_2O_7$ from elements and component oxides obtained in this study are compared with the reported literature values in Table 2. The enthalpy and entropy of formation obtained in this study agree well with the reported values [4].

3.2. The compound Na_2NiO_2

The X-ray diffraction pattern of the compound Na_2NiO_2 obtained in this study matches with the published pattern [11]. The variation of the emf of cell-II with temperature in the range 673 to 773 K is shown in Fig. 3. The least-squares regression analysis of the emf data yields

$$E = 1383 + 0.230T\ (\pm 1.5)\ \text{mV}. \qquad (12)$$

The overall cell reaction can be represented as

$$2Na_2Mo_2O_7 + Na_2NiO_2 + Ni = 3Na_2MoO_4 + MoO_2 + 2NiO.. \qquad (13)$$

The standard Gibbs energy change corresponding to Eq. (13) is related to the cell emf by the expression

$$\Delta G_{13}^\circ = -nFE, \qquad (14)$$

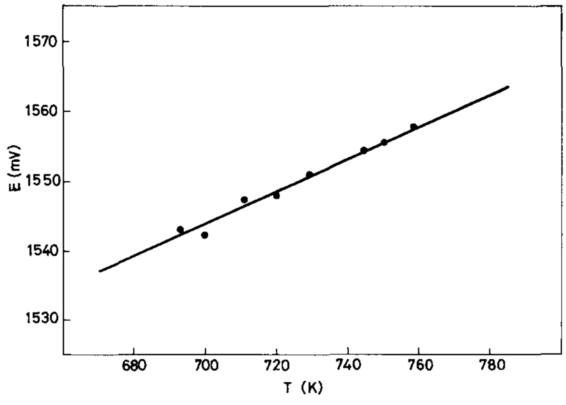

Fig. 3. Temperature dependance of the emf of cell-II.

where $n = 2$ and can be expressed as

$$\Delta G_{13}^\circ = -266.88 - 0.044T\ (\pm 0.2)\ \text{kJ}. \qquad (15)$$

The standard free energy change corresponding to the reactions

$$2Na(l) + Ni(s) + O_2(g) = Na_2NiO_2(s) \qquad (16)$$

and

$$Na_2O(s) + NiO(s) = Na_2NiO_2(s) \qquad (17)$$

can be obtained from cell emf and auxiliary information on $Na_2Mo_2O_7$ from this work and on Na_2MoO_4, MoO_2 and NiO from the literature [14]. These are expressed as

$$\Delta G_{16}^\circ = -684.12 + 0.257T\ (\pm 7)\ \text{kJ mol}^{-1}\ [673\text{–}773\ \text{K}], \qquad (18)$$

$$\Delta G_{17}^\circ = -27 + 0.030T\ (\pm 11)\ \text{kJ mol}^{-1}. \qquad (19)$$

For Eq. (17) Shaiu et al. [9] obtained the free energy change in the temperature range 800–1040 K, from the emfs of the cell based on CaF_2 solid electrolyte, as

$$\Delta G_{17}^\circ = 15.73 - 0.048T\ \text{kJ mol}^{-1}. \qquad (20)$$

This indicates that in the temperature range 800–1040 K the compound Na_2NiO_2 is unstable with respect to NiO and Na_2O. Hence, Shaiu et al. [9] themselves considered their results unreliable.

4. Conclusion

The standard Gibbs' energy of formation of $Na_2Mo_2O_7$ and Na_2NiO_2 were first determined by using a solid state emf technique based on Na^+ ion conducting electrolyte. The standard enthalpy and entropy of formation of $Na_2Mo_2O_7$ computed from the results obtained in this study agrees well with the reported values.

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