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Potentiometric determination of the thermodynamic stability of $SrO–RuO_2$ system

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Abstract

A partial phase diagram for $SrO–RuO_2$ system in the temperature range 1023 to 1473K under 1 atmosphere of oxygen was determined for the purpose of galvanic cell studies. The e.m.f. of the galvanic cells using 15 wt.% CaO-stabilized ZrO_2 (15 CSZ) solid electrolyte and air ($P_{O_2}=0.21$ atm)/Pt as the reference electrode yielded the following least-squares expressions for the test electrodes $SrO/Sr_2RuO_4/Ru$ (I), $Sr_2RuO_4/Sr_3Ru_2O_7/Ru$ (II) and $Sr_3Ru_2O_7/SrRuO_3/Ru$ (III) over the temperature ranges 1044 to 1235, 926 to 1164 and 991 to 1282K respectively:

$$E_{(\mathrm{I})}=1009.25-0.40411\ T\pm3.37\ \mathrm{mV} \qquad (1)$$

$$E_{(\mathrm{II})}=1060.67-0.46896\ T\pm3.26\ \mathrm{mV} \qquad (2)$$

$$E_{(\mathrm{III})}=1010.50-0.43449\ T\pm3.78\ \mathrm{mV} \qquad (3)$$

These e.m.f. results, after correcting for the standard state of oxygen in the air reference electrode, were combined with the $\Delta G_f^\circ(RuO_2)$ from literature and the standard Gibbs energies of formation, $\Delta G^\circ_{f,\,ox}$, of Sr_2RuO_4, $Sr_3Ru_2O_7$ and $SrRuO_3$ were determined.

1. Introduction

The ruthenates of strontium have evoked considerable interest in materials science and technology owing to their peculiar electrical, magnetic and catalytic properties [1–14]. The alkaline earth ruthenates $CaRuO_3$ and $SrRuO_3$ are good conductors of electricity [1, 3] and the latter finds use as a high temperature conductive paste [8, 9, 14]. Incidentally $SrRuO_3$ is the only known ferromagnetic oxide containing only a second row transition metal while $CaRuO_3$ is antiferromagnetic [2, 4, 11, 13, 15]. Besides $SrRuO_3$, the other ternary phases reported in the $SrO–RuO_2$ system are Sr_2RuO_4, $Sr_3Ru_2O_7$ and $Sr_4Ru_3O_{10}$ [16, 17]. Rao *et al.* [10] have reported the electrical resistivity of Sr_2RuO_4 to be one order of magnitude higher than that of $SrRuO_3$. The perovskite-type $CaRuO_3$ is the only ruthenate in the $CaO–RuO_2$ pseudo-binary system in contrast to the more complex $SrO–RuO_2$ system. The Gibbs energy data on $CaRuO_3$ was earlier reported by Mallika and Sreedharan [18] using the solid oxide electrolyte e.m.f. method, while there is not a single reliable report on the thermodynamic properties of any strontium ruthenate in the published literature. However, Gibbs energy data on these ruthenates could be of interest in nuclear technology as both Sr and Ru happened to be among the predominant fission products in fast reactor fuels [19]. In addition, the higher the thermodynamic stability of such ternary ruthenates, the greater is the probability of the retention of the radiologically hazardous as well as volatile RuO_4 during reactor accidents. Hence a potentiometric study of the ternary phases in the $SrO–RuO_2$ system was undertaken.

2. Experimental details

The starting materials were $SrCO_3$ with a purity better than 99% (Loba-Chemie, India) and $RuCl_3$ (purity greater than 99.9%, Johnson-Matthey Chemicals, UK). The latter was oxidized to RuO_2 by heating in oxygen at 923 K for 6 h followed by reduction with hydrogen at 873 K as reported earlier [18]. Though $SrCO_3$ exhibited a sharp weight loss step at 1200 K in static air during its thermal decomposition in a thermogravimetric run, nevertheless for the purpose of synthesis and e.m.f. studies, the preparation of SrO was carried out by heating the carbonate at a much higher temperature of 1473 K in a stream of CO_2-free argon for several hours in order to ensure completeness of decomposition. Several mixtures of SrO:Ru in the mole ratios ranging from 2:1 to 1:1 were intimately

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ground and compacted into cylindrical pellets of 10 mm diameter and 2–3 mm thickness at 100 MPa pressure. These pellets were heated in the range 1023–1473 K for about 24 h in dry oxygen. This procedure of grinding, compaction and heating was repeated two or three times employing higher temperatures in the second and third stage of heat treatments. The phase analyses were carried out by X-ray powder diffraction (XRD) to ensure completeness of the reactions as well as for phase equilibrium studies within its 5 mass% limits of detection of impurity phases. Generally pre-equilibrated biphasic mixtures of ternary compounds were used in conjunction with Ru for e.m.f. studies instead of mixing the compounds prepared in the respective stoichiometric compositions. This precaution was taken to prevent interference in e.m.f. studies by a third phase, the amount of which is within the threshold of detection by XRD.

The following galvanic cells were constructed and studied:

Pt, SrO, Sr_2RuO_4, Ru/15 CSZ/O_2

($P_{O_2}=0.21$ atm), Pt (I)

Pt, Sr_2RuO_4, $Sr_3Ru_2O_7$, Ru/15 CSZ/O_2

($P_{O_2}=0.21$ atm), Pt (II)

and

Pt, $Sr_3Ru_2O_7$, $SrRuO_3$, Ru/15 CSZ/O_2

($P_{O_2}=0.21$ atm), Pt (III)

A two compartment galvanic cell assembly using cylindrical solid electrolyte tubes with one end closed and closed end flat having a composition of 15 wt.% CaO-stabilized ZrO_2 (15 CSZ, Corning, USA) conforming to the dimensions 12.7 mm outer diameter, 9.8 mm inner diameter and 350 mm length were employed in all these studies. Tests for the absence of asymmetric potentials, details for purification of helium and temperature control and measurement using a calibrated Pt–10%Rh/Pt thermocouple in addition to reversibility tests conducted during e.m.f. measurements are the same as described elsewhere [20, 21]. In general an e.m.f. reading was taken only when it was stable within 0.2 mV for at least 1 h after attainment of thermal equilibrium. Reproducibility of cell voltages on thermal cycling and their invariance with varying relative amounts of the coexisting phases were the other checks employed for ascertaining the equilibrium nature of the e.m.f. results. The electrodes were examined by XRD at the end of each experiment to confirm the absence of changes in phase composition.

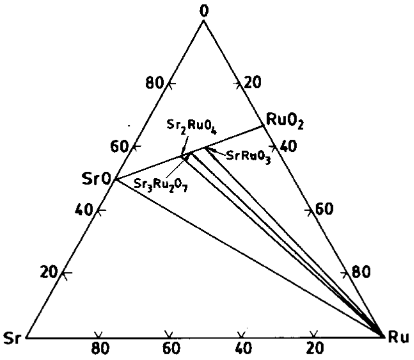

Fig. 1. Partial phase equilibrium diagram of Sr–Ru–O system in oxygen.

3. Results

3.1. Phase equilibrium in SrO–RuO2 system

The compacted mixtures which were equilibrated in oxygen in the temperature range mentioned above, namely, 1023–1473 K corresponded to Sr:Ru ratios in the interval 2 to 1. The two end compositions yielded pure Sr_2RuO_4 and $SrRuO_3$. Four other mixtures with Sr:Ru ratios of 1.75, 1.42, 1.33 and 1.16 were analyzed by XRD to be biphasic comprising $Sr_2RuO_4+Sr_3Ru_2O_7$ and $Sr_3Ru_2O_7+SrRuO_3$ depending on the metal ratio. No trace of $Sr_4Ru_3O_{10}$ (reported earlier [17]) could be found even in the mixture with a value of 1.33 for the Sr:Ru ratio. Further, the oxygen-rich phase $SrRu_2O_6$ which was synthesized at 973K under an oxygen pressure of 300 MPa by Sleight [9] was also not expected to be formed in the present studies under 0.13 MPa pressure of oxygen. The XRD examination of used pellets from e.m.f. studies confirm the coexistence of Ru metal with the three biphasic mixtures used in the galvanic cells (I) to (III). These observations facilitated the construction of a phase diagram for the Sr–Ru–O system valid over the range 1023 to 1473K as shown in Fig. 1.

3.2. E.m.f. results

The results of e.m.f. on cells (I) to (III), shown in Fig. 2, could be represented by the least-squares expressions (1)–(3) which are valid over the temperature ranges 1044 to 1235, 926 to 1164 and 991 to 1282 K respectively.

$$E_{(I)}=1009.25-0.40411\ T\pm 3.37\ \text{mV} \quad (1)$$

$$E_{(II)}=1060.67-0.46896\ T\pm 3.26\ \text{mV} \quad (2)$$

$$E_{(III)}=1010.50-0.43449\ T\pm 3.78\ \text{mV} \quad (3)$$

4. Discussion

Randall and Ward [16] had heat treated mixtures of SrO and Ru with two composition ranges, namely,

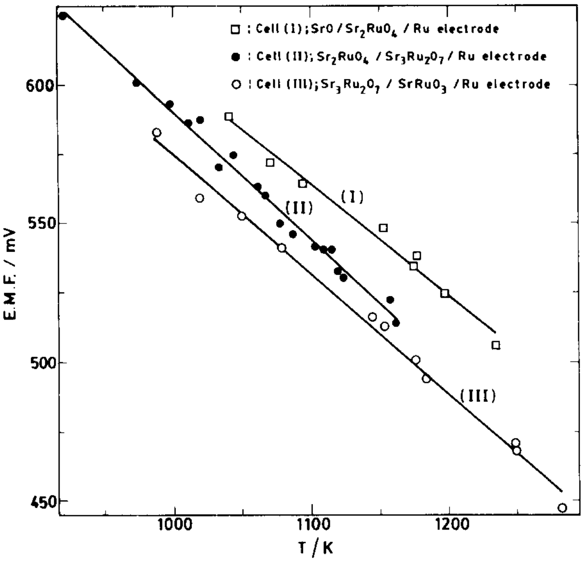

Fig. 2. Experimental e.m.f. results of the cells (I)–(III).

between values of 1–1.5 and 1.5–2 for Sr:Ru at 1473 K. Over the first range of composition they found the formation of $SrRuO_3$ while over the second range they found the existence of Sr_2RuO_4 and evidence of another phase crystallographically similar to $Sr_3Ti_2O_7$. Kafalas and Longo [17] synthesized a series of ternary compounds which are poly-types of stoichiometry $(ABO_3)(AO)_n$ where n could assume values of 0, 1/3, 1/2 and 1. For these values of n, when $A \equiv Sr$ and $B \equiv Ru$ the ternary compounds happened to be $SrRuO_3$, $Sr_4Ru_3O_{10}$, $Sr_3Ru_2O_7$ and Sr_2RuO_4. In the phase equilibrium studies reported here formation of the latter two could be verified in the appropriate composition range in agreement with the report by Randall and Ward. However, no evidence could be found for the formation of $Sr_4Ru_3O_{10}$ during synthesis at ambient pressures. Therefore, it is inferred that this phase could be formed only under high pressures as employed by Kafalas and Longo. These studies, in addition to the phase analyses of mixtures thermally equilibrated with Ru justified the choice of coexisting phases for e.m.f. studies.

The least-squares expressions (1)–(3) were corrected for the standard state of oxygen in the reference air electrode and for the passage of 4 F of electricity, the standard Gibbs energy changes, ΔG_r° for the three cells were found to be

$$\Delta G^\circ_{r(I)} = -389519 + 142.959\ T \pm 1300\ \mathrm{J\ mol^{-1}} \qquad (4)$$

$$\Delta G^\circ_{r(II)} = -409364 + 167.990\ T \pm 1260\ \mathrm{J\ mol^{-1}} \qquad (5)$$

and

$$\Delta G^\circ_{r(III)} = -390002 + 154.683\ T \pm 1460\ \mathrm{J\ mol^{-1}} \qquad (6)$$

These Gibbs energy expressions would correspond to the following overall galvanic cell reactions respectively, with oxygen also in its standard state:

$$2\ SrO + Ru + O_2(g) \rightleftharpoons Sr_2RuO_4 \qquad (IA)$$

$$3\ Sr_2RuO_4 + Ru + O_2(g) \rightleftharpoons 2\ Sr_3Ru_2O_7 \qquad (IIA)$$

and

$$Sr_3Ru_2O_7 + Ru + O_2(g) \rightleftharpoons 3\ SrRuO_3 \qquad (IIIA)$$

It is thus seen that the ΔG_r° expressions for the three cells are identical with the oxygen potentials, $\Delta \bar{G}_{O_2}$ ($RT \ln P_{O_2}$) for the respective three-phase coexisting mixtures. Plots of log P_{O_2} derived from eqns. (4)–(6) against reciprocal temperatures for these sets of phases in equilibrium are shown in Fig. 3.

In order to derive the standard Gibbs energies of formation, $\Delta G^\circ_{f,\ ox}$, of the ternary phases from the constituent binary oxides it is necessary to subtract the following ΔG_f° expression for RuO_2 (reported earlier from similar studies in an identical experimental setup [20]) from the eqns. (4)–(6):

$$\Delta G_f^\circ(RuO_2) = -305464 + 172.70\ T$$
$$\pm 1245\ \mathrm{J\ mol^{-1}} \quad (751\text{–}1200\ \mathrm{K}) \qquad (7)$$

The solid state reactions and the corresponding numerical expressions for ΔG° thus derived are listed in Table 1. The first three expressions in Table 1 were obtained by subtracting eqn. (7) from each of eqns. (4)–(6). Equation (11) was derived by combining eqns. (8) and (9) while eqn. (12) was obtained by adding up eqns. (10) and (11). Consequently the precision in the derived $\Delta G^\circ_{f,\ ox}$ values have wider limits as compared with what could be achieved in the individual e.m.f. measurements. Efforts to improve the precision by adopting stacked pellet assembly with Ru/RuO_2 as the reference electrode in the place of air

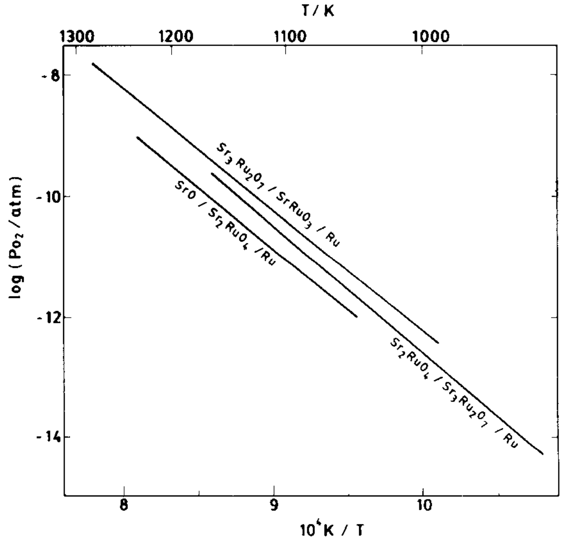

Fig. 3. Plot of the partial pressures of oxygen over the equilibrium buffer mixtures in the Sr–Ru–O system.

TABLE 1. Standard Gibbs energy data for the solid state reactions between SrO and RuO$_2$

Sl. no.	Solid state reaction	ΔG° (J mol^{-1}) $=A+BT$(K) $-A$	 $-B$	Precision (J mol^{-1})	Eqn. no.
1	$2\,SrO+RuO_2 \rightleftharpoons Sr_2RuO_4$	84 055	29.74	2550	(8)
2	$3\,Sr_2RuO_4+RuO_2 \rightleftharpoons 2\,Sr_3Ru_2O_7$	103 901	4.71	2510	(9)
3	$Sr_3Ru_2O_7+RuO_2 \rightleftharpoons 3\,SrRuO_3$	84 538	18.02	2710	(10)
4	$3\,SrO+2\,RuO_2 \rightleftharpoons Sr_3Ru_2O_7$	187 956	34.45	5060	(11)
5	$SrO+RuO_2 \rightleftharpoons SrRuO_3$	272 494	52.47	7770	(12)

($P_{O_2}=0.21$ atm)/Pt reference was not fruitful on account of the transport of RuO$_2$ from the reference to the test electrode. An examination of the $\Delta S^\circ_{f,\,ox}$ values from eqns. (8), (11) and (12) shows that although they agree in sign with the spontaneous process of mixing of solids, their magnitudes are somewhat larger than about 10–20 J mol^{-1}K^{-1} expected for ΔS^M_{ideal}. A third-law analysis of the Gibbs energy data (in order to assess their temperature dependence) could not be done owing to the non-availability of C°_p and S°_f values for any of the ternary compounds. However, the overall magnitude of the standard Gibbs energy data for the solid state reactions listed in Table 1 seem to be reasonable although the stability of the three ternary compounds do not appear to differ too largely from each other.

Using the expressions (8), (9) and (10), log a_{RuO_2} could be plotted as a function of composition in the three biphasic fields at the two interpolated temperatures 1000 and 1200 K as shown in Fig. 4. The increasing activity of RuO$_2$ with RuO$_2$ content in the adjacent phase fields is consistent with the expectation on thermodynamic basis.

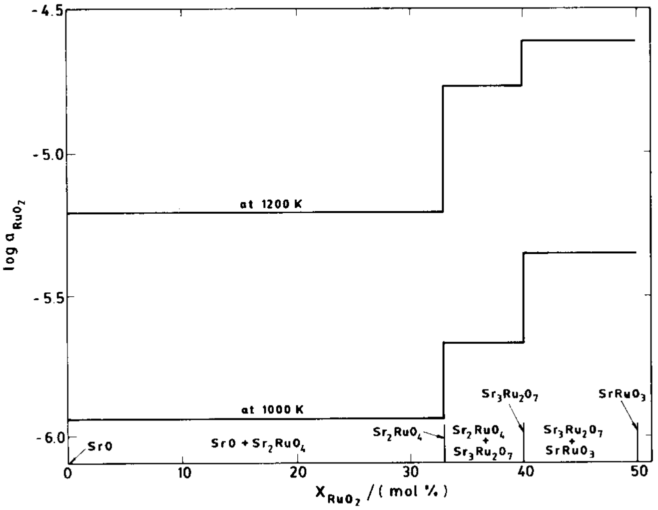

Fig. 4. Activity isotherms for RuO$_2$ in the Sr–Ru–O system at 1000 and 1200 K.

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