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Standard Gibbs' energy of formation of La_2CoO_4 and comparison of stability of La_2MO_4 (M = Cu, Ni or Co) compounds

O. M. SREEDHARAN, R. PANKAJAVALLI
Metallurgy Programme, Reactor Research Centre, Kalpakkam, Tamilnadu 603102, India

Ternary compounds formed between La_2O_3 and first period transition metal oxides have been of considerable interest as electrode materials in MHD generators [1] and as oxidation catalysts [2, 3]. Of the two types of oxides, $LaMO_3$ and La_2MO_4, the thermodynamic properties of La_2NiO_4 [4] and La_2CuO_4 [5] have been studied in addition to those of $LaCoO_3$ [6]. For completion of characterization of La_2MO_4 compounds and of the system La–Co–O, a study of the stability of La_2CoO_4 has been undertaken. Nakamura *et al.* [3] have reputed a log $[p_{O_2}/\text{atm}]$ value of −13.3 for the reduction of La_2CoO_4 into La_2O_3 and Co at 1273 K by controlled atmosphere thermogravimetry. However, no ΔG^0 value is available at any other temperature. But the solid electrolyte galvanic cell technique can provide this data over a range of temperature with high precision commensurate with e.m.f. measurements [7].

La_2O_3 and Co_3O_4 (both of purity 99.99%) were used as starting materials. CoO was prepared by heating Co_3O_4 in a flowing argon atmosphere at 1273 K. An intimate mixture of La_2O_3 and CoO in the molar ratio 1 : 1 was compacted into pellets and was heated to 1273 K for 24 h in evacuated and sealed silica ampoules. This procedure was repeated once again to ensure completion of the solid state reaction. Pellets of dimensions 6 mm diameter by 3 mm height were made by compacting three different mixtures of La_2O_3, Co and La_2CoO_4 at a pressure of 100 MPa; the ratio of the three phases was 3 : 1 : 2 by weight which was deliberately varied by about 10% in order to check the equilibrium nature of the e.m.f.

A two compartment galvanic cell assembly with the solid electrolyte tube separating the gaseous environments of the two electrodes was employed for the e.m.f. measurements. The electrolyte was made of 15 wt % yttria stabilized zirconia in the form of a one end closed tube with the closed end flat and was of the dimensions of 305 mm length by 12.7 mm outer diameter and 9.5 mm inner diameter. Other experimental details are described elsewhere [8, 9].

The e.m.f. of the galvanic cell Pt, La_2CoO_4, La_2O_3, Co/15 YSZ/O_2 ($p_{O_2} \approx 10^{-3}$ atm in N_2–O_2), Pt I (15 YSZ: 15 wt % yttria stabilized zirconia) is shown as a function of temperature in Fig. 1 and can be represented by the following least square expression

$$(E_\text{I} \pm 3.7)(\text{mV}) = 1167.5 - 0.4326T\,(\text{K}) \quad (1)$$
$$(973 \text{ to } 1375\,\text{K})$$

The oyxgen potential ($RT \ln p_{O_2}$) of the reference gas mixture of N_2–O_2 was determined [8] from the galvanic cell Pt, O_2 ($p_{O_2} \approx 10^{-3}$ atm in N_2–O_2)/15 YSZ/Air ($p_{O_2} = 0.2$ atm), Pt II whose e.m.f. is given by the expression

$$(E_\text{II} \pm 0.1)(\text{mV}) = 2.72 + 0.0908T\,(\text{K}) \quad (2)$$

Equations 1 and 2 are combined and then corrected for the change of reference state of oxygen in ambient air to the standard state of pure oxygen to yield for the reaction

$$La_2O_3(s) + Co(s) + \tfrac{1}{2}O_2(g) \rightleftharpoons La_2CoO_4(s) \quad (3)$$

the following expressions for the standard Gibbs energy change

$$(\Delta G^0_{(3)} \pm 0.72)(\text{kJ}) = -224.86 + 0.0584T(\text{K})$$
$$(973 \text{ to } 1375\,\text{K}) \quad (4)$$

Combining Equation 4 with the ΔG^0_f (CoO, s) of Sreedharan *et al.* [10], $\Delta G^0_{f,\,ox,\,T}$ for the Reaction 5.

$$La_2O_3(s) + CoO(s) \rightleftharpoons La_2CoO_4(s) \quad (5)$$

$$(\Delta G^0_{f,\,ox,\,T} \pm 1.02)(\text{kJ}) = 12.24 - 0.0149T\,(\text{K}) \quad (6)$$

The log p_{O_2} value for the reduction of

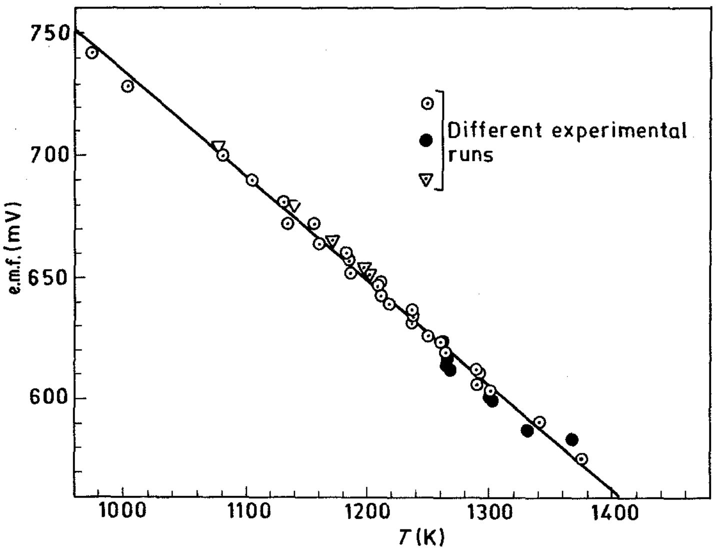

Figure 1 The e.m.f. of the cell Co, La_2CoO_4, La_2O_3/15 YSZ/O_2 ($p_{O_2} \approx 2.4 \times 10^{-3}$ atm).

$La_2CoO_4(s)$ into $La_2O_3(s)$ and Co(s) at 1273 K was found to be -13.3 ± 0.1 by Nakamura *et al.* [3] as compared to -12.35 ± 0.1 from Equation 4. The reasons for a similar discrepancy have been discussed elsewhere [8].

The high temperature thermodynamic stability of lanthanum-transition metal–oxygen compounds with K_2NiF_4 structure are of interest from the view point of assessing any systematic trend [3]. Thus it would be worthwhile to compare the standard Gibbs energy change $\Delta G^0_{f,\,ox,\,T}$ for the general

$$La_2O_3(s) + MO(s) \rightleftharpoons La_2MO_4(s) \qquad (7)$$

where M stands for Cu, Ni or Co. Chandrasekharaiah *et al.* [5] had reported the e.m.f. of the cells

$$\text{Pt, Ni, NiO/15 YSZ/}La_2CuO_4\text{, }LaCuO_2\text{, }La_2O_3\text{, Pt III}$$

and

$$\text{Pt, Ni, NiO/15 YSZ/}LaCuO_2\text{, }La_2O_3\text{, Cu, Pt IV}$$

to be

$$(E_{III} \pm 2.0)(\text{mV}) = 443.0 - 0.063\,T(\text{K}) \quad (970 \text{ to } 370\,\text{K}) \qquad (8)$$

and

$$(E_{IV} \pm 5.0)(\text{mV}) = 293.0 - 0.044\,T(\text{K}) \quad (1140 \text{ to } 1260\,\text{K}) \qquad (9)$$

for the cell reactions

$$Ni(s) + 2La_2CuO_4(s) \rightleftharpoons \rightleftharpoons 2LaCuO_2(s) + NiO(s) + La_2O_3(s) \qquad (10)$$

and

TABLE I $\Delta G^0_{f,\,ox,\,T}$ for La_2CuO_4 from e.m.f. data from literature [5]

Reactions	ΔG^0 (kJ)	Range T (K)	Precision (± kJ)	Reference
1. $Ni(s) + 2La_2CuO_4(s) \rightleftharpoons 2LaCuO_2(s) + NiO(s) + La_2O_3(s)$	$-85.487 + 0.01216\,T$	970–1370	+ 0.39	[5]
2. $Ni(s) + 2LaCuO_2(s) \rightleftharpoons NiO(s) + La_2O_3(s) + 2Cu(s)$	$-56.541 + 0.00849\,T$	1140–1260	± 0.96	[5]
3. $Ni(s) + \frac{1}{2}O_2(g) \rightleftharpoons NiO(s)$	$-234.304 + 0.08527\,T$	900–1300	± 0.5	[11]
4. $2Cu(s) + \frac{1}{2}O_2(g) \rightleftharpoons Cu_2O(s)$	$-166.7 + 0.0713\,T$	924–1328	± 0.4	[12]
5. $Cu_2O(s) + \frac{1}{2}O_2(g) \rightleftharpoons 2CuO(s)$	$-130.445 + 0.09391\,T$	900–1300	± 0.5	[13]
6. $La_2CuO_4 \rightleftharpoons La_2O_3 + CuO$ $\frac{1}{2}\{(1) + (2) + (4) + (5) - 2(3)\}$	$14.7175 + 0.00766\,T$	970–1370	± 1.6	Computed in this work

TABLE II $\Delta G^0_{f,\mathrm{OX},T}$ for the formation of La_2MO_4 (M = Cu, Ni or Co) from La_2O_3 and Mo

M	$\Delta G^0_{f,\mathrm{OX},T}$ (kJ)	Precision (kJ)	Range T (K)	$\Delta G^0_{f,\mathrm{OX},1273}$	Reference
Cu	$-14.7-0.0077T$	1.6	970–1370	−24.5	Computed in this work
Ni	$25.57-0.0302T$	0.19	1123–1373	−12.64	[5]
Co	$12.24-0.0149T$	1.02	973–1373	−6.73	This work

$$Ni + 2LaCuO_2(s) \rightleftharpoons NiO(s) + La_2O_3(s) + Cu(s) \qquad (11)$$

respectively.

Combining Equations 8 and 9 with the ΔG^0_f of NiO, Cu_2O and CuO, the $\Delta G^0_{f,\mathrm{OX},T}$ for Reaction 7 where M is Cu can be obtained as shown in Table I. The $\Delta G^0_{f,\mathrm{OX},T}$ expressions for the formation of La_2MO_4 (M = Cu, Ni or Co) are compared in Table II. It can be seen from Table II that at a temperature of 1273 K, the values of $\Delta G^0_{f,\mathrm{OX},1273}$ are −24.6, −12.6 and −6.7 kJ mol^{-1} for La_2CuO_4, La_2NiO_4 and La_2CoO_4, respectively. This trend in Gibbs energy may indicate a rather small positive or negative value for $\Delta G^0_{f,\mathrm{OX},T}$ for the values formation of La_2FeO_4 or La_2MnO_4; this explains why these compounds are not reported.

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