Chemistry of Materials **1989,** *1,* 515–519

Gibbs Energies of Formation of $CuYO_2$ and $Cu_2Y_2O_5$ and Phase Relations in the System Cu–Y–O

G. M. Kale and K. T. Jacob*

Department of Metallurgy, Indian Institute of Science, Bangalore 560 012, India

Received March 27, 1989

Thermodynamic properties of cuprous and cupric yttrates ($CuYO_2$ and $Cu_2Y_2O_5$) and oxygen potentials corresponding to three three-phase fields in the system Cu–Y–O have been determined by using solid-state galvanic cells: Pt, Cu + $CuYO_2$ + Y_2O_3||(Y_2O_3)ZrO_2||Cu + Cu_2O, Pt; Pt, $CuYO_2$ + $Cu_2Y_2O_5$||(Y_2O_3)ZrO_2||Cu_2O + CuO, Pt; and Pt, $CuYO_2$ + $Cu_2Y_2O_5$ + Y_2O_3||(Y_2O_3)ZrO_2||Cu_2O + CuO, Pt. Yttria-stabilized zirconia was used as the solid electrolyte in the temperature range 873–1323 K. The compound $CuYO_2$ was prepared by the reduction of $Cu_2Y_2O_5$ at 1373 K under argon gas with a residual oxygen partial pressure of ~1 Pa. For the reaction $^1/_2Cu_2O(s) + {}^1/_2Y_2O_3(s) \rightarrow CuYO_2(s)$, $\Delta G° = -5800 + 3.90T$ (±30) J mol^{-1}, and for $2CuO(s) + Y_2O_3(s) \rightarrow Cu_2Y_2O_5(s)$, $\Delta G° = 11\,210 - 15.07T$ (±120) J mol^{-1}. The oxygen potentials corresponding to the coexistence of phases $CuYO_2$ + $Cu_2Y_2O_5$ and $CuYO_2$ + $Cu_2Y_2O_5$ + Y_2O_3 were found to be the same over the temperature range of measurement, thus indicating negligible solid solubility of Y_2O_3 in $CuYO_2$ and $Cu_2Y_2O_5$. On the basis of the present results and auxiliary thermodynamic data from the literature, phase relations in the Cu–Y–O system at 723, 950, and 1373 K have been deduced.

Introduction

The thermodynamic properties of ternary phases in the Cu–Y–O system are of interest because the pseudobinary CuO–Y_2O_3 constitutes one boundary of the pseudoternary system CuO–Y_2O_3–BaO, containing the superconducting compound $YBa_2Cu_3O_{7-x}$. To develop a phase diagram for the ternary system, it is necessary to know the stability of different phases existing in the constituent binaries as a function of temperature. Nevriva et al.[1-3] determined the temperature–composition diagram for the pseudobinary $BaCuO_2$–$YCuO_{2.5}$ between 1173 and 1573 K and for CuO–$YCuO_{2.5}$ in the temperature range 1298–1473 K at an oxygen partial pressure of 10^5 Pa by X-ray phase analysis and differential thermal analysis (DTA). They did not report the existence of a $CuYO_2$ compound. Ishiguro et al.[4] have synthesized polycrystalline $CuYO_2$ at the oxygen partial pressures ranging from 10 to 10^3 Pa at 1373 K. Ishiguro et al.[4] have also grown single crystals of $CuYO_2$ from the melt at $P_{O_2} = 10$ Pa. Tretyakov et al.[5] (1170–1340 K) and Pankajavalli and Sreedharan[6] (1097–1292 K) have measured the oxygen potential for the coexistence of $Cu_2Y_2O_5$, Y_2O_3, and Cu_2O phases using the galvanic cell

$$\mathrm{Pt,\ Y_2O_3 + Cu_2O + Cu_2Y_2O_5\|(Y_2O_3)ZrO_2\|air}\quad (P_{O_2} = 2.1 \times 10^4\ \mathrm{Pa}) \tag{I}$$

If the phases Y_2O_3 + Cu_2O + $Cu_2Y_2O_5$ coexist at equilibrium, then the compound $CuYO_2$ must be unstable. Since a complete set of phase relations in the Cu–Y–O system have not been reported in the literature, the present study focuses on the determination of the Gibbs energy of formation of $CuYO_2$ and $Cu_2Y_2O_5$ from component oxides employing solid-state galvanic cells:

$$\mathrm{Pt,\ Cu + Y_2O_3 + CuYO_2\|(Y_2O_3)ZrO_2\|Cu + Cu_2O,\ Pt} \tag{II}$$

$$\mathrm{Pt,\ CuYO_2 + Cu_2Y_2O_5\|(Y_2O_3)ZrO_2\|CuO + Cu_2O,\ Pt} \tag{III}$$

$$\mathrm{Pt,\ CuYO_2 + Cu_2Y_2O_5 + Y_2O_3\|(Y_2O_3)ZrO_2\|CuO + Cu_2O,\ Pt} \tag{IV}$$

in the temperature range 873–1323 K. From the thermodynamic data, phase relations in the ternary Cu–Y–O system are evaluated at different temperatures.

Experimental Section

Materials. High-purity CuO, Cu_2O, and Y_2O_3 were supplied by Aldrich Chemical Co. The argon gas, used to provide an inert blanket over the reference and measuring electrodes of the cells, was 99.99% pure. It was further dried by passing over anhydrous P_2O_5 and deoxidized by passing over copper wool at 675 K. The compound $Cu_2Y_2O_5$ was prepared by heating an intimate mixture of CuO and Y_2O_3 in an appropriate molar ratio at 1273 K for 25 h in flowing oxygen. The compound $Cu_2Y_2O_5$ was identified by X-ray analysis to be single phase. The compound $CuYO_2$ was prepared by intimately mixing the powders of CuO/Cu_2O and Y_2O_3 in equimolar proportions and heating at 1273 K in an alumina crucible in air for 35 h. The product ($Cu_2Y_2O_5$) was then heated at 1373 K in flowing argon atmosphere with a residual oxygen partial pressure of ~1 Pa for 100 h. The resulting powder was identified as $CuYO_2$ by X-ray diffraction analysis. This compound could not be obtained by heating Cu_2O and Y_2O_3 directly. The yttria-stabilized zirconia solid electrolyte tube was obtained from commercial sources.

Apparatus and Procedure. The experimental arrangement of cell II was similar to that discussed by Jacob et al.[7] Both the electrodes of cell II were flushed by separate streams of prepurified argon gas at a flow rate of ~1.5 mL s^{-1}. A schematic diagram of the apparatus used for cells III and IV is shown in Figure 1. The cells III and IV were designed to reduce the volume of free space above the electrodes. The electrodes of cells III and IV were initially flushed with argon gas. The argon flow was then cut off, and the electrodes were allowed to establish their equilibrium oxygen partial pressure. The cell assembly was housed inside a vertical furnace such that the electrodes were maintained in the constant-temperature zone. A foil of stainless steel was wrapped around the outer alumina tube of the cell. The foil was grounded to minimize induced voltage on the platinum leads. The cell temperature was measured by a Pt/Pt–13% Rh thermocouple placed adjacent to the measuring electrode. The temperature of

---

* Person to whom correspondence should be addressed.

(1) Nevriva, M.; Pollert, E.; Matejkova, L.; Triska, A. *J. Cryst. Growth* **1988,** *91,* 434.

(2) Nevriva, M.; Pollert, E.; Matejkova, L.; Triska, A. *Physica B+C (Amsterdam)* **1988,** *153,* 377.

(3) Nevriva, M.; Pollert, E.; Sestak, J.; Matjekova, L.; Triska, A. *Thermochim. Acta,* in press.

(4) Ishiguro, T.; Ishizawa, N.; Mizutani, M.; Kato, M. *J. Solid State Chem.* **1983,** *49,* 232.

(5) Tretyakov, Yu. D.; Kaul, A. R.; Makukhini, N. V. *J. Solid State Chem.* **1976,** *17,* 183.

(6) Pankajavalli, R.; Sreedharan, O. M. *J. Mater. Sci. Lett.* **1988,** *7,* 714.

(7) Jacob, K. T.; Kale, G. M.; Iyengar, G. N. K. *Metall. Trans. B,* in press.

0897-4756/89/2801-0515$01.50/0

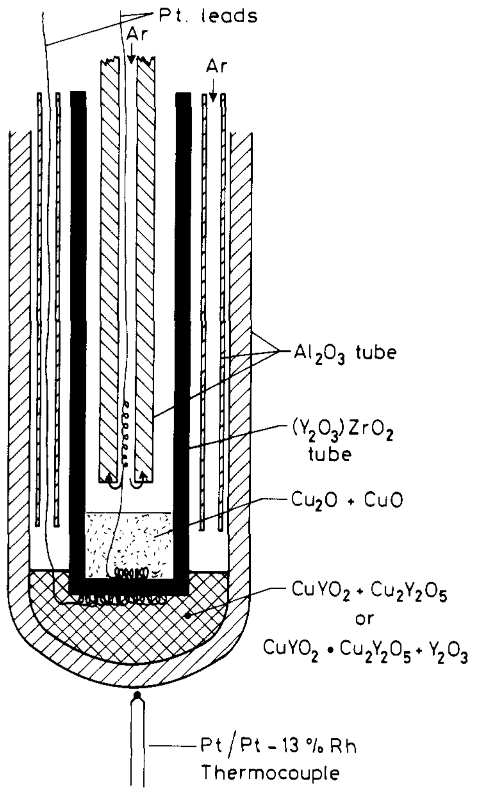

Figure 1. Schematic diagram of cells III and IV.

the cell was controlled within ±1 K.

The reference electrode for cell II was prepared by intimately mixing an equimolar ratio of Cu + Cu_2O. The mixture was compacted inside the solid electrolyte tube with a platinum lead buried in it. The reference electrodes for cells III and IV were prepared by compacting Cu_2O and CuO in the molar ratio of 1:2 inside a solid electrolyte tube with a platinum lead immersed in the mixture. The working electrode for cell II was prepared by pelletizing an intimate equimolar mixture of Cu, $CuYO_2$, and Y_2O_3 at 100 MPa and sintering at 1300 K in an inert atmosphere. The pellet was then spring loaded against the outer flat surface of the $(Y_2O_3)ZrO_2$ electrolyte tube by a system of alumina slabs and supports.[7] The measuring electrodes for cells III and IV were prepared by ramming an intimate equimolar mixture of component phases against the closed end of an alumina tube. The stabilized zirconia tube was spring loaded against the electrode mixture.

The emf of the solid-state galvanic cells II, III, and IV was measured as a function of temperature in the range 873–1323 K with a high-impedance ($>10^{12}\ \Omega$) digital voltmeter. The reversibility of the cell was checked by passing small currents ($\sim$50 μA) in either direction through the cell for $\sim$200 s. In each case the emf was found to return to the original value before the microcoulometric titration. The emf of each cell was found to be reproducible on temperature cycling. The emf of cell II was found to be independent of the flow rate of argon over each electrode in the range of 1–2.5 mL s^{-1}. The electrodes of each cell were examined before and after the experiment by X-ray diffraction analysis. The phase composition of the electrodes was not altered during the experiment.

Results

The variation of the emf of cells II, III, and IV with temperature is shown in Figures 2 and 3. The numbers on the plot indicate the sequence of measurement. The emf of cell IV was found to be identical with that of cell III. The least-squares regression analysis of the emf data gives

$$E_{II} = 60.10 - 0.0404T\ (\pm 0.3)\ \text{mV} \qquad (1)$$

$$E_{III} = E_{IV} = -118.20 + 0.1185T\ (\pm 0.3)\ \text{mV} \qquad (2)$$

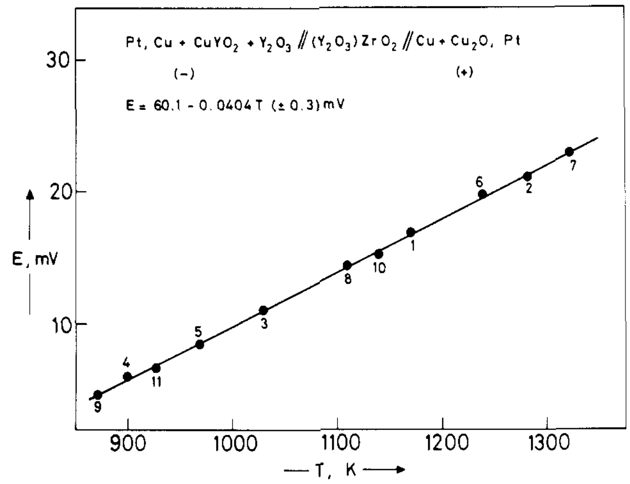

Figure 2. Variation of the emf of cell II as a function of temperature.

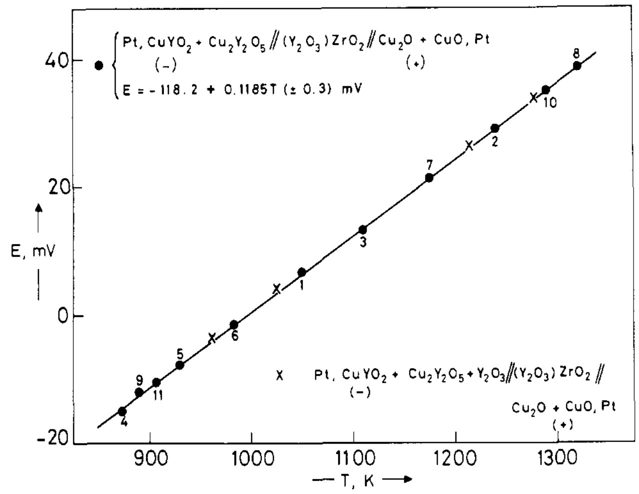

Figure 3. Temperature dependence of the emf of cells III and IV.

The error limits correspond to twice the standard deviation. The cathodic reaction for cell II can be written as

$$Cu(s) + \tfrac{1}{2}Y_2O_3(s) + \tfrac{1}{2}O^{2-} \rightarrow CuYO_2(s) + e^- \qquad (3)$$

and the anodic reaction is

$$\tfrac{1}{2}Cu_2O(s) + e^- \rightarrow Cu(s) + \tfrac{1}{2}O^{2-} \qquad (4)$$

The overall virtual reaction corresponding to cell II can be written as

$$\tfrac{1}{2}Cu_2O(s) + \tfrac{1}{2}Y_2O_3(s) \rightarrow CuYO_2(s) \qquad (5)$$

The emf of cell II is related to the Gibbs energy change for reaction 5 by the Nernst equation:

$$\Delta G^\circ_5 = -nFE_{II} = -5800 + 3.90T\ (\pm 30)\ \text{J mol}^{-1} \quad (873 \le T \le 1323\ \text{K}) \qquad (6)$$

where $n = 1$ is the number of electrons participating in the electrode reaction, F is the Faraday constant, and E is the emf. The formation of cuprous yttrate is exothermic. The Gibbs energy of formation of $CuYO_2$ at 1273 K is only −835 J mol^{-1}. The small driving force at high temperatures partly accounts for the difficulty in direct synthesis of $CuYO_2$ from Cu_2O and Y_2O_3.

The cathodic reaction for cells III and IV is

$$2CuYO_2(s) + O^{2-} \rightarrow Cu_2Y_2O_5(s) + 2e^- \qquad (7)$$

The corresponding anodic reaction is

$$2CuO(s) + 2e^- \rightarrow Cu_2O(s) + O^{2-} \quad (8)$$

Combining reactions 7 and 8 gives the net cell reaction:

$$2CuYO_2(s) + 2CuO(s) \rightarrow Cu_2O(s) + Cu_2Y_2O_5(s) \quad (9)$$

From the measured emf of cells III and IV the Gibbs energy change for the reaction 9 is

$$\Delta G^\circ_9 = -nFE_{III/IV} =$$
$$22\,810 - 22.87T\ (\pm 60)\ J\ mol^{-1} \quad (873 \le T \le 1323\ K) \quad (10)$$

The standard Gibbs energy change for reaction 9 is zero at 977 K, thus suggesting an inversion of phase relations at this temperature. The emf of cells III and IV were found to be identical over the temperature range of measurement. This indicates that the solubility of Y_2O_3 in $CuYO_2$ and $Cu_2Y_2O_5$ is negligible. Combination of eq 6 and 10 gives the standard Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides:

$$2CuO(s) + Y_2O_3(s) \rightarrow Cu_2Y_2O_5(s) \quad (11)$$

$$\Delta G^\circ_{11} =$$
$$11\,210 - 15.07T\ (\pm 85)\ J\ mol^{-1} \quad (873 \le T \le 1323\ K) \quad (12)$$

The formation of $Cu_2Y_2O_5$ from component oxides is endothermic. The thermodynamic data indicate that this entropy-stabilized compound will decompose into component oxides below 744 (±10) K. Arjomand and Machin[8] suggested that there is a ferromagnetic ordering in $Cu_2Y_2O_5$ at low temperatures. The disordered magnetic moments at high temperature partly contribute to the high entropy of $Cu_2Y_2O_5$. Although the site occupancy of cations in $Cu_2Y_2O_5$ is not known, the mixing of cations on crystallographically nonequivalent sites may also give an additional configurational contribution to the entropy of $Cu_2Y_2O_5$. Combining eq 10 with the oxygen chemical potential for the coexistence of Cu_2O and CuO from Jacob and Alcock[9] gives for the oxidation of cuprous yttrate to cupric yttrate

$$4CuYO_2(s) + O_2(g) \rightarrow 2Cu_2Y_2O_5(s) \quad (13)$$

$$\Delta G^\circ_{13} = -215\,260 + 142.08T\ (\pm 200)\ J\ (mol\ of\ O_2)^{-1} \quad (14)$$

Phase Diagrams

The phase relations in the Cu–Y–O system at 1373, 950, and 723 K, calculated from the thermodynamic data obtained in this study and phase diagrams for constituent binaries available in the literature,[10] are shown in Figures 4–6, respectively. The partial pressures of oxygen corresponding to various three-phase regions are also shown, three of which are calculated from the present results and the rest from the literature.[9,11] The partial pressures of oxygen in phase fields containing Cu–Y alloys or intermetallics cannot be computed because of the lack of data on the activity of components in the Cu–Y system. It is apparent from Figures 4–6 that the topology of phase relations in the Cu–Y–O system is sensitive to temperature. At 1373 K, Cu_2O coexists with the two yttrates $CuYO_2$ and $Cu_2Y_2O_5$, whereas Cu_2O + CuO + $Cu_2Y_2O_5$ from another

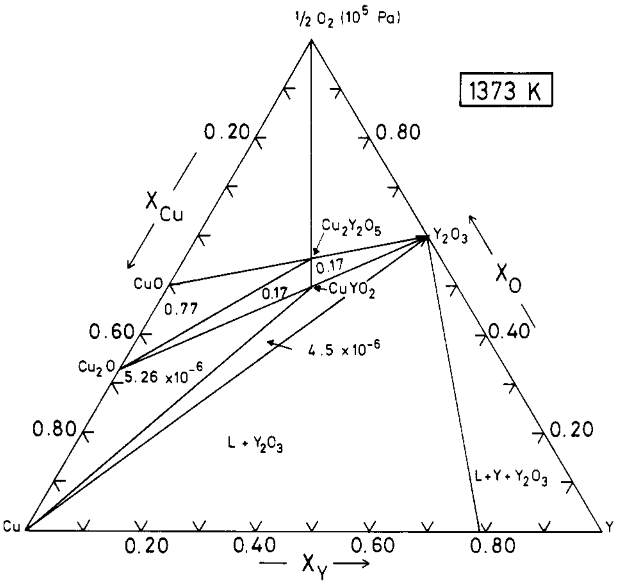

Figure 4. Isothermal section of Cu–Y–O ternary phase diagram at 1373 K.

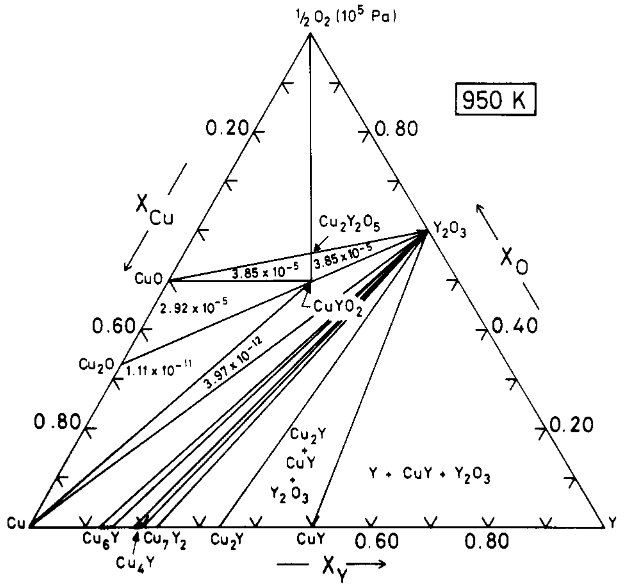

Figure 5. Phase diagram of Cu–Y–O system at 950 K.

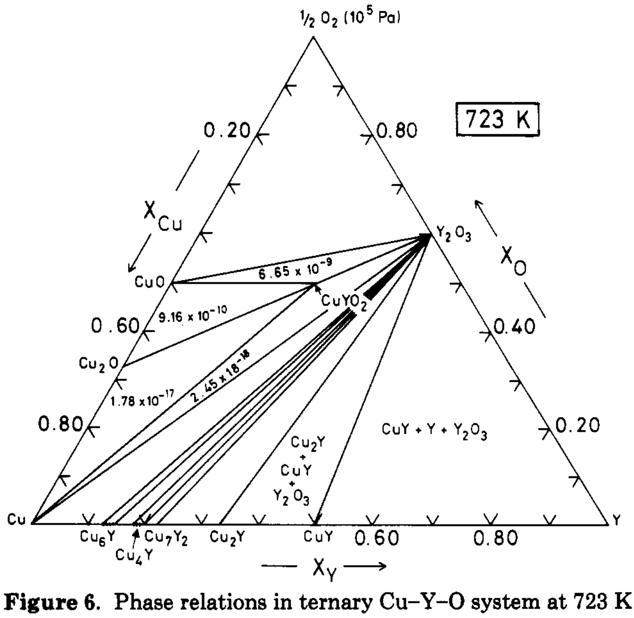

Figure 6. Phase relations in ternary Cu–Y–O system at 723 K.

---

[8] Arjomand, M.; Machin, D. J. *J. Chem. Soc., Dalton Trans.* **1975**, *11*, 1061.

[9] Jacob, K. T.; Alcock, C. B. *J. Am. Ceram. Soc.* **1975**, *8*, 192.

[10] *Binary Alloy Phase Diagrams*; Massalski, T. B., Ed.; American Society of Metals: Metals Park, OH, 1986.

[11] Jacob, K. T.; Jeffes, J. H. E. *Trans. Inst. Mining Met., Sec. C* **1971**, *80*, 32.

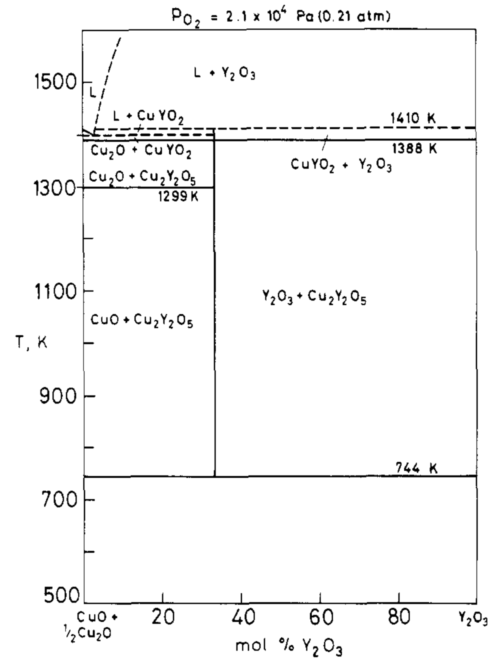

Figure 7. Isobaric (P_{O_2} = 2.1 × 10^4 Pa) representation of phase relations in the system $CuO-Cu_2O-Y_2O_3$.

three-phase field. At 950 K, Cu_2O + CuO coexist with $CuYO_2$, and the cuprous and cupric yttrate are in equilibrium with CuO. The change in the topology of the phase diagram occurs at 977 K. At temperatures less than 744 K, the ternary oxide $Cu_2Y_2O_5$ becomes unstable and gives rise to a three-phase field, CuO + Y_2O_3 + $CuYO_2$, which does not exist at 950 and 1373 K. The compound $YCuO_3$ was not detected in this study. It is known to form from the oxides at 1073 K at an oxygen pressure of 4 × 10^7 Pa.[8]

When three condensed phases and a gas phase are in equilibrium in a ternary system such as $CuO-Cu_2O-Y_2O_3$, the system is monovariant; at a given P_{O_2}, three condensed phases coexist at a unique temperature. Since 1 mol of CuO gives 0.5 mol of Cu_2O on dissociation, the number of moles of Cu remains unchanged when 0.5 mol of Cu_2O is one of the components. Hence the composition can be expressed in terms of CuO + $^1/_2Cu_2O$ and Y_2O_3. On the basis of the present thermodynamic data and auxiliary data from the literature,[9,11] an isobaric (P_{O_2} = 2.1 × 10^4 Pa) section of the $CuO-Cu_2O-Y_2O_3$ ternary system has been composed as shown in Figure 7. The vertical line in Figure 7 corresponds to the interoxide compounds $CuYO_2$ and $Cu_2Y_2O_5$, as they have the same Cu/Y ratio. The cupric yttrate is stable below 1388 (±10) K. The horizontal lines in Figure 7 indicate the invariant equilibria involving three condensed phases and oxygen gas at a partial pressure of 2.1 × 10^4 Pa. The incongruent melting point of Cu_2O (1407 K) at P_{O_2} = 2.1 × 10^4 Pa is taken from the Cu–O phase diagram.[10] The composition of liquid phase is ~37.5 at. % O. The solubility of Y_2O_3 in liquid copper oxide is estimated. Consequently the eutectic and peritectic temperatures are approximate.

Discussion

The Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides is compared in Figure 8 as a function of temperature with the data reported in the literature.[5,6] The results of Tretyakov et al.[5] agree with the results obtained in this study, being more positive by only 250 J mol^{-1} at 1200 K and more negative by 500 J mol^{-1} at 1300 K. The values suggested by Pankajavalli and Sreedharan[6] are more positive than the results of this study by 1500–2000 J mol^{-1}. Both groups of investigators equilibrated a mixture of $Cu_2Y_2O_5$ and Y_2O_3 with Cu_2O. According to the phase diagram (Figures 4 and 5) Cu_2O cannot coexist with Y_2O_3. The reasonable agreement between their[5,6] reported values for the Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides and that obtained in this study suggests that their measurements correspond to a metastable equilibrium that is rendered possible by extremely slow kinetics of the reaction between Cu_2O and Y_2O_3. The Gibbs energy of formation of $CuYO_2$ has not been measured previously.

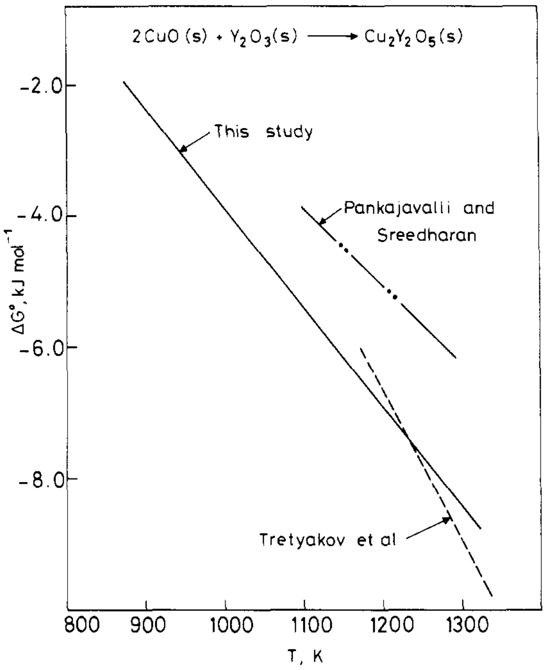

Figure 8. Comparison of the Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides as a function of temperature.

Pankajavalli and Sreedharan[6] have tried to seek support for their emf measurements from DTA studies on the decomposition of $Cu_2Y_2O_5$ in air and oxygen. The broad endothermic peak in air (P_{O_2} = 2.1 × 10^4 Pa) during heating at 10 K min^{-1} starts at approximately 1330 K in their study[6] and culminates at ~1412 K with a small shoulder at 1405 K. The profile of the endothermic peak shows a maximum slope at around 1390 K. This agrees closely with the temperature of 1388 (±10) K for the decomposition of $Cu_2Y_2O_5$ to $CuYO_2$ shown in Figure 7. Pankajavalli and Sreedharan[6] suggest that the decomposition of $Cu_2Y_2O_5$ to solid Cu_2O and Y_2O_3 occurs at 1361 (±10) K, in agreement with a value of 1369 K calculated from their thermodynamic data for $Cu_2Y_2O_5$. They ignore the presence of $CuYO_2$. The small shoulder appearing in their DTA peak at P_{O_2} = 2.1 × 10^4 Pa may be related to the formation of a liquid phase. The start of the endothermic peak at ~1330 K probably indicates the formation of $Cu_2Y_2O_5$ from traces of unreacted CuO and Y_2O_3 in their samples. They synthesized $Cu_2Y_2O_5$ at 1273 K.

The DTA trace at P_{O_2} = 10^5 Pa shows a sharp endothermic peak commencing at 1471 K.[6] This was interpreted by Pankajavalli and Sreedharan[6] as decomposition of $Cu_2Y_2O_5$ into solid Cu_2O and Y_2O_3. Their thermodynamic data give a temperature of 1474 K for this decomposition. However, at P_{O_2} = 10^5 Pa a melt containing ~39.5 at. % O appears at 1394 K according to the phase diagram for the binary Cu–O system.[10] Solid Cu_2O cannot be present at 1471 K and P_{O_2} = 10^5 Pa. The experimental phase diagram at P_{O_2} = 10^5 Pa by Nevriva et al.[1] indicates the decomposition of $Cu_2Y_2O_5$ into a liquid Cu–O melt containing ~4.5 mol % dissolved Y_2O_3 and solid Y_2O_3.

Summary

The Gibbs energy of formation of $CuYO_2$ from component oxides has been determined by electrochemical measurements for the first time. Previous measurements on the Gibbs energy of formation of $Cu_2Y_2O_5$[5,6] were based on the coexistence of this compound with Cu_2O and Y_2O_3, ignoring the presence of $CuYO_2$. Although the phases $Cu_2O + Y_2O_3 + Cu_2Y_2O_5$ are not in stable equilibrium, they can coexist metastably due to the slow rate of formation of $CuYO_2$ from Cu_2O and Y_2O_3. The use of stable equilibrium phase assemblages in the present study gives values for the Gibbs energy of formation of $Cu_2Y_2O_5$ from component oxides in reasonable agreement with earlier measurements,[5,6] which were inadvertently based on metastable conditions. Ternary phase diagram of the system Cu–Y–O at 723, 950, and 1373 K have been composed by using thermodynamic data obtained in this study and auxiliary information from the literature. The isobaric section at $P_{O_2} = 2.1 \times 10^4$ Pa has also been constructed.

Registry No. $CuYO_2$, 87588-40-7; $Cu_2Y_2O_5$, 12158-85-9; Cu, 7440-50-8; Y, 7440-65-5; O_2, 7782-44-7; Y_2O_3, 1314-36-9.

Morphological Control of Electropolymerization on Porous Substrates

W. Cahalane and M. M. Labes*

Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

Received April 24, 1989

Unique morphologies are achieved when pyrrole and 3-methylthiophene are electrochemically polymerized on two porous substrates, Nuclepore and stainless steel mesh. Polypyrrole forms highly oriented tubular whiskers on Nuclepore with striations along the direction of growth having conductivities between 2000 and 3000 S cm^{-1}, higher than those observed in typical preparations of polypyrrole films. On the other hand, poly(3-methylthiophene) forms whiskers with an interesting spiral morphology, having relatively poor conductivities.

Introduction

The degree of preferential orientation that can be achieved in a film prepared from a highly anisotropic polymeric conductor controls the magnitude of its conductivity. It is for this reason that considerable attention has been devoted to the mode of polymerization and to processing conditions in the synthesis of these polymers. In the cases of polypyrrole and polythiophene, variation in conductivity has been achieved by controlling the electrosynthetic conditions, since the polymer itself, once prepared, is intractable. Some substituted polythiophenes are soluble, allowing solution processing techniques to be employed.

One way of controlling the morphology of electrochemically grown materials is to utilize structured, porous substrates. Indeed, Penner and Martin[1] utilized the dielectric membrane Nuclepore as a template for the growth of polypyrrole fibrils. Nuclepore is a polycarbonate or polyester that has been "drilled" by a nuclear process to provide cylindrical pores of 0.015–14.0 μm size. Penner and Martin attempted to fill these pores with conducting polymer to provide conducting pathways through the Nuclepore membrane. They noted some "blooming" of polymer from the surface of the film as well. Bi et al.[2] noted the formation of PPY nucleated at the surface of a wire net anode in a regular array with "hollow bowl" morphology. It occurred to us to attempt the growth of oriented fibrils at the surfaces of these substrates and to correlate measurements of the conductivities with the morphologies of these fibrils.

In related work published while this paper was under review, Cai and Martin[3] stated that PPY and poly(3-methylthiophene) (P3MT) can be synthesized within the pores of Nuclepore via diffusion of monomer and chemical oxidizing agent from opposite sides of the membrane. Thin films are formed on the walls of the pores, which ultimately become larger to appear to fill the pore (although the homogeneity throughout the pore was not as yet studied). Provided that the films on the walls are very thin (less than 200 nm), they report the conductivities, measured by a two-probe technique, of both polymers to be enhanced to values of approximately 10^3 S cm^{-1} (highest value 1550 S cm^{-1}) and surmise the effect to be caused by alignment of the polymers along the pores.

The usual preparation of PPy films from an acetonitrile solution with tetraalkylammonium salts has been studied in great detail,[4] giving conductivities of the order of 100 S cm^{-1}.[5] A conductivity of 400 S cm^{-1} has been reported for films made in a propylene carbonate solution.[6] Satoh et al.[7,8] have made films with a room-temperature conductivity of 500 S cm^{-1} from an aqueous solution with sodium *p*-toluenesulfonate as the electrolyte. Warren et al.[9] have studied the effects of various aqueous dopants,

---

[1] Penner, R. M.; Martin, C. R. *J. Electrochem. Soc.* **1986**, *133*, 2206–2207.

[2] Bi, X.; Yao, Y.; Wan, M.; Wang, P.; Xiao, K.; Yang, Q.; Qian, R. *Makromol. Chem.* **1985**, *186*, 1101–1108.

[3] Cai, Z.; Martin, C. R. *J. Am. Chem. Soc.* **1989**, *111*, 4138–4139.

[4] Waltman, R. J.; Bargon, J. *Can. J. Chem.* **1986**, *64*, 76–95.

[5] Salomon, M.; Diaz, A. F.; Logan, J. A.; Krouhbi, M.; Bargon, J. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 265–273.

[6] Yamaura, M.; Hagiwara, T.; Iwata, K. *Synth. Met.* **1988**, *26*, 209–224.

[7] Satoh, M.; Kaneto, K.; Yoshino, K. *Synth. Met.* **1986**, *14*, 289–296.

[8] Satoh, M.; Kaneto, K.; Yoshino, K. *Jpn. J. Appl. Phys.* **1985**, *24*, L423.

[9] Warren, L. F.; Anderson, D. P. *J. Electrochem. Soc.* **1987**, *134*, 101–105.

0897-4756/89/2801-0519$01.50/0