

Table 1. Summary of Analytical Curves of N-methylcarbamates

carbamates	slope ^a	R square ^b	LOD(pg)
Sevin ^d	0.98	0.9665	130
Carbofuran ^e	0.96	0.9885	300 ^f
Baygon ^g	0.95	0.9962	140

^aSlope from the analytical curves. ^bCorrelation coefficients. ^cLimits of detection. ^d1-Naphthyl-N-methylcarbamate. ^e2,3-Dihydro-2,2-dimethyl-7-benzofuranyl-N-methylcarbamate. ^fThe original sample assay was shown as 75%. ^g2-Isopropoxyphenyl-N-methylcarbamate.

In this study, we propose another micro-determination method of N-methyl carbamates which is simpler and more sensitive than the conventional fluorimetric determination of the post-column derivatives with OPA (o-phthalaldehyde)¹⁴. The presence of other carbamates such as N,N-dimethylcarbamates certainly will interfere the measurement but the quantification of N-methyl carbamate can be made without any problem because they exhibit different retention behavior³. The main limitation of this method is no capability of differentiating N-methyl carbamates in the mixture. Only the total amount will be provided.

Acknowledgement. The financial support from the Korea Science and Engineering Foundation is greatly appreciated. One of the author(CP) expresses his sincere

thanks to the Dae Woo Foundation for supporting him with pre-doctoral fellowship.

References

1. T. Cairns, E. G. Sigmund, M. A. Luke, and G. M. Doose, *Anal. Chem.* **59**, 2055 (1987).
2. A. J. Beery, D. E. Games, and J. R. Perkins, *J. Chromatogr.* **363**, 147 (1986).
3. J. F. Lawrence and R. W. Frei, *Anal. Chem.* **44**, 2046 (1972).
4. R. T. Krause, *J. Chromatogr. Sci.* **16**, 281 (1978).
5. R. T. Krause, *J. Assoc. Off. Anal. Chem.* **63**, 1114 (1980).
6. C. S. P. Sastry and D. Vijaya, *Talanta* **34**, 372 (1987).
7. A. D. Campiglia and C. G. de Lima, *Anal. Chem.* **59**, 2822 (1987).
8. J. F. Lawrence and R. W. Frei, *J. Chromatogr.* **66**, 93 (1972).
9. J. Chamberlain, "Analysis of Drugs in Biological Fluids"; CRC Press: Boca Raton, FL, 1985.
10. C. Park, M. Jung, Y. Kim, and H. Kim, to be published.
11. H. Kim, C. Park, E. Hwang, and Q. Choi, *Bull. Kor. Chem. Soc.* **5**, 253 (1984).
12. J. E. Knoll, *J. Chromatogr. Sci.* **23**, 422 (1985).
13. S. Y. Su, E. R. Asafu-Adjaye, and S. Ocak, *Analyst* (London) **109**, 1019 (1984).
14. R. T. Krause, *J. Assoc. Off. Anal. Chem.* **68**, 386 (1985).

Polarographic Behavior of Cadmium-Tartrate Complexes in Weak Acid and Alkaline Media

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Received January 12, 1989

The electrochemical behavior of cadmium(II) in tartrate solution has been studied over the pH range of 6 to 13.6 in order to explain the phenomena of the changes in limiting current depending on the pH. The polarographic limiting current showed a constant value up to pH of 7.8, after which it decreased sharply to show a minimum at pH between 11 and 12. The limiting current, then, increased again with increasing pH. The number of peaks in cyclic voltammogram was 1 to 3 depending on the pH of the solution. Two other voltammetric peaks could be observed when the main reduction peak diminished. The decrease of limiting current at $7.5 < \text{pH} < 9$ was explained as the formation of complex $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)^-$. The increase of limiting current at strong alkaline solution, however, was due to the complex $\text{Cd}(\text{Tart})_2(\text{OH})_2^{4-}$.

Introduction

Lingane¹ first reported the limiting current obtained during the reduction of cadmium in basic tartrate supporting electrolyte was unusually small. Koh² observed that the limiting current and half-wave potential were constant up to

pH 7.8, then the limiting current decreased sharply when pH was greater than 7.8 and the half-wave potential shifted to more negative potential as the pH exceeded 8.2. The limiting current was minimum at pH 11.2-11.4, then the current increased as pH was raised. He suggested that the process responsible for the decrease of the current in the pH between

Table 1. Analytical Results of Solid Precipitates and Possible Molar Composition

ppt #	pH*	wt % of Cd(II)	Molar Composition		
			[Cd ²⁺]:[Tart ²⁻]	[Cd ²⁺]:[OH ⁻]	[Cd ²⁺]:[Tart ²⁻]:[OH ⁻]
1	5.6	54.6	1.6:1		
2	7.8	42.3	1.0:1		
3	12	74	3.7:1	1:2.3	
4	13	82	6.0:1	1:1.5	
5	13.6	20.7	0.35:1	6.7:1	1:2:2

*pH of the solution from which the precipitate was obtained.

8 and 11 was



where (Tart) was tartrate anion. His explanation was reasonable when H was around 10, but the sharp decrease of current at the range of pH 7.5–9 could not be explained. The increase of current in strong alkaline solution also was not possible to explain.

It has been known that the tartrate ion forms very stable complexes with metal ions and both the carboxylic and the alcoholic hydroxyl groups take part in complex formation in alkaline solution³.

In the present work, the polarographic behavior of cadmium(II) and pH titration were studied at various concentrations of tartrate and hydroxide ions to explain the phenomenon of the variation of the limiting current with the change of pH.

Experimental

Reagents and Polarography. Cd(II) solution was prepared by dissolving cadmium metal(>99.99%, Fluka AG) in nitric acid. All experiments were carried out in a double-walled glass cell maintained at $25 \pm 0.2^\circ\text{C}$. An EG & G Princeton Applied Research model 173 potentiostat with a model 175 universal programmer and a Watanabe X-Y recorder were used for polarographic measurement.

The HMDE(Hanging Mercury Drop Electrode) experiments were performed with EG&G PAR model 174A Polarographic Analyzer and model 303 SMDE(Static Mercury Drop Electrode). Ag/AgCl electrode was mainly used as a reference electrode, and all the potential values were reported against this reference electrode.

pH Titration. Chemtrix type 60A pH meter was used for pH titration. Carbonate-free sodium hydroxide solution was prepared and standardized by potentiometric titration against potassium biphthalate.

Potentiometric titration of sodium tartrate($\text{Na}_2(\text{Tart})$) with sodium hydroxide solution in the absence and presence of cadmium(II) ion was performed. The range of tartrate concentration was from 0.06 M to 1.5 M and the solutions were kept at an ionic strength of 2.00 with potassium nitrate.

Preparation of Complexes in Solid Form. The following solid precipitates were prepared at different experimental condition.

The precipitate one (ppt. 1) was obtained by mixing solutions (original mixture) of 25 ml of 1 M Cd(II) and 25 ml of 2 M sodium tartrate.

Sodium hydroxide of the same equivalent as cadmium(II)

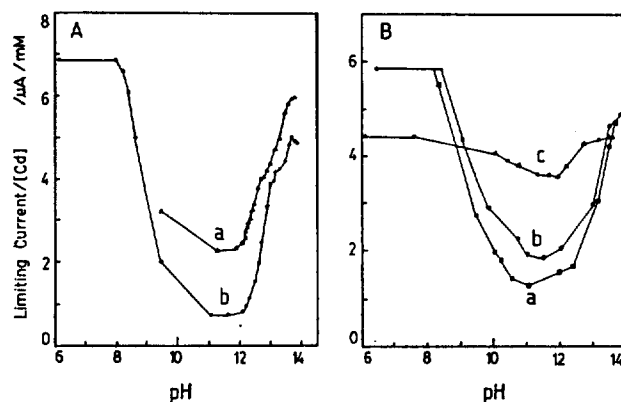


Figure 1. Plots of limiting current at different pH; A: 0.15 M Na_2Tart with different concentration of Cd(II), a; 0.42 mM, b; 2.1 mM. B: $[\text{Cd(II)}] = 0.42\text{ mM}$ with different concentration of Na_2Tart , a; 0.06 M, b; 0.12 M, c; 0.75 M.

was added to the above original mixture(pH of the solution became 7.8). The precipitate obtained when the solution was evaporated to one forth of the initial volume by boiling was designated as ppt. 2. The precipitate was filtered while it was hot.

Sodium hydroxide of twice as much as cadmium(II) was added to the original mixture (pH of the solution became 12.0). The media became syrup-like solution and the obtained precipitate was assigned as ppt. 3.

The ppt. 4 was obtained by adding four equivalent of sodium hydroxide to Cd(II) to the original mixture. The pH of the solution was 13.

The ppt. 5 was prepared by adding sodium hydroxide to the solution of Cd:Tart = 1:10 until pH became 13.6.

All the precipitates were dissolved in 1M HCl solution and analyzed for cadmium by polarography. The analyzed data are given at Table 1. The concentration ratio of hydroxide and tartrate was calculated from the remainder subtracting weight percent of cadmium.

Results and Discussion

Polarography. The polarographic limiting currents measured at different pHs are shown in Figure 1. One of which(A) shows the effect of cadmium(II) concentration at one tartrate concentration and the other(B) also shows the effect of the tartrate concentration at a fixed cadmium concentration. From these figures, the limiting current decreased more rapidly when the concentration of tartrate was low. Also it showed that the range of pH where the limiting cur-

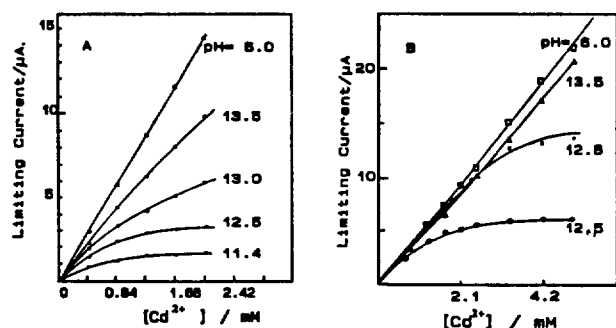


Figure 2. Effect of cadmium concentration on limiting current. A: 0.15M Na₂Tart, B: 0.75M Na₂Tart.

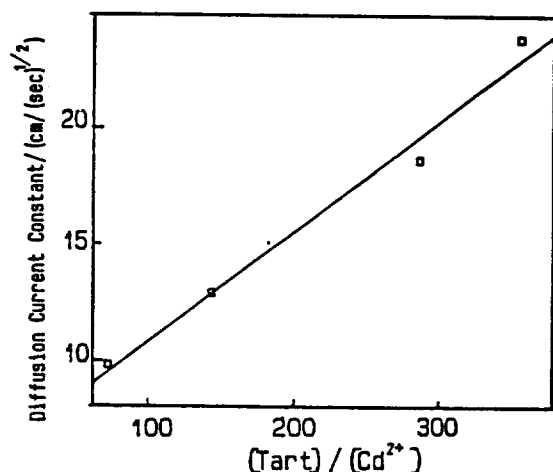


Figure 3. Variation of diffusion current constant by concentration ratio of tartrate to cadmium at pH 11.5.

rent was unusually low was getting narrower when the concentration ratio of tartrate to cadmium increased.

Complex formation between cadmium and nitrate was reported negligible in the concentration range studied⁴. So the complexation between cadmium and tartrate was the main concern in this study. The diffusion current constants of Cd(II) in 0.15M tartrate solution were calculated to be 2.80 cm/(sec)^{1/2} at pH 6.0, and 2.6 cm/(sec)^{1/2} at pH 13.6 with $m=1.91$ mg/sec and $t=4.40$ sec. Therefore, the diffusion coefficients of Cd(II) at pH=6.0 and pH=13.6 were 3.9×10^{-6} cm²/sec and 3.4×10^{-6} cm²/sec, respectively.

At pH=6.0 and with constant concentration of tartrate (0.15 M), the limiting current increased linearly according to the concentration of cadmium(II). The limiting current, however, was not proportional to the concentration of cadmium (Figure 2(A)) at pH value where the current exhibited strong dependence on pH. In sufficiently high concentration of tartrate compared with that of cadmium, the limiting current varied linearly with cadmium concentration even in strong alkaline solution (Figure 2(B)).

The limiting current at pH of the minimum current increased with the increase of tartrate concentration (Figure 3). Therefore, it is reasonable to conclude that the concentration of electrochemically reducible complex increases with the increase of the ratio of tartrate to Cd(II).

The individual number of ligand species in the complexes can be obtained from the shift of half-wave potential with respect to either pH or tartrate concentration⁵. It was

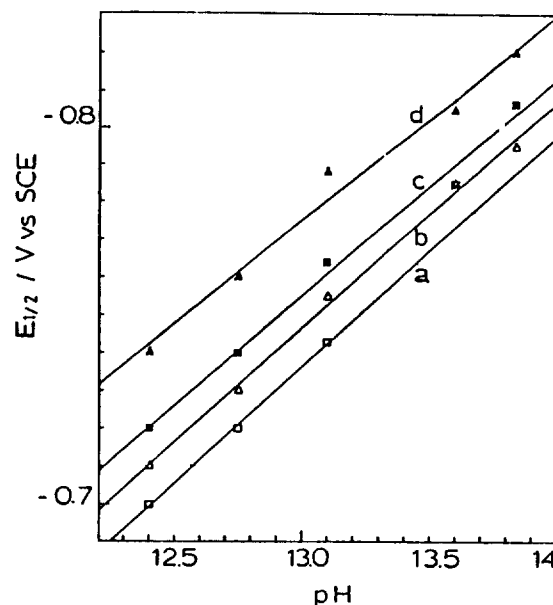


Figure 4. Shift of half-wave potential by pH with tartrate concentrations of (a); 0.09M, (b); 0.15M, (c); 0.30M, and (d); 0.75M.

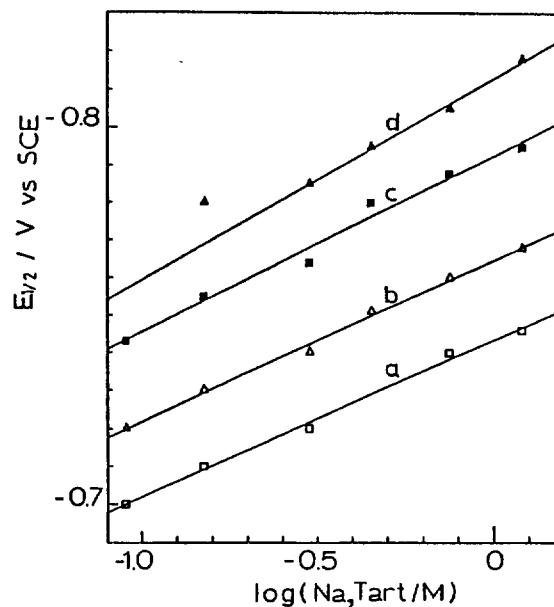


Figure 5. Shift of half-wave potential by tartrate concentration at pH values of (a); 12.4, (b); 12.7, (c); 13.1, and (d) 13.6.

1.85–2.08 from Figure 4 at pH 12.4–13.8 while the number of tartrate varied from 1.41 to 1.82 depending on pH from 12.4 to 13.6 (Figure 5). The analysis result of cadmium complex (ppt. 5 of Table 1) obtained at pH 13.6 was $[\text{Cd}^{2+}]:[\text{Tart}^{2-}]:[\text{OH}^-]=1:2:2$. Therefore, the complex in solution of sufficiently high pH and high ratio of tartrate to cadmium is $\text{Cd}(\text{Tart})_2(\text{OH})_4^{4-}$.

pH Titration. The pH titration curve of the solution containing Cd(II) and an excess sodium tartrate with sodium hydroxide showed a distinct inflection point between pH 7 and 11 as shown in Figure 6 and 7. The inflection point appeared at the point where the titration fraction corresponded to the amount of cadmium. Therefore, the titration curve

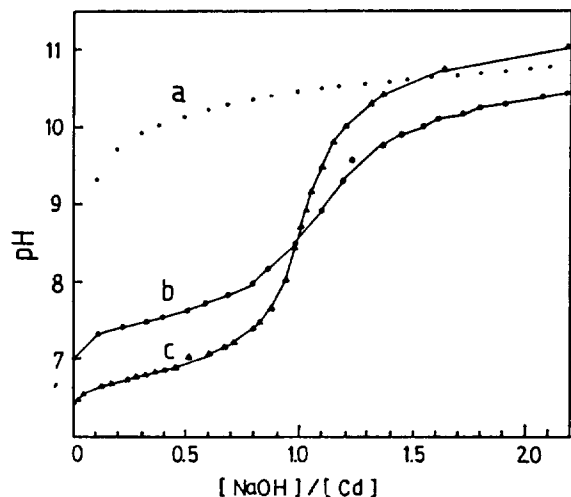


Figure 6. Titration curves of 0.1M tartrate and cadmium, of which the concentrations are (a); 0, (b); 2 mM, and (c) 10 mM.

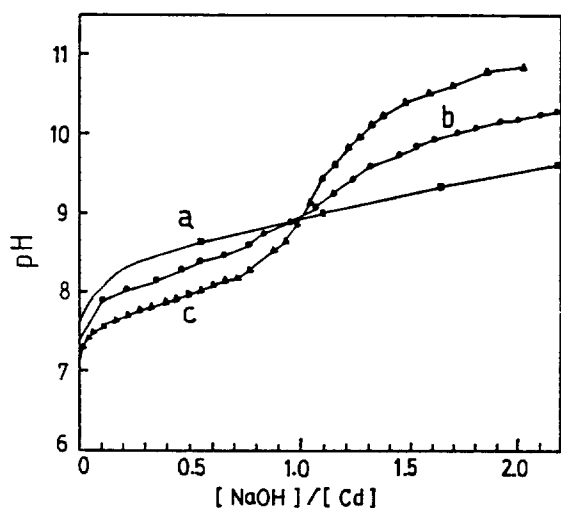


Figure 7. Titration curve of 1M tartrate and cadmium, of which the concentrations are (a); 0.4mM, (b); 2mM, and (c) 10mM.

with one inflection point indicated the presence of replaceable proton coming from cadmium complex. When the pH of the solution was below 8 during titration, only tartrate must be involved as a ligand in the complex. So a proton from hydroxyl group in tartrate must be released because two carboxylic protons were already dissociated. The possibility of hydrolysis of tartrate to bitartrate which responded with titration curve will be slim because the first and the second acid dissociation constant of tartaric acid are 9.2×10^{-4} and 4.3×10^{-5} , respectively. Besides, the inflection point varies as the concentration of cadmium as shown in Figure 6 and 7. Therefore, the complex of cadmium tartrate in neutral and weak alkaline solution is $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)$.

Cyclic Voltammetry at HMDE. Due to its superior sensitivity to polarography, other peaks were also observed with cyclic voltammetry at various potential depending on the experimental condition (pH and tartrate ion concentration). A single main reduction peak was observed when pH was either below 8.3 or above 12.5. Its peak potential ($-0.68 \text{ V vs. Ag/AgCl}$) did not change with pH up to pH value of 8.3. So it is possible to conclude that either cadmium ion does not form

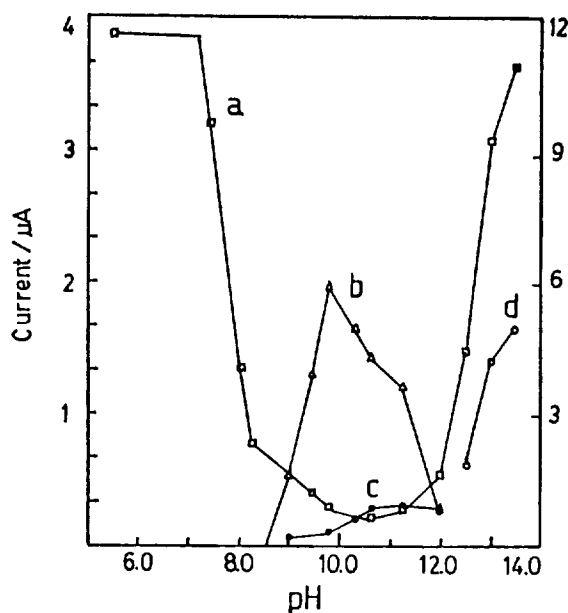
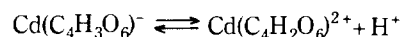


Figure 8. Dependence of peak current on pH. Concentration of tartrate; 0.06M, Concentration of Cadmium; 1.1mM, (a); Peak 1 (peak potential of $-0.68 \text{ V vs. Ag/AgCl}$) (b); Peak 2 (-0.87 V), (c); Peak 3 (-1.16 V), (d); Peak 4 (adsorption Peak at -0.8 V), Curve (a) should use the scale at the right.

a complex with hydroxide up to that pH or it forms a very weak complex. The peak current, however, decreased sharply as observed in polarography.

The variation of peak current of different peaks at different pH are shown in Figure 8. From this curves, it is obvious to note that more than two other electrochemically reducible species are present at $9 < \text{pH} < 12.5$. But the total current is much less than the one measured at acidic media and this indicates that there exist other species which are not electrochemically active in the potential region assuming that the diffusion coefficients of the reducible species are not different very much. This assumption is true as seen in the above that the diffusion coefficients of $\text{Cd}(\text{Tart})$ and $\text{Cd}(\text{Tart})_2(\text{OH})_2^{4-}$ are almost the same. Furthermore, small secondary waves were observed when the pH of the solution was greater than 9, and they could be from the ones complexed with deprotonated tartrate and hydroxide.

The surface related peak⁷ which could be observable when pH was greater than 12 was present at -0.8 V . The peak current increased with slower scan rate. Because of its scan rate dependence, it could be not only adsorbed species but also related to the kinetics of chemical equilibria in the media. It is known that the equilibrium constant of the following reaction is $10^{10.28}$ ⁸.



Therefore, it is possible to conclude that other species such as $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)^-$, $\text{Cd}(\text{C}_4\text{H}_2\text{O}_6)^{2-}$, $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)(\text{OH})^{2-}$, and $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)(\text{OH})_2^{3-}$ can exist at $9 < \text{pH} < 12$. Besides, it is also known that the complexes of tartrate exhibits binuclear structure due to a large stereoselective effect⁹⁻¹⁰. Thus, $\text{Cd}(\text{C}_4\text{H}_3\text{O}_6)^-$ and $\text{Cd}(\text{C}_4\text{H}_2\text{O}_6)^{2-}$ may also form dimers with oxygen bridge from hydroxyl group of tartrate. So one or more of the above species which are not electrochemically active account for the low total peak current at $9 < \text{pH} < 12.5$.

Acknowledgement. The financial support from the Ministry of Education through the Research Institute for Basic Science is greatly appreciated.

References

1. J. J. Lingane, *Ind. Eng. Chem. Ed.*, **15**, 584 (1943).
2. K. H. Koh, *J. Kora. Chem. Soc.*, **11**, 179 (1967).
3. B. Csiszar and P. Szarvas, *Nature* **3**, 846 (1960).
4. D. D. DeFord and D. L. Andersen, *J. Am. Chem. Soc.* **72**, 3918 (1950).
5. D. N. Hume, D. D. DeFord, and G. C. B. Cave, *J. Am. Chem. Soc.*, **73**, 5323 (1951).
6. O. I. Komolev and Z. G. Galanets, *Chem. Abstra.* **51**, 11906g (1957).
7. R. W. Murray and D. J. Gross, *Anal. Chem.* **38**, 392 (1966).
8. K. K. Tripathy, R. K. Patnaik and S. Pari, *J. Indian Chem. Soc.* **49**, 345 (1972).
9. G. L. Robbins and R. E. Tapscott, *Inorg. Chem.* **15**, 154 (1976).
10. R. E. Tapscott, R. E. Belford, and I. C. Paul, *Coord. Chem. Rev.*, **4**, 323 (1969).

Electrical Properties of Pure and Cadmium-Doped Indium Sesquioxide

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Cadmium-doped indium sesquioxide systems with a variety of CdO mol % were prepared to investigate the effect of doping on the electrical properties of indium sesquioxide. The electrical conductivities of pure In_2O_3 and Cd-doped In_2O_3 systems were measured in the temperature range from 25 to 1200 °C and P_{O_2} range from 10^{-7} to 10^{-1} atm, and the thermoelectric power was measured in the same temperature range. The electrical conductivity and thermopower decreased with increasing CdO mol % indicating that all the samples are n-type semiconductors. The electrical conductivities of pure In_2O_3 and lightly doped In_2O_3 were considerably affected by the chemisorption O_2 at temperatures of 400 to 560 °C and then gaseous oxygen was reversibly chemisorbed at the temperature. The predominant defects in In_2O_3 are believed to be triply-charged interstitial indiums at temperatures above 560 °C and oxygen vacancies below 560 °C. In Cd-doped In_2O_3 systems, cadmium acts as an electron acceptor and inhibits the transfer of lattice indium to interstitial sites, which give rise to the decrease of the electrical conductivity.

Introduction

Indium sesquioxide has been known to be an n-type semiconductor. Pure and impurity-doped indium sesquioxides find use in a variety of applications such as electrodes in solar cells¹, gas detectors², and heterogeneous oxidation-reduction catalysts^{3,4}. The electrical properties of In_2O_3 along with its defect structure have been extensively studied, but the detailed conduction mechanism is not yet fully understood. Ovadyahu *et al.*⁵ suggested the existence of In atoms with different valences in In_2O_3 based on the results of stoichiometry measurements, Hall effect and crystal structure data. In view of these reports, the electrical conduction mechanism in indium sesquioxide may be more complicated than hitherto assumed.

Indium sesquioxide doped with acceptor or donor impurities is expected to become p-type or a highly resistive n-type due to the compensation effect in wide band gap semiconductors. Wit *et al.*^{6,7} reported that the electrical behavior of In_2O_3 between 25 and 800 °C is influenced by impurities, the impurity effect is overshadowed by intrinsic properties

above 800 °C. Kanai investigated the electrical conduction in a Mg-doped In_2O_3 single crystal between -173 and 25 °C and found that the electrical conduction was electronic with the electron concentration and electron mobility in the crystal almost independent of temperature⁸. Until now, few results have been reported for the electrical properties of indium sesquioxide polycrystals doped with other elements. In the present work, we report on the electrical properties of Cd-doped In_2O_3 systems and suggest the nature of the electrical conduction mechanism based on the results.

Experimental

Sample Preparation. Specpure indium sesquioxide (99.999% pure, Aldrich Co.) and cadmium oxide (99.999% pure, Johnson-Matthey Co.) powders were used for the preparation of Cd-doped In_2O_3 systems. Finely screened CdO and In_2O_3 powders were uniformly dispersed in various mole ratios in pure ethanol for 48 hrs and the mixtures were filtered and dried at 150 °C. CdO- In_2O_3 solid solutions were prepared by allowing direct solid-state reaction between the