

LITHIUM ACTIVITIES IN LITHIUM TRANSITION METAL DOUBLE OXIDES

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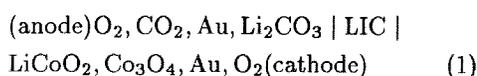
INTRODUCTION

Many researchers investigate cathode materials, such as LiCoO_2 and LiMn_2O_4 , for a lithium second battery. To keep a constant output voltage, the cathode material should be stable thermodynamically. When we have thermodynamic data, we can estimate the phase stability. However, there is few thermodynamic data in thermodynamic data tables.

In the present study, to determine standard Gibbs free energy of formation of LiCoO_2 , LiFeO_2 , LiCrO_2 , LiMn_2O_4 and LiFe_5O_8 , the lithium activity equilibrated between the lithium transition metal double oxide and a transition metal oxide is measured by using a solid-state electrochemical cell at high temperature.

EXPERIMENTAL

When the lithium activity equilibrated between LiCoO_2 and Co_3O_4 was measured, the lithium concentration cells with Li ion conductor (LIC) as electrolyte was constructed as follows:



where LIC was Li glass composed of Li_2O , TiO_2 , P_2O_5 and Al_2O_3 [1]. Separation between anode and cathode atmospheres was obtained by Ag seal. Premixed gas, N_2 -21% O_2 -1% CO_2 , was flowed on anode at which lithium activity was determined by the equilibrium between Li_2CO_3 - O_2 - CO_2 . The anode was worked as a reference electrode. The oxygen partial pressure at cathode was controlled by gas mixture of N_2 -21% O_2 .

The lithium activities of other lithium transition metal double oxides were measured by using similar cell construction. The electromotive force (emf) were measured at about 623 ~ 923 K using an electrometer with an input impedance of $10^{12} \Omega$.

RESULTS AND DISCUSSION

The emf showed good linearity as a function of temperature. In the case of the equilibria between LiCoO_2 and Co_3O_4 , the least squares fits give the emf, E , in the following expression.

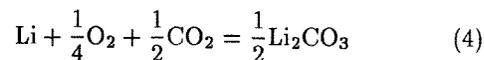
$$E/\text{mV} = 288 \pm 2 - 0.672T \quad (723 \sim 823 \text{ K}) \quad (2)$$

The emf is related to the lithium activities, a_{Li} , as

follows.

$$E = \frac{RT}{F} \ln \frac{a_{\text{Li}}^{\text{cathode}}}{a_{\text{Li}}^{\text{anode}}} \quad (3)$$

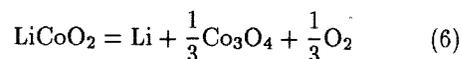
The anode reaction and its Gibbs energy change are represented by



$$\Delta G_{(4)} = \Delta G_{(4)}^\circ + RT \ln \frac{a_{\text{Li}_2\text{CO}_3}^{1/2}}{a_{\text{Li}}^{1/4} p_{\text{O}_2}^{1/2} p_{\text{CO}_2}} \quad (5)$$

where $\Delta G_{(4)}^\circ$ is the standard Gibbs free energy change of the reaction (4) and can be calculated by using values in thermodynamic table[2]. When the anode was at equilibrium, $\Delta G_{(4)}$ was equal to zero. Since p_{O_2} and p_{CO_2} was fixed by gas supply and $a_{\text{Li}_2\text{CO}_3}$ was equal to unity, we can calculate a_{Li} at anode. Using calculated $a_{\text{Li}}^{\text{anode}}$, obtained E and eq. (3), $a_{\text{Li}}^{\text{cathode}}$ can be determined.

The cathode reaction of the cell and its Gibbs energy change are represented by



$$\Delta G_{(6)} = \Delta G_{(6)}^\circ + RT \ln \frac{a_{\text{Li}} a_{\text{Co}_3\text{O}_4}^{1/3} p_{\text{O}_2}^{1/3}}{a_{\text{LiCoO}_2}} \quad (7)$$

Using the condition, $\Delta G_{(6)} = 0$, $a_{\text{Co}_3\text{O}_4} = 1$, $p_{\text{O}_2} = 0.21$ and determined $a_{\text{Li}}^{\text{cathode}}$, we can calculate $\Delta G_{(6)}^\circ$. From $\Delta G_{(6)}^\circ$ and the standard Gibbs energy of formation of Co_3O_4 [3], the standard Gibbs energy of formation of LiCoO_2 is obtained as

$$\begin{aligned} \Delta_f G^\circ(\text{LiCoO}_2, T = 648 \sim 823\text{K})/\text{kJmol}^{-1} \\ = (-677.8 \pm 0.56) + (0.228 \pm 0.001)T \end{aligned} \quad (8)$$

Using same treatments, $\Delta_f G^\circ$ of other compounds are represented by

$$\begin{aligned} \Delta_f G^\circ(\text{LiFeO}_2, T = 623 \sim 923\text{K})/\text{kJmol}^{-1} \\ = (-767.1 \pm 1.35) + (0.201 \pm 0.002)T \end{aligned} \quad (9)$$

$$\begin{aligned} \Delta_f G^\circ(\text{LiCrO}_2, T = 623 \sim 798\text{K})/\text{kJmol}^{-1} \\ = (-801.7 \pm 0.78) + (0.181 \pm 0.001)T \end{aligned} \quad (10)$$

$$\begin{aligned} \Delta_f G^\circ(\text{LiMn}_2\text{O}_4, T = 673 \sim 923\text{K})/\text{kJmol}^{-1} \\ = (-1313.9 \pm 2.12) + (0.312 \pm 0.003)T \end{aligned} \quad (11)$$

$$\begin{aligned} \Delta_f G^\circ(\text{LiFe}_5\text{O}_8, T = 623 \sim 823\text{K})/\text{kJmol}^{-1} \\ = (-2385.4 \pm 2.95) + (0.701 \pm 0.004)T \end{aligned} \quad (12)$$

REFERENCES

1. J. Fu, *Solid State Ionics*, **96**, 195 (1997)
2. *MALT2 Materials-oriented Little Thermodynamic Database*, The Japan Society of Calorimetry and Thermal Analysis, (Kagaku Gijutsu Sha, Japan, 1992)