

LITHIUM TRANSPORT IN TERNARY LITHIUM-COPPER-OXYGEN CATHODE MATERIALS

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An understanding of the Li-Cu-O ternary phase diagram was undertaken in order to predict Lithium Copper Oxide battery performance. The slow kinetics of this system are manifested in lower observed open circuit voltages than those predicted thermodynamically, approximately 1.6-1.8V versus 2.2-2.4V, respectively. Electrochemical titration of both copper (II) oxide and copper (I) oxide resulted in two-plateau discharges. The ternary compound LiCuO was formed during initial discharge of both compounds. The free energy of LiCuO was determined to be -88.3 kcal/mole. The slow kinetics of the initial displacement reaction is discussed in terms of the morphological changes undergone during titration with lithium.

Introduction

A number of lithium/first-row transition metal/oxygen electrochemical cells were investigated previously^{1a,b}. The relationships among electrochemical cells, thermodynamic principles, and phase diagrams is explained more fully in these earlier publications¹. Lithium/copper (II) oxide cells are of practical interest, and are currently being manufactured by SAFT. They are low rate cells which polarize strongly beyond approximately 1-2 mA/cm². These apparent slow kinetics are also manifested in lower observed open circuit voltages (after partial discharge) than those predicted thermodynamically, approximately 1.6-1.8V versus 2.2-2.4V, respectively.

An understanding of the Li-Cu-O ternary phase diagram was undertaken in order to predict battery performance. Both equilibrium (OCV) voltages and plateau capacities can be predicted from such information. In addition, laboratory cells of the type: Li / PC, 1.0 M LiClO₄ / CuO were investigated in order to determine thermodynamic properties of several discharge products which were not available in the literature.

Hypothetical Treatment if No Ternary Oxides Exist

The free energy of formation (ΔG_f) of all the binary oxides (MO_y; M=Li,Cu) in the Li-Cu-O ternary system have been measured previously. Their values at 25°C are listed in Table I².

TABLE I

Free Energy of Formation of Binary Oxides

Binary Oxide	$\Delta G_f(25^\circ\text{C})$ (kcal/mole)
Li	0.00
Cu	0.00
O ₂	0.00
Li ₂ O	-134.35
Li ₂ O ₂	-136.47
Cu ₂ O	-35.30
CuO	-30.62

If no ternary oxides (Li_xCuO_y) existed in this system, the calculation of the ternary phase diagram would be simple and straightforward, as is shown in Figure 1 on the Gibbs composition isotherm at 25°C. Each open triangle represents a three-phase equilibria of the phases lying at the corners of each tie triangle.

Furthermore, the theoretical open circuit voltages of cells of the type:

Li / Li⁺ Electrolyte / Li_xCuO_y
(where Li_xCuO_y represents any mixture of the three phases within one tie triangle) may be calculated directly from the Nernst Equation.

The activity of all three elements (including Li) must be constant and equal anywhere within a single tie triangle, from the Gibbs Phase Rule at constant temperature and pressure: $V = C - P$ (1)

where V is the variance, C is the number of components ($=3$) and P is the number of phases in equilibrium ($=3$). Therefore, the variance (or degree of freedom) is zero in any tie triangle.

If a lithium battery cathode material is made with some initial composition lying on the Gibbs composition triangle, then the change occurring in composition within the cathode during electrochemical discharge may also be plotted on the phase diagram. This is represented by the dashed lines emanating from the Li corner of the diagram, Figure 1. Electrochemical discharge proceeds in a direction toward the Li corner; if the cell is reversible, then charging would proceed in a direction away from the Li corner. Battery voltage "plateaus" are thus simply seen to be movement through tie triangles, or three-phase equilibria.

Effect of Intermediate Ternary Oxides

The presence of ternary oxides (Li_xCuO_y) in the Li-Cu-O system simply increases the number of tie triangles; and hence, the number of "voltage plateaus" in a battery using them as cathode materials. However, the free energies of formation (ΔG_f) are not known as well for the ternary compounds as was the case for the binary compounds.

Two ternary Li-Cu-O compounds were found to exist in the literature: $\text{LiCuO}^{3,4}$ and $\text{Li}_2\text{CuO}_2^5$. In order for them to exist as stable compounds, their respective free energies of formation must be lower (more negative) than the weighted average of their neighboring binary oxides. "Maximum" ΔG_f values result if the unknown compound lies in composition between two known binary compounds (Table II), whereas "minimum" ΔG_f values result when the composition of the unknown compound lies outside the two known binary compounds^{1a}.

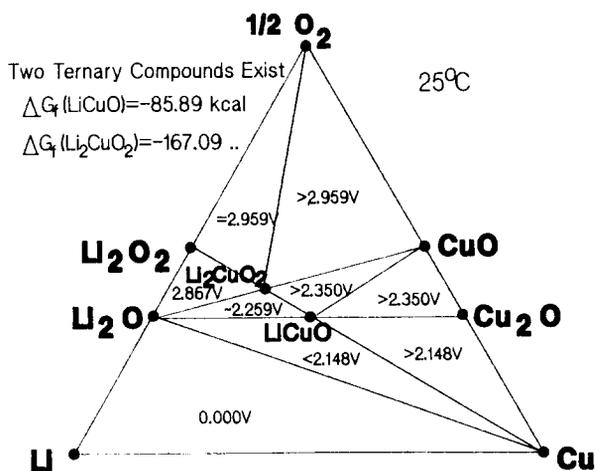
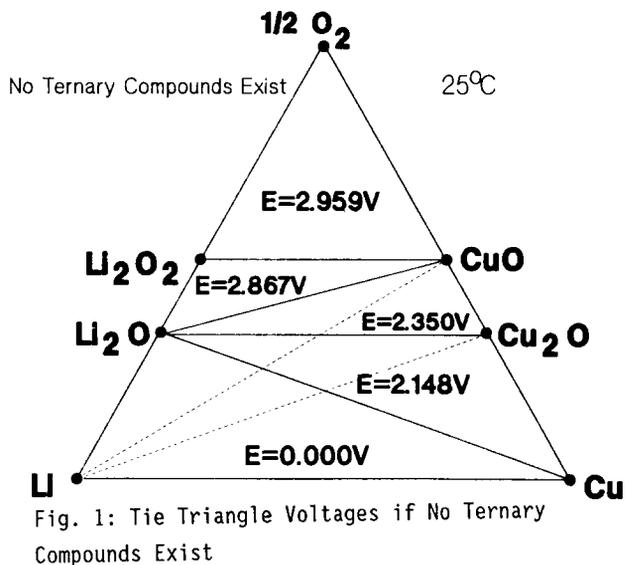


Fig. 2: Tie Triangle Voltages if the LiCuO/CuO Tie Line Exists

TABLE II
Maximum Free Energies of Formation of Ternary Li-Cu-O Compounds

Reaction	$\Delta G_f(\text{Product}, 25^\circ\text{C})$ (kcal/mole)
1. $\text{Li}_2\text{O} + \text{Cu}_2\text{O} \rightarrow 2(\text{LiCuO})$	<-84.83
2. $\text{Li}_2\text{O} + \text{CuO} \rightarrow (\text{Li}_2\text{CuO}_2)$	<-164.97
3. $\text{Li}_2\text{O}_2 + 2\text{Cu} \rightarrow 2(\text{LiCuO})$	<-68.24
4. $\text{Li}_2\text{O}_2 + \text{Cu} \rightarrow (\text{Li}_2\text{CuO}_2)$	<-136.47
5. $\text{Li} + \text{CuO} \rightarrow (\text{LiCuO})$	<-30.62

In either case, the extreme possibilities of ΔG_f for the unknown compound are given by setting a zero free energy of reaction (ΔG_r) between the unknown compound and the two binary compounds with known free energies of formation:



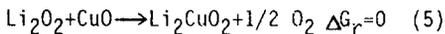
$$(-134.35) + (-35.30) = 2 \Delta G_f(\text{LiCuO}) \quad (3)$$

$$\Delta G_f(\text{LiCuO}) < -84.83 \text{ kcal/mole} \quad (4a)$$

Similarly,

$$\Delta G_f(\text{Li}_2\text{CuO}_2) < -164.97 \text{ kcal/mole} \quad (4b)$$

It is further possible to predict how the phase equilibria will change based on assumptions about the actual stability of the two ternary oxides, relative to their maximum values given in Equation 4. For instance, one can calculate what stability of Li_2CuO_2 is required in order that the $\text{O}_2/\text{Li}_2\text{CuO}_2$ tie line exists in preference to the $\text{Li}_2\text{O}_2/\text{CuO}$ tie line, shown in Figure 2. This is accomplished through the use of the "clear-cross principle"⁶, where once again, the ΔG_r of a reaction is set equal to 0:

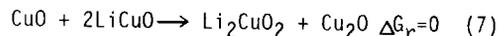


$$\Delta G_f(\text{Li}_2\text{CuO}_2) < -167.09 \text{ kcal/mole} \quad (6)$$

It is more likely that Figure 2 represents the actual phase diagram than Figure 1, since Li_2CuO_2 is known to exist ($\Delta G_f < -164.97$ kcal/mole) and the "balance" point for the $\text{Li}_2\text{CuO}_2/\text{O}_2$ tie line is slightly more stable than this value ($\Delta G_f = -167.09$ kcal/mole).

Unfortunately, the most difficult line in the phase diagram to predict is also the most important one to practical Li/CuO batteries. The discharge path of a cathode, composed initially of

only CuO, exactly follows the CuO/LiCuO tie line of Figure 2. However, if Li_2CuO_2 is even more stable than -167.09 kcal/mole, the $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ tie line might exist in preference to the CuO/LiCuO tie line.



$$\Delta G_f(\text{Li}_2\text{CuO}_2) - 2\Delta G_f(\text{LiCuO}) = 4.68 \text{ kcal/mole}$$

That is, if Li_2CuO_2 is more stable than twice LiCuO plus 4.68 kcal/mole, then the $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ tie line would exist, rather than the CuO/LiCuO tie line shown in Figure 2.

In other words, this "clear-cross principle" calculation involves two unknowns, rather than only one as before. Using the new "maximum" value for $\Delta G_f(\text{Li}_2\text{CuO}_2)$ of -167.09 kcal/mole means that any value of $\Delta G_f(\text{LiCuO})$ less (more negative) than -85.89 kcal/mole results in the presence of the CuO/LiCuO tie line, Figure 2. Any value for LiCuO between -85.89 and -84.83 kcal/mole (its maximum value) results in the presence of the $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ tie line. This holds especially important implications for the Li/CuO battery, because the first case results in a considerably longer (50%) initial plateau on discharge than does the second case.

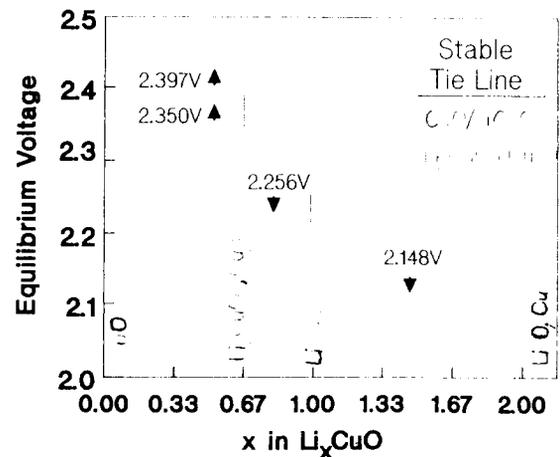


Fig. 3: Theoretical Discharge Curves if LiCuO/CuO (Dashed) or $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ (Solid) is Stable

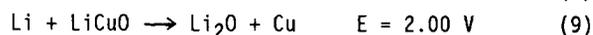
The length and voltages predicted for the battery discharge curve are compared for each of these two cases in Figure 3. The second case predicts two distinct plateaus between $x=0.0$ and $x=1.0$ in Li_xCuO , whereas the first case predicts only one. The total energy (area under the discharge curve) is the same for both cases, but the presence of a $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ tie line would raise the voltage of the first tie triangle (plateau) and lower the voltage of the second tie triangle (plateau) relative to the 2.350V which would be present if the $\text{Li}_2\text{CuO}_2/\text{Cu}_2\text{O}$ tie line were not present. The greater the stability of Li_2CuO_2 over that of LiCuO , the larger the difference will be between the two plateau voltages. The two tie lines cross each other at a value (x) of 0.67 Li per Cu on the discharge curve.

Not only are the number and voltages of the plateaus different in the two cases, but also the battery chemistry (between $x=0.0$ and $x=1.0$) is completely different. In the first case, the compound LiCuO is being formed during discharge (at the expense of of the initial CuO); whereas, in the second case, two new compounds (Li_2CuO_2 and Cu_2O) are nucleated and grow at the expense of the initial CuO , followed by the formation of LiCuO after all the CuO is exhausted.

Electrochemical Experiments

The Li-Cu-O system was found to be kinetically slow; only currents below 2 mA/cm^2 resulted in acceptable polarizations. Not only is this unfortunate in a practical battery aspect, but it also resulted in very long times to perform electrochemical experiments. Most importantly, equilibration times (OCV) for each datum point on the equilibrium potential curves (Figures 4 and 5) required 2 to 24 hours after current was terminated.

Nevertheless, the Li/CuO cell discharge mechanism was determined from the two equilibrium potential curves. Four experiments were performed along the Li/CuO titration line, Figure 4. Three of these used the initial cathode composition of CuO only; the fourth cell started with synthetically prepared LiCuO ($x=1.0$, circles). The overall reproducibility of the voltage plateaus was poor, unless very long equilibration times were allowed. Furthermore, discharge capacities were not as long as theoretically expected. However, the first plateau did extend beyond $x=0.67$, indicating that initial discharge of CuO did not involve Li_2CuO_2 . Voltages between $x=0.1$ and 1.00 were between 1.9 and 2.5 volts, with the highest values resulting from the longest equilibration times. This two-step discharge of Figure 4 is indicative of the formation of LiCuO , rather than Li_2CuO_2 , followed by the formation of lithium oxide and elemental copper:



Because these cells developed very slow kinetics after $x=0.5$ to 0.85, the range $x>1.0$ was investigated using a new cell with synthetically prepared LiCuO . It exhibited a voltage of 1.95 to 2.0V vs. Li, Figure 4.

X-ray diffraction results afforded good confirmation of these electrochemical reactions. Samples removed from the cells after electrochemical addition of 0.25 and 0.44 Li atoms per Cu both exhibited diffraction lines of two new phases (LiCuO and slight Cu) along with the original CuO . These results predict the phase diagram of Figure 6 and the dashed line of Figure 3 (rather than the solid line).

In order to confirm the phase diagram and obtain a free energy of formation for the ternary compound LiCuO , two cells were also prepared along the Li/ Cu_2O titration line, Figure 5.

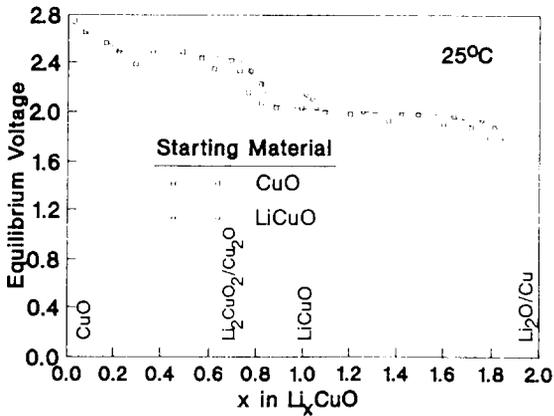


Fig. 4: Equilibrium Potential Curve of CuO Cells

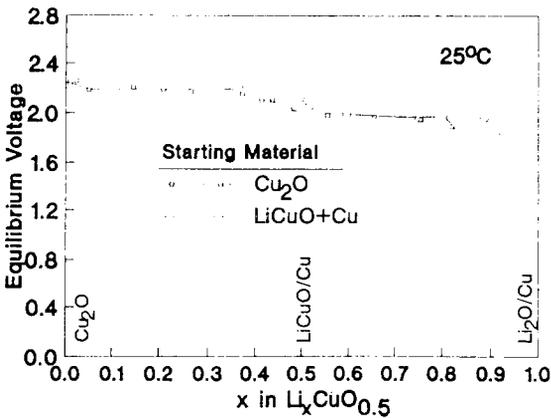


Fig. 5: Equilibrium Potential Curve of Cu₂O Cells

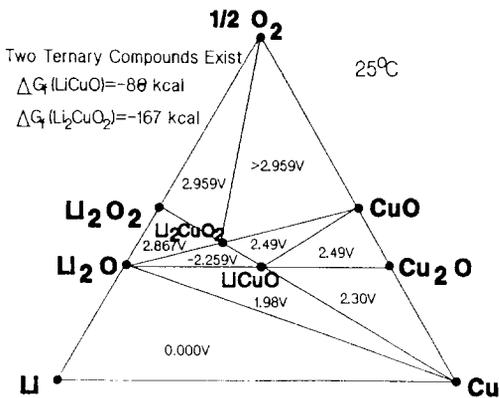
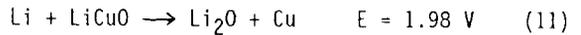
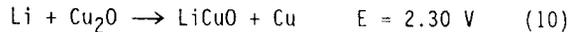


Fig. 6: Experimentally Determined Li-Cu-O Diagram

These results suggest a two-plateau discharge of Cu₂O:



This results in a calculated value of ΔG_f (LiCuO) of -88.3 kcal/mole. X-ray analysis at x=0.45 also confirmed the first displacement reaction, since strong Cu lines were observed. The experimentally determined ternary phase diagram is illustrated in Figure 6.

Morphological Considerations

The morphological changes undergone by the initial CuO cathode particles during cell discharge are illustrated schematically in Figure 7. During low rate discharge, the new LiCuO phase is nucleated on the CuO surface and continues to grow as discharge proceeds at the expense of the CuO, Figure 7(b). This is an "equilibrium" process, and corresponds to movement along the CuO/LiCuO tie line of Figure 6.

However, during higher-rate discharge, the kinetics of Reaction 8 are apparently too slow to satisfy the cell current, so that Li begins to react with the LiCuO according to Reaction 9 before all the CuO is exhausted. This is equivalent to a "non-equilibrium" situation, since the resulting Li₂O,Cu products are not stable with respect to the interior CuO, Figure 7(c). In terms of Figure 6, this is equivalent to the cell discharging as if the cathode composition was in the lower tie triangle (1.98V), even though its actual composition remains in the upper tie triangle (2.49V). This is believed to be the primary reason that Lithium Copper Oxide cells discharge at a much lower voltage (1.2 to 1.7V) than expected (2.0 to 2.49V), even at low currents. Even with this principle in mind, copper oxide cells polarize very strongly at low currents, since these discharge voltages are still 0.3 to 0.7V below the "non-equilibrium" open-circuit voltage of 1.98V. This may be due to poor electronic conduction through the exterior Li₂O and LiCuO phases.

In the limit of infinitely small currents, a CuO cathode eventually discharges at equilibrium according to Equation 9, once all of the original CuO is converted to LiCuO (at $x=1.0$), Figure 7(d).

MORPHOLOGICAL CONSIDERATIONS

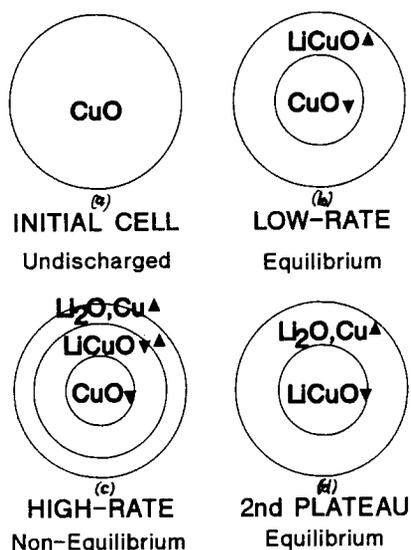


Fig. 7: Morphological Changes of CuO Cathodes

Conclusions

The battery reactions occurring within a Li/CuO cell at low currents could be predicted exactly if the free energy of formations of all compounds in the Li-Cu-O phase diagram were known. Furthermore, the number of discharge plateaus, the voltage of each plateau, and the length (capacity) of each plateau could also be predicted exactly. The relationship between battery performance and the thermodynamic phase diagram is therefore seen to be of utmost importance.

Unfortunately, the free energy of formation (ΔG_f) of the two ternary compounds in the system (LiCuO and Li_2CuO_2) were previously unknown, though all the binary compounds were

known. The free energy of formation of LiCuO was measured in electrochemical cells and found to be -88.3 kcal/mole. The free energy of formation of Li_2CuO_2 was not determined, because it was found not to occur in the cell reactions.

Electrochemical experiments conducted at small currents yielded Li/CuO cells with a two-plateau discharge, with open circuit voltages of 2.49 and 1.98V, respectively. At practical currents ($>1\text{mA/cm}^2$), Li/CuO cells were found to initially discharge according to the second plateau reaction, due to kinetic limitations in the first plateau reaction. This is believed to explain the difference observed between thermodynamic and actual discharge voltages.

Acknowledgments

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