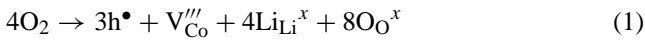


Letter to the Editor

Charge compensation in LiCoO₂

Recently, Tukamoto and West investigated the electronic conductivity of undoped LiCoO₂ and Mg-doped LiCoO₂ [1]. They studied the electrical conductivity of undoped LiCoO₂ over a temperature range 25–700 °C at three different oxygen partial pressures. They observed that at a given temperature that as the oxygen partial pressure increased there was increase in the electronic conductivity of undoped LiCoO₂. From this result they suggested that undoped LiCoO₂ was a p-type semiconductor, due to the presence of a small amount of Co⁴⁺ in the material. Tukamoto and West proposed two different charge-compensating defects for Co⁴⁺. The defect reactions for these two cases are given further. Kroger–Vink [2] notation is used for the point defects:



where $h^\bullet = \text{Co}^{4+}$, and



In the first case, the holes (Co⁴⁺) are charge compensated by Co vacancies and in the second case, they are compensated by Li vacancies. Tukamoto and West [1] suggested because of the possibility of lithia loss by volatilization during synthesis that hole charge compensation by Li vacancies was the most likely possibility. This was only the explanation given for choosing charge compensation by Li vacancies. No conclusive evidence to support this suggestion was given.

It is the purpose of this note to show that by using the laws of mass action for the defect reactions above in conjunction with the dependency of the electronic conductivity on oxygen partial pressure it is possible to determine conclusively the correct compensation defect (Co or Li vacancies) for Co⁴⁺ in undoped LiCoO₂.

It is known for oxides containing transition metal ions that the electronic conductivity, σ , depends on the oxygen partial pressure because, the concentration of holes or electrons depends on the partial pressure of oxygen, P_{O_2} [3–8]. An example, for the case of a p-type semiconductor where holes are the dominant electronic defect is given:

$$\sigma \propto [h^\bullet] \propto P_{\text{O}_2}^m \quad (3)$$

where $[]$ is concentration and m the oxygen partial pressure exponent. The sign and magnitude of m are indication of the rate-controlling species and charge-compensating defect. For example, a positive value of m implies holes while a negative value implies electrons. The magnitude of m determined from the dependence of the electronic conduc-

tivity on oxygen partial pressure can be compared to predicted m values from the laws of mass action for the various charge-compensating defects to determine the correct charge compensating point defect for the holes or electrons. For example, applying the law of mass action to Eq. (1) yields the following:

$$K_1 = \frac{[h^\bullet]^3 [V_{\text{Co}}'''] [\text{Li}_{\text{Li}}^x]^4 [\text{O}_{\text{O}}^x]^8}{(P_{\text{O}_2})^4} \quad (4)$$

Applying the law of mass action to Eq. (2) yields:

$$K_2 = \frac{[h^\bullet] [V_{\text{Li}}'] [\text{O}_{\text{O}}^x]^2}{P_{\text{O}_2}} \quad (5)$$

where K_1 and K_2 are the reaction constants. Eqs. (4) and (5) can be simplified since, $[\text{Li}_{\text{Li}}^x]$ and $[\text{O}_{\text{O}}^x] \approx 1$:

$$(P_{\text{O}_2})^4 = [h^\bullet]^3 [V_{\text{Co}}'''] \quad (6)$$

$$P_{\text{O}_2} = [h^\bullet] [V_{\text{Li}}'] \quad (7)$$

Eqs. (6) and (7) can be combined with the charge neutrality equations for reactions (1) and (2) to predict the dependence of the hole concentration in undoped LiCoO₂ on oxygen partial pressure for charge compensation by Co or Li vacancies, respectively.

The charge neutrality condition for reaction (1) is as follows:

$$[h^\bullet] = 3[V_{\text{Co}}'''] \quad (8)$$

The charge neutrality condition for reaction (2) is as follows:

$$[h^\bullet] = [V_{\text{Li}}'] \quad (9)$$

Substituting Eq. (8) into Eq. (6) and Eq. (9) into Eq. (7) yields the following:

$$[h^\bullet] \propto P_{\text{O}_2} \quad (10)$$

$$[h^\bullet] \propto (P_{\text{O}_2})^{0.5} \quad (11)$$

From Eq. (10), it can be observed for the case where the holes are compensated by Co vacancies the hole concentration and consequently, from Eq. (3) the electronic conductivity should vary with oxygen partial pressure to the first power ($m = 1$), whereas for compensation by Li vacancies the electronic conductivity should vary with oxygen partial pressure to the one-half power ($m = 0.5$). Thus, examination of the dependence of the electronic conductivity of undoped LiCoO₂ as a function of oxygen partial pressure should allow for determination of the correct charge-compensating defect.

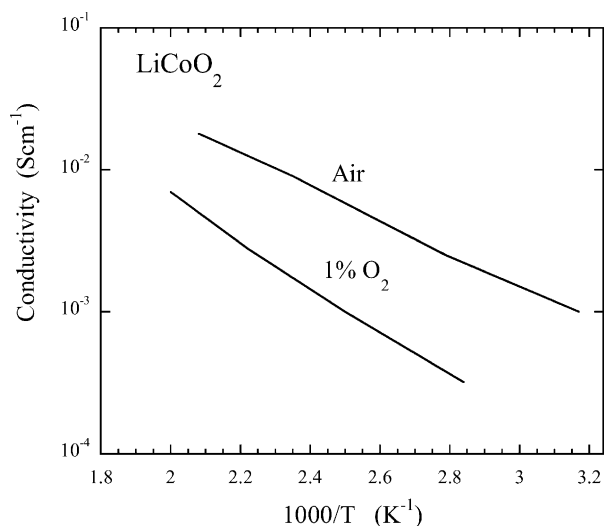


Fig. 1. The electronic conductivity data of undoped LiCoO₂ from Tukamoto and West [1] as a function of inverse temperature at two different oxygen partial pressures.

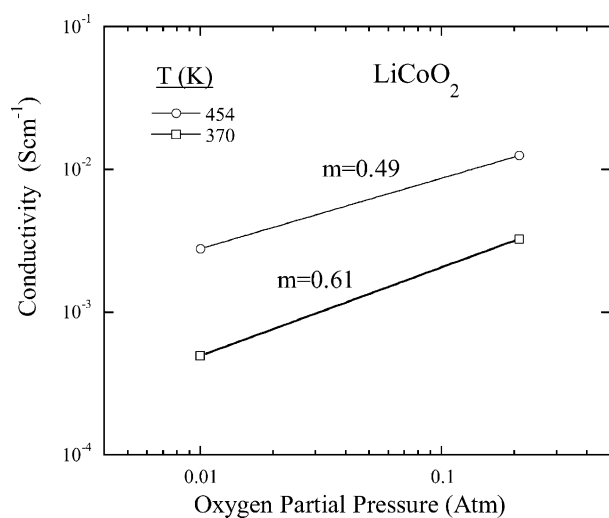


Fig. 2. The electronic conductivity data of undoped LiCoO₂ as a function of oxygen partial pressure at two different temperatures.

The electronic conductivity data of undoped LiCoO₂ from Tukamoto and West [1] as a function of inverse temperature at two different oxygen partial pressures (1% O₂ and air) is shown in Fig. 1. Tukamoto and West also measured the electronic conductivity at a lower oxygen partial using argon gas. Since, no oxygen partial pressure was given for this gas, data obtained in this atmosphere are not included in Fig. 1. From Fig. 1, it is observed that as the oxygen partial pressure increases the electronic conductivity increases, in agreement

with a p-type semiconducting oxide [1]. From Eq. (3), it can be seen that a plot of logarithm of σ versus logarithm of P_{O_2} at a given temperature should yield a straight line with a slope equal to m . Such a plot is shown in Fig. 2 based on data from Fig. 1 at two different temperatures ($T = 370$ and 454 K). From Fig. 2, it is observed that at $T = 454$ K, $m = 0.49$ and $T = 370$, $m = 0.61$. The experimental m values for undoped LiCoO₂ range from ≈ 0.5 to 0.6 . A comparison of these values to predicted m values of 1 for Co vacancies (Eq. (10)) and 0.5 for Li vacancies (Eq. (11)) suggests that Li vacancies are the charge-compensating defect for the holes in undoped LiCoO₂. This result confirms the suggestion of Tukamoto and West [1].

A comparison of the dependence of the electronic conductivity on oxygen partial pressure for undoped LiCoO₂ with the predicted dependence of possible charge-compensating point defects on oxygen partial pressure gives conclusive proof that the holes (Co⁴⁺) in undoped LiCoO₂ are charge compensated by Li vacancies.

Acknowledgements

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