NONSTOICHIOMETRY AND DEFECT STRUCTURE OF γ-Na_xCoO_2

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γ-Na_xCoO_2, has long been known to be the best ever p-type oxide thermoelectric, but its oxygen nonstoichiometry and defect structure remains unelucidated. In this work, we measured oxygen nonstoichiometry and electrical conductivity on the system of γ-Na_xCoO_2 against oxygen activity (a_{O2}) across its widest ever range below a_{O2}=1 for a fixed Na-content x=0.706 at different temperatures in the range of 773-973 K, and at a fixed temperature 973 K for x=0.664, 0.706 and 0.731, respectively. It has been deduced therefrom that as a_{O2} decreases, the majority disorder type shifts from $[V_{Na}']\approx p$ to either $[V_{Na}']\approx[Co_{Na}^{\bullet}]$ or $[V_{Na}']\approx[Co_i^{\bullet\bullet\bullet}]$, however, exhibiting a positive deviation from the ideal defect behavior. The latter is attributed to the positive deviation of holes due to their degeneracy. By taking into appropriate account of the activity coefficient of holes in terms of the Fermi-Dirac integral of order 1/2, the nonstoichiometry and electrical conductivity have been precisely and consistently depicted to evaluate the defect-chemical parameters including the effective mass and mobility of holes and the redox equilibrium constant. The phase-stability limit of γ-Na_xCoO_2 is also reported against temperature and Na-content.