Experimental Errors in Studying the Defect Mobility in Nonstoichiometric Metal Oxides

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Important information on the mobility of predominant defects in transition metal oxides may be obtained in studying the kinetics of nonstoichiometry changes as a function of temperature and oxidant activity using modern microthermogravimetric techniques. One of the most important methods enabling the determination of chemical diffusion coefficient in these compounds is so-called re-equilibration kinetic method. As the chemical diffusion is a process of ambipolar migration of defects under their concentration gradient, the chemical diffusion coefficient in nonstoichiometric compounds can be determined from mass changes of a given sample when going from one equilibrium state to another. If no hysteresis is observed in oxidation and reduction runs, it may be considered that the rate determined step is the ambipolar diffusion of defects. The main goal of the present paper is an attempt to show that several systematic errors in such experiments may lead to erroneous results. First of all, geometry of the sample should be rationally chosen in order to eliminate the influence of corner effect on re-equilibration kinetics. However, one of the most important systematic errors may originate from carrier gasses used to obtain the necessary oxygen partial pressure. If only one carrier gas is used – as usually – the Archimedes effect is to be expected when the oxygen partial pressure is changed. This source of systematic errors may be eliminated by using two carrier gases (Ar and He), in which the Ar/He ratio is chosen in such a way that the density of this gas mixture is exactly the same as that of oxygen. Another systematic error may result from insufficient supply of the oxidizing gas to the surface of re-equilibrated sample. All these problems are illustrated by the results obtained on nonstoichiometric nickel and cobalt oxides.