QUASI-EQUILIBRIUM OXYGEN RELEASE METHOD FOR STUDYING MATERIALS WITH MIXED IONIC - ELECTRONIC CONDUCTIVITY

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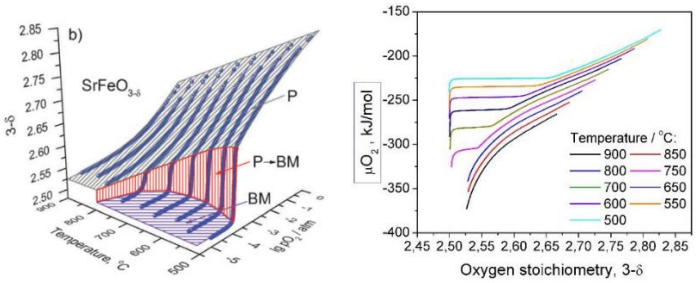
Nonstoichiometric oxides with mixed oxygen ionic and electron conductivity (MIEC), which typically possess a perovskite-like structure, have attracted sustained interest over the past several decades because they are promising materials for oxygen-permeable membranes and cathodes of solid oxide fuel cells (SOFCs) [1, 2]. The oxygen non-stoichiometry of MIEC oxides determines both the fundamental functional properties of membrane and electrode materials and the operating efficiency of catalytic membrane reactors and SOFCs. At the Institute of Solid State Chemistry and Mechanochemistry, a new method of quasi-equilibrium oxygen release (QEOR) has been developed, which makes it possible to obtain equilibrium dependences of oxygen nonstoichiometry on the partial pressure of oxygen (pO_2) and temperature (see figure) and to calculate thermodynamic parameters ($\Delta\mu(3-\delta)$, $\Delta H(3-\delta)$, $\Delta S(3-\delta)$) of oxygen exchange [3].



Equilibrium isotherms 3-δ - lg pO_2 and calculated from them chemical potential of oxygen in $SrFeO_{3-\delta}$ vs oxygen nonstoichiometry

Since changes in oxygen stoichiometry in MIEC oxides are accompanied by changes in the charge carrier concentration, the obtained data can be used to estimate the dependence of the density of states near the Fermi level on δ. The nature of the $\Delta H(3-\delta)$ and $\Delta S(3-\delta)$ dependences can be used to determine the conductivity type (metal-like or semiconductor). In addition, using the QEOR method, the dependence of the oxygen exchange reaction rate constant on the MIEC oxide surface on its chemical potential can be established in the form of the Brønsted-Evans-Polanyi relationship. Thus, thermodynamic parameters determine the important functional properties of MIEC materials and the operational efficiency of devices based on them.

1. Wei Bai et al. *International journal of hydrogen energy*, 2021, 46, 36257- 36290.
2. M. Fallah Vostakola et al., B. *Energies* 2021, 14, 1280-1333.
3. I. Starkov, S. Bychkov, A. Matvienko, A. Nemudry, *Phys. Chem. Chem. Phys*. 2014, 16, 5527- 5535

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