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REVIEW

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Research on the electrochemistry of oxygen ion conductors in the former Soviet Union. II. Perovskite-related oxides

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Abstract The review is devoted to the analysis of experimental results on electrochemical and physicochemical properties of the perovskite-related oxide phases obtained at scientific centers of the former Soviet Union. The main attention is focused on oxides with high electronic conductivity, which are potentially useful as electrodes for high-temperature electrochemical cells with oxygen-ion conducting solid electrolytes and interconnectors of solid oxide fuel cells, and on mixed ionic-electronic conductors for oxygen separation membranes. Along with perovskite-like solid solutions based on $LnMO_{3-\delta}$ (Ln is a rare-earth element, M = Cr, Mn, Fe, Co, Ni) and $SrCoO_{3-\delta}$, properties of the oxide phases $Ln_2MO_{4\pm\delta}$ (M = Cu, Ni, Co) with the K_2NiF_4-type structure are briefly reviewed.

Key words Perovskite · Conductivity · Oxygen permeability · Electrode · Thermal expansion

Introduction

Perovskite-related oxides are of great interest as materials for solid oxide fuel cells (SOFCs), oxygen separation membranes, membrane reactors for hydrocarbon partial oxidation, solid electrolyte oxygen pumps and sensors. Properties of such oxides, determined by cations occupying A and B sites of the ABO_3 perovskite crystal lattice as well as external conditions such as temperature and oxygen partial pressure, vary over a wide range and can be controlled by a partial substitution in both cation sublattices. In addition, there exist several derivative structures exhibiting unique transport properties (brownmillerite, orthoferrite, K_2NiF_4-type phases, Aurvillius and Ruddlesden-Popper series). This offers considerable scope for developing novel materials with predetermined characteristics required by specific applications.

The present part of our review, devoted to the developments of oxygen ion conductors in the former Soviet Union, is focused on the experimental results from studying perovskite-related oxide phases. Among the variety of such oxides, we have chosen only materials which are considered to be applicable in high-temperature electrochemical devices. This is, firstly, oxides with high electronic conductivity, promising for electrodes of solid-electrolyte cells and interconnectors of SOFCs. Secondly, our attention is given to the developments of mixed conductors for oxygen electrochemical membranes of various types. Since the number of recent publications concerning high-temperature superconductors and K_2NiF_4-type oxides is very large, we have made an attempt to briefly list the articles which may be interesting from the viewpoint of oxygen electrochemistry. Analogously, the research articles concerning perovskite-type proton conductors, the synthesis and processing of ceramics, and the thermodynamic properties of the oxides are only listed in order to provide corresponding references for scientists interested in such information. The authors did not take into consideration the mechanisms of electronic transport in perovskites and defect equilibria, more detailed analysis of which can be found in monographs [1, 2].

Perovskite-type $LnCrO_3$ (Ln = La–Lu, Y)

Rare-earth element (REE) chromites with perovskite-like structure find wide applications as materials for interconnectors of SOFCs, heaters of high-temperature furnaces, and electrodes of various solid-electrolyte cells [1]. This is caused by such properties of the chromites as a high electronic conductivity at temperatures above

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