Abstract

This review is focused on the analysis of experimental results on oxygen ion-conducting ceramic materials based on HfO₂, CeO₂, and ThO₂, published in the former Soviet Union. In particular, the physicochemical and transport properties of fluorite-related oxides and the characteristics of electronic conduction in these solid electrolytes are briefly reviewed. Emphasis is given to electrocatalytic and electrochemical properties of cerium-containing oxides, which are promising materials for electrodes of electrochemical cells operating in reducing atmospheres, and mixed-conducting membranes. A comparative analysis of specific features of the solid-electrolyte ceramics based on hafnia, zirconia, ceria, and thoria is performed in order to reveal basic tendencies of oxygen ionic transport in fluorite-type oxides, and to identify the potential applicability of these materials in various high-temperature electrochemical devices.

Key words

Stabilized hafnia · Doped ceria · Thoria · Solid electrolyte · Ionic conductivity

Introduction

Oxygen ion-conducting solid electrolytes find numerous technological applications in solid oxide fuel cells (SOFCs), sensors of various types, high-temperature electrolyzers, and ceramic membranes for partial oxidation of hydrocarbons. Each of these applications has specific requirements in terms of materials properties. In particular, the main requirement for solid electrolytes used in SOFCs and sensors is maximum oxygen ionic conductivity and minimum electronic conduction under typical operating conditions. On the other hand, the ability to optimize properties of ion-conducting materials is relatively limited, and both construction and performance of electrochemical cells are often determined by the properties of materials available. Therefore, the development of materials with satisfactory properties for high-temperature electrochemical applications is an important scientific task. At the same time, numerous results in this field obtained in the former Soviet Union, and published mainly in Russian, are practically unknown to Western scientists.

This work focused on studies on oxygen ion-conducting ceramic materials based on HfO₂, CeO₂, and ThO₂, performed in the former USSR. Among other goals, the authors tried to analyze the results considered of present interest for the state-of-the-art in the field of high-temperature electrochemistry of oxygen. Particular emphasis was also given to list briefly a number of articles published in less-known issues and journals, in order to assist people looking for information on these themes. In this review, no attempt was made to compare the results obtained in Soviet and Western scientific centers. Such comparison would obviously show enormous coherence between such results, as any reader familiar to the subject might conclude from the present paper. Lastly, references to papers published in international journals included in this work were only selected to show relationships between selected sets of experimental results.

HfO₂-based ceramic materials

Most of the phase relationships in the oxide systems based on hafnium dioxide are close to those found in
zirconia-based oxides, discussed in the Part I of this review [1]; the properties of these groups of oxides are also alike, owing to the similar electronic configuration of zirconium and hafnium cations. However, HfO$_2$-based ceramics have found fewer electrochemical applications than zirconia owing to several important differences in the transport properties and stability of these materials. Firstly, the oxygen ionic conductivity of the most-conducting solid electrolytes of stabilized hafnia, with the fluorite-type structure, is significantly lower than that of zirconia-based oxides. Secondly, stabilized fluorite-type phases of hafnium dioxide, having the highest ionic conductivity, are less stable at low temperatures than those based on stabilized zirconia. Another significant difference is a considerably higher chemical stability and mechanical strength of HfO$_2$-based ceramics with respect to stabilized ZrO$_2$, which could enhance the applicability domain of these materials, but also prevents the easy synthesis and processing of hafnia-based ceramics.

When reviewing the literature on HfO$_2$-containing oxides, one should mention separately a monograph [2], which presents a large amount of data on phase diagrams, kinetics of solid-state synthesis and properties of these materials.

Hafnium dioxide and the systems HfO$_2$-MO (M = Be, Mg, Ca, Sr, Ba)

As found for zirconium dioxide, HfO$_2$ has a monoclinic structure at low temperature; increasing the temperature results in a transition of the monoclinic (M) phase to tetragonal (T) and then to a cubic fluorite-type (F) phase [2, 3]. However, the temperatures for M → T and T → F phase transitions for hafnia are higher than those for zirconia: the M → T transformation for HfO$_2$ takes place at approximately 2100–2270 K, depending on impurity content, and the cubic phase of HfO$_2$ forms only at temperatures close to the melting point (~2970 K). Under high pressure (40–110 kbar) and at temperatures up to 1970 K, an orthorhombic phase can be obtained [4]. This phase, being metastable at ordinary conditions, decomposes rapidly when heating, even at temperatures as low as 770 K. Thermodynamic properties of hafnium dioxide and other oxides of the binary Hf-O system have been reported [5–7].

In oxidizing conditions, monoclinic HfO$_2$ shows mixed oxygen ionic and p-type electronic conductivity; the oxygen ion transference numbers in air do not exceed 0.3 at 970–1270 K (Table 1). The total electrical conductivity of monoclinic HfO$_2$ decreases with reducing oxygen partial pressure owing to decreasing p-type conductivity, which can be approximated by [8]:

$$\sigma_p = 35.5 p_{O_2}^{1/4} \exp \left( - \frac{15780}{T} \right)$$

with the pre-exponential term expressed in S cm$^{-1}$ atm$^{-1/4}$. The activation energy for hole conduction in undoped hafnia is higher than for ionic transport [8]. As a result, the ion transference number of HfO$_2$ increases with decreasing oxygen pressure and temperature. Thermal expansion coefficients (TECs) of hafnium dioxide, determined from dilatometric [10] and high-temperature X-ray diffraction [11, 12] data, are given in Table 2.

The HfO$_2$ F-phase, which is the most interesting as a solid electrolyte in the hafnia-based oxide systems, can be stabilized to temperatures lower than the pure hafnium dioxide T ↔ F transition temperature, by addition of rare-earth or some alkaline-earth metal oxides.

Phase diagrams and selected phase relationships in the binary systems HfO$_2$-MO (M = Be, Mg, Ca, Sr, Ba) have been reported [13, 15, 16, 18–39]. Numerous research articles presented detailed ternary phase diagrams like HfO$_2$-ZrO$_2$-MgO [16], HfO$_2$-ZrO$_2$-CaO [18], HfO$_2$-Y$_2$O$_3$-MgO [35, 36], HfO$_2$-Y$_2$O$_3$-CaO [25, 26, 31–34, 38], or separate phase relationships in these systems. Thermodynamic properties of different hafnia-based oxide phases, stability, and kinetics of solid-state reactions involved in their synthesis were studied under various conditions [13, 23, 40–51]. When summarizing these results and comparing them to data on zirconia-based ceramics [1], one can select the following specific features:

1. In the phase diagrams with hafnia, the domains of formation of tetragonal and cubic fluorite-type solid solutions are shifted to higher temperatures in comparison to those of zirconia (Fig. 1). For a given temperature, the concentration range of the HfO$_2$-based fluorite phase is, as a rule, narrower than for the corresponding zirconia phase, and the minimum dopant concentration necessary to stabilize the F-phase is higher for hafnia. This results in poor stability of the hafnia-based fluorites at temperatures below 1600 K, in comparison with the corresponding zirconia phases.

2. In the systems HfO$_2$-MO, there are no stable fluorite-type phases to be used as solid electrolytes in the

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>973 K</th>
<th>1023 K</th>
<th>1073 K</th>
<th>1123 K</th>
<th>1173 K</th>
<th>1223 K</th>
<th>1273 K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_2$/air</td>
<td>0.31</td>
<td>0.26</td>
<td>0.23</td>
<td>0.16</td>
<td>0.14</td>
<td>0.11</td>
<td>0.09</td>
<td>[9]</td>
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<td>O$_2$/air</td>
<td>0.12</td>
<td>–</td>
<td>0.10</td>
<td>0.07</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
<td>[8]</td>
</tr>
<tr>
<td>O$_2$/CO + CO$_2$ (10% CO)</td>
<td>0.73</td>
<td>0.67</td>
<td>0.69</td>
<td>0.61</td>
<td>0.59</td>
<td>0.43</td>
<td>0.35</td>
<td>[8]</td>
</tr>
<tr>
<td>O$_2$/CO + CO$_2$ (66% CO)</td>
<td>0.82</td>
<td>–</td>
<td>0.75</td>
<td>–</td>
<td>0.60</td>
<td>–</td>
<td>0.49</td>
<td>[8]</td>
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