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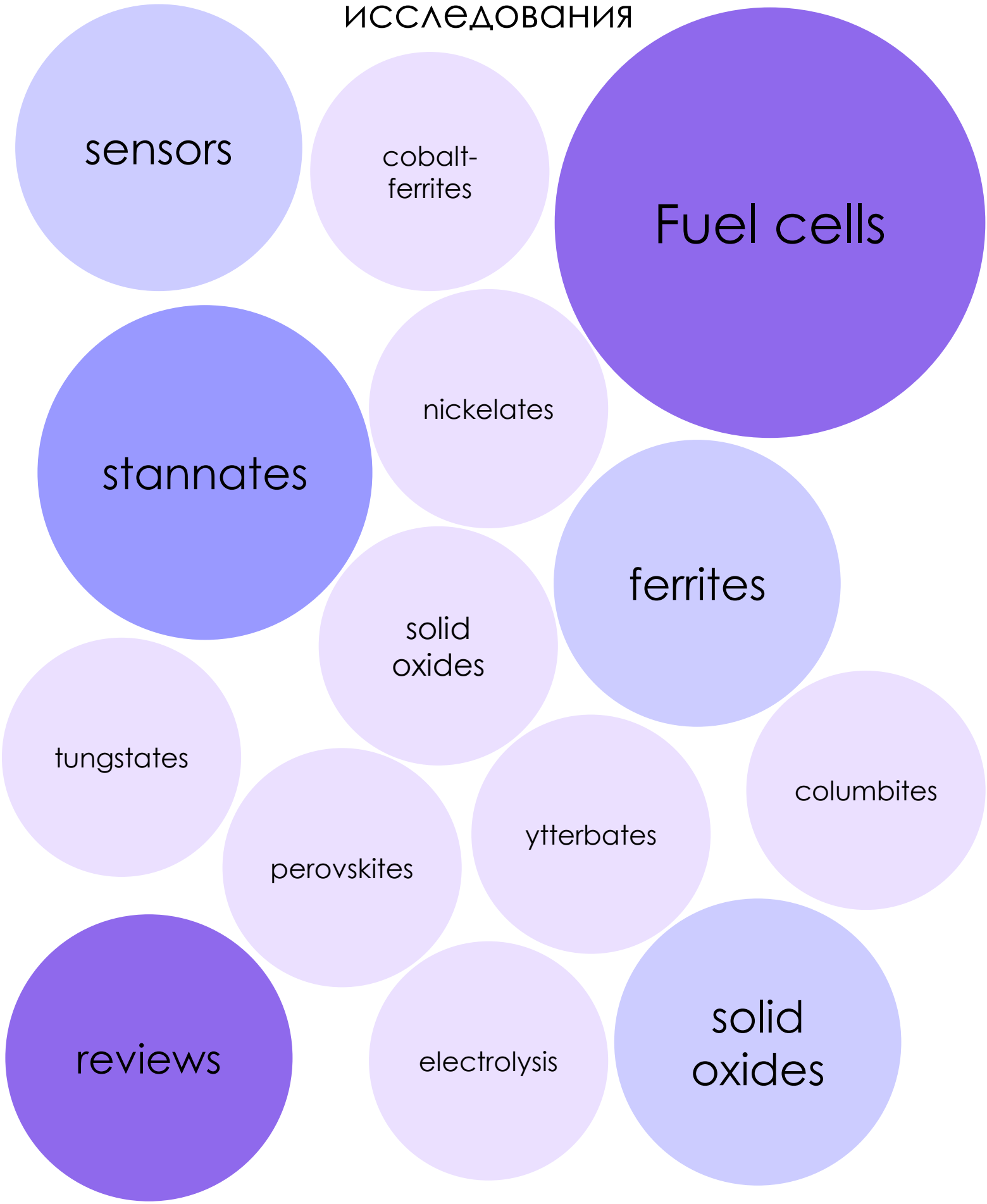
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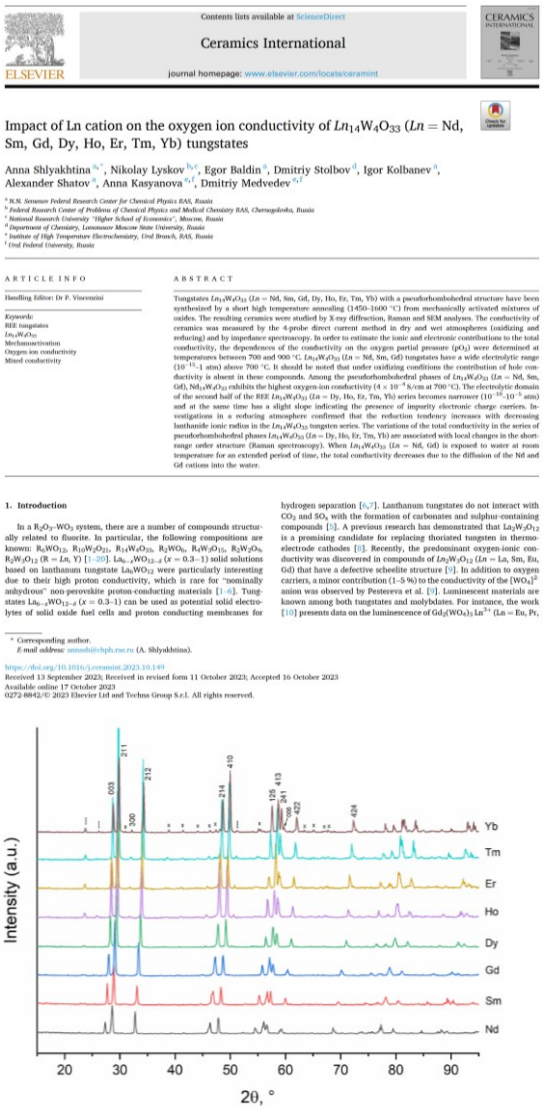
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Impact of Ln cation on the oxygen ion conductivity of $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb) tungstates

- *Anna Shlyakhtina*
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- *Anna Kasyanova*
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- *REE tungstates*
- *$Ln_{14}W_4O_{33}$*
- *Mechanoactivation*
- *Oxygen-ion conductivity*
- *Mixed conductivity*

Tungstates $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb) with a pseudorhombohedral structure have been synthesized by a short high temperature annealing (1450–1600 °C) from mechanically activated mixtures of oxides. The resulting ceramics were studied by X-ray diffraction, Raman and SEM analyses. The conductivity of ceramics was measured by the 4-probe direct current method in dry and wet atmospheres (oxidizing and reducing) and by impedance spectroscopy. In order to estimate the ionic and electronic contributions to the total conductivity, the dependences of the conductivity on the oxygen partial pressure (pO_2) were determined at temperatures between 700 and 900 °C. $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd) tungstates have a wide electrolytic range (10^{-15}–1 atm) above 700 °C. It should be noted that under oxidizing conditions the contribution of hole conductivity is absent in these compounds. Among the pseudorhombohedral phases of $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd), $Nd_{14}W_4O_{33}$ exhibits the highest oxygen-ion conductivity (4×10^{-4} S/cm at 700 °C). The electrolytic domain of the second half of the REE $Ln_{14}W_4O_{33}$ (Ln = Dy, Ho, Er, Tm, Yb) series becomes narrower (10^{-10}–10^{-5} atm) and at the same time has a slight slope indicating the presence of impurity electronic charge carriers. Investigations in a reducing atmosphere confirmed that the reduction tendency increases with decreasing lanthanide ionic radius in the $Ln_{14}W_4O_{33}$ tungsten series. The variations of the total conductivity in the series of pseudorhombohedral phases $Ln_{14}W_4O_{33}$ (Ln = Dy, Ho, Er, Tm, Yb) are associated with local changes in the short-range order structure (Raman spectroscopy). When $Ln_{14}W_4O_{33}$ (Ln = Nd, Gd) is exposed to water at room temperature for an extended period of time, the total conductivity decreases due to the diffusion of the Nd and Gd cations into the water.



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Impact of Ln cation on the oxygen ion conductivity of $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb) tungstates

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ABSTRACT

Tungstates $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb) with a pseudorhombohedral structure have been synthesized by a short high temperature annealing (1450–1600 °C) from mechanically activated mixtures of oxides. The resulting ceramics were studied by X-ray diffraction, Raman and SEM analyses. The conductivity of ceramics was measured by the 4-probe direct current method in dry and wet atmospheres (oxidizing and reducing) and by impedance spectroscopy. In order to estimate the ionic and electronic contributions to the total conductivity, the dependences of the conductivity on the oxygen partial pressure (pO_2) were determined at temperatures between 700 and 900 °C. $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd) tungstates have a wide electrolytic range (10^{-15}–1 atm) above 700 °C. It should be noted that under oxidizing conditions the contribution of hole conductivity is absent in these compounds. Among the pseudorhombohedral phases of $Ln_{14}W_4O_{33}$ (Ln = Nd, Sm, Gd), $Nd_{14}W_4O_{33}$ exhibits the highest oxygen-ion conductivity (4×10^{-4} S/cm at 700 °C). The electrolytic domain of the second half of the REE $Ln_{14}W_4O_{33}$ (Ln = Dy, Ho, Er, Tm, Yb) series becomes narrower (10^{-10}–10^{-5} atm) and at the same time has a slight slope indicating the presence of impurity electronic charge carriers. Investigations in a reducing atmosphere confirmed that the reduction tendency increases with decreasing lanthanide ionic radius in the $Ln_{14}W_4O_{33}$ tungsten series. The variations of the total conductivity in the series of pseudorhombohedral phases $Ln_{14}W_4O_{33}$ (Ln = Dy, Ho, Er, Tm, Yb) are associated with local changes in the short-range order structure (Raman spectroscopy). When $Ln_{14}W_4O_{33}$ (Ln = Nd, Gd) is exposed to water at room temperature for an extended period of time, the total conductivity decreases due to the diffusion of the Nd and Gd cations into the water.

1. Introduction

In a R_2O_3–WO_3 system, there are a number of compounds structurally related to fluorite. In particular, the following compositions are known: R_6WO_{12}, $R_{10}W_2O_{21}$, $R_{14}W_4O_{33}$, $R_{16}W_2O_{27}$, $R_{18}W_2O_{33}$, R_2WO_6, $R_2W_2O_9$, $R_2W_3O_{12}$ (R = Ln, Y) [1–20]. $Ln_{6-x}WO_{12-x}$ (x = 0.3–1) solid solutions based on lanthanum tungstate La_6WO_{12} were particularly interesting due to their high proton conductivity, which is rare for "nominally anhydrous" non-perovskite proton-conducting materials [1–6]. Tungstates $Ln_{6-x}WO_{12-x}$ (x = 0.3–1) can be used as potential solid electrolytes of solid oxide fuel cells and proton conducting membranes for hydrogen separation [6,7]. Lanthanum tungstates do not interact with CO_2 and SO_x with the formation of carbonates and sulphur-containing compounds [8]. A previous research has demonstrated that $La_2W_2O_{12}$ is a promising candidate for replacing thoriated tungsten in thermo-electrode cathodes [9]. Recently, the predominant oxygen-ionic conductivity was discovered in compounds of $Ln_2W_2O_{12}$ (Ln = La, Sm, Eu, Gd) that have a defective scheelite structure [9]. In addition to oxygen carriers, a minor contribution (1–5 %) to the conductivity of the $[WO_4]^{2-}$ anion was observed by Pesterева et al. [9]. Luminescent materials are known among both tungstates and molybdates. For instance, the work [10] presents data on the luminescence of $Gd_2(WO_4)_3:Ln^{3+}$ (Ln = Eu, Pr,

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Insight into grain and grain-boundary transport of proton-conducting ceramics: A case report of $BaSn_{0.8}Y_{0.2}O_{3-\delta}$.

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- *D.A. Osinkin*
- *B. Py*
- *A. Maradesa*
- *F. Ciucci*
- *D.A. Medvedev*

- *distribution of relaxation times*
- *electrochemical impedance spectroscopy*
- *grain and grain-boundary transport*
- *proton-conducing electrolytes*

Proton-conducting ceramic electrolytes offer great potential for the development of low- and intermediate-temperature solid oxide electrochemical devices, e.g., fuel cells and electrolyzers. However, the electrolyte constitutes the main bottleneck in such devices, especially at reduced temperatures, determining their overall performance and efficiency. Herein, for the first time the low-temperature transport properties of $BaSn_{0.8}Y_{0.2}O_{3-\delta}$ as a representative of proton-conducting materials are investigated. The attention is focussed on grain and grain boundary conductivity of this ceramic material over a wide range of experimental conditions, including temperatures of 400–550 °C, oxygen partial pressures of 10^{-22}–0.21 atm, and water vapor partial pressures of 10^{-5}-0.03 atm. After analyzing $BaSn_{0.8}Y_{0.2}O_{3-\delta}$ with electrochemical impedance spectroscopy under these experimental conditions, the distribution of relaxation times is leveraged to evaluate the resistance, capacitance, and frequency of each electrolytic process. The data show that the BSY ceramic, prepared with CuO as a sintering additive, is characterized by three distinct processes: one is due to grain response, and two others are understood to be related to the responses of the pure and CuO-covered grain boundaries. Therefore, this work opens a new path for the analysis of ionic, including protonic, transport along grains and grain boundaries.



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Insight into Grain and Grain-Boundary Transport of Proton-Conducting Ceramics: A Case Report of $BaSn_{0.8}Y_{0.2}O_{3-\delta}$

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1. Introduction

Proton-conducting oxides are interesting research objects due to their proton conduction characteristics, which co-exist with oxygen-ionic transport. The distinctiveness of these oxides consists in the fact that, in contrast to low-temperature proton-conducting materials, the proton charge carriers are not original elements of a crystal (or molecular) structure.[1–3] Most often, protons ($OH_O^{\bullet}$) are generated as a consequence of the dissociative adsorption of oxygen vacancies ($V_O^{\bullet\bullet}$), which originate via an acceptor-doping mechanism:

$$H_2O + V_O^{\bullet\bullet} + O_O^{\times} \rightleftarrows 2OH_O^{\bullet} \quad (1)$$

Due to the higher mobility of proton defects relative to oxygen vacancies (or oxygen ions), such complex oxides often exhibit high ionic conductivity, representing attractive characteristics in many applications. In particular, proton conductors have been used as electrolytes in low- (below 500 °C) and intermediate- (500–700 °C) temperature protonic ceramic fuel cells (PCFCs) and electrolysis cells (PCECs).[4–7] which are derivatives of the traditional solid oxide fuel cells (SOFCs) and electrolysis cells (SOECs) based on oxygen-conducting electrolytes. The lower operating temperatures permit robust stability of the electrochemical devices, which explains their simultaneous high efficiency and performance.[8–11]

Proton-conducting electrolytes are generally polycrystalline materials, thus possessing grains and grain boundaries. The transport mechanism through the grains and grain boundaries of such oxide materials differs due to the distinct chemistry of the grains and grain boundaries, including the presence of space charge layers in grains, local crystal structure misalignments, and different defect compositions.[13–17] However, both parameters can be purposefully altered by means of rational chemical design. The grain (bulk) transport can be regulated by tailoring the crystal structure and altering the chemical properties of defect formation and interaction. On the other hand, the application of novel technological solutions can affect grain boundary

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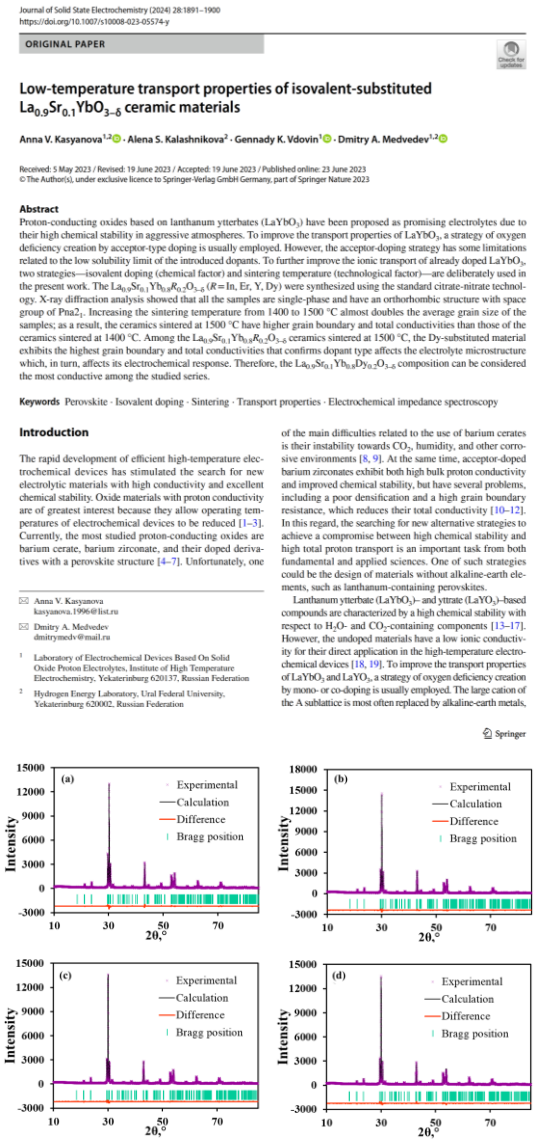
2024

Low-temperature transport properties of isovalent-substituted $La_{0.9}Sr_{0.1}YbO_{3-\delta}$ ceramic materials.

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- *A.S. Kalashnikova*
- *G.K. Vdovin*
- *D.A. Medvedev*

- *Perovskite*
- *Isovalent doping*
- *Sintering*
- *Transport properties*
- *Electrochemical impedance spectroscopy*

Proton-conducting oxides based on lanthanum ytterbates ($LaYbO_3$) have been proposed as promising electrolytes due to their high chemical stability in aggressive atmospheres. To improve the transport properties of $LaYbO_3$, a strategy of oxygen deficiency creation by acceptor-type doping is usually employed. However, the acceptor-doping strategy has some limitations related to the low solubility limit of the introduced dopants. To further improve the ionic transport of already doped $LaYbO_3$, two strategies—isovalent doping (chemical factor) and sintering temperature (technological factor)—are deliberately used in the present work. The $La_{0.9}Sr_{0.1}Yb_{0.8}R_{0.2}O_{3-\delta}$ (R = In, Er, Y, Dy) were synthesized using the standard citrate-nitrate technology. X-ray diffraction analysis showed that all the samples are single-phase and have an orthorhombic structure with space group of $Pna2_1$. Increasing the sintering temperature from 1400 to 1500 °C almost doubles the average grain size of the samples; as a result, the ceramics sintered at 1500 °C have higher grain boundary and total conductivities than those of the ceramics sintered at 1400 °C. Among the $La_{0.9}Sr_{0.1}Yb_{0.8}R_{0.2}O_{3-\delta}$ ceramics sintered at 1500 °C, the Dy-substituted material exhibits the highest grain boundary and total conductivities that confirms dopant type affects the electrolyte microstructure which, in turn, affects its electrochemical response. Therefore, the $La_{0.9}Sr_{0.1}Yb_{0.8}Dy_{0.2}O_{3-\delta}$ composition can be considered the most conductive among the studied series.



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ORIGINAL PAPER

Low-temperature transport properties of isovalent-substituted $La_{0.9}Sr_{0.1}YbO_{3-\delta}$ ceramic materials

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Abstract
Proton-conducting oxides based on lanthanum ytterbates ($LaYbO_3$) have been proposed as promising electrolytes due to their high chemical stability in aggressive atmospheres. To improve the transport properties of $LaYbO_3$, a strategy of oxygen deficiency creation by acceptor-type doping is usually employed. However, the acceptor-doping strategy has some limitations related to the low solubility limit of the introduced dopants. To further improve the ionic transport of already doped $LaYbO_3$, two strategies—isovalent doping (chemical factor) and sintering temperature (technological factor)—are deliberately used in the present work. The $La_{0.9}Sr_{0.1}Yb_{0.8}R_{0.2}O_{3-\delta}$ (R = In, Er, Y, Dy) were synthesized using the standard citrate-nitrate technology. X-ray diffraction analysis showed that all the samples are single-phase and have an orthorhombic structure with space group of $Pna2_1$. Increasing the sintering temperature from 1400 to 1500 °C almost doubles the average grain size of the samples; as a result, the ceramics sintered at 1500 °C have higher grain boundary and total conductivities than those of the ceramics sintered at 1400 °C. Among the $La_{0.9}Sr_{0.1}Yb_{0.8}R_{0.2}O_{3-\delta}$ ceramics sintered at 1500 °C, the Dy-substituted material exhibits the highest grain boundary and total conductivities that confirms dopant type affects the electrolyte microstructure which, in turn, affects its electrochemical response. Therefore, the $La_{0.9}Sr_{0.1}Yb_{0.8}Dy_{0.2}O_{3-\delta}$ composition can be considered the most conductive among the studied series.

Keywords Perovskite · Isovalent doping · Sintering · Transport properties · Electrochemical impedance spectroscopy

Introduction

The rapid development of efficient high-temperature electrochemical devices has stimulated the search for new electrolytic materials with high conductivity and excellent chemical stability. Oxide materials with proton conductivity are of greatest interest because they allow operating temperatures of electrochemical devices to be reduced [1–3]. Currently, the most studied proton-conducting oxides are barium cerate, barium zirconate, and their doped derivatives with a perovskite structure [4–7]. Unfortunately, one of the main difficulties related to the use of barium cerates is their instability towards CO_2, humidity, and other corrosive environments [8, 9]. At the same time, acceptor-doped barium zirconates exhibit both high bulk proton conductivity and improved chemical stability, but have several problems, including a poor densification and a high grain boundary resistance, which reduces their total conductivity [10–12]. In this regard, the searching for new alternative strategies to achieve a compromise between high chemical stability and high total proton transport is an important task from both fundamental and applied sciences. One of such strategies could be the design of materials without alkaline-earth elements, such as lanthanum-containing perovskites.

Lanthanum ytterbate ($LaYbO_3$)- and yttrate ($LaYO_3$)-based compounds are characterized by a high chemical stability with respect to H_2O- and CO_2-containing components [13–17]. However, the undoped materials have a low ionic conductivity for their direct application in the high-temperature electrochemical devices [18, 19]. To improve the transport properties of $LaYbO_3$ and $LaYO_3$, a strategy of oxygen deficiency creation by mono- or co-doping is usually employed. The large cation of the A sublattice is most often replaced by alkaline-earth metals,

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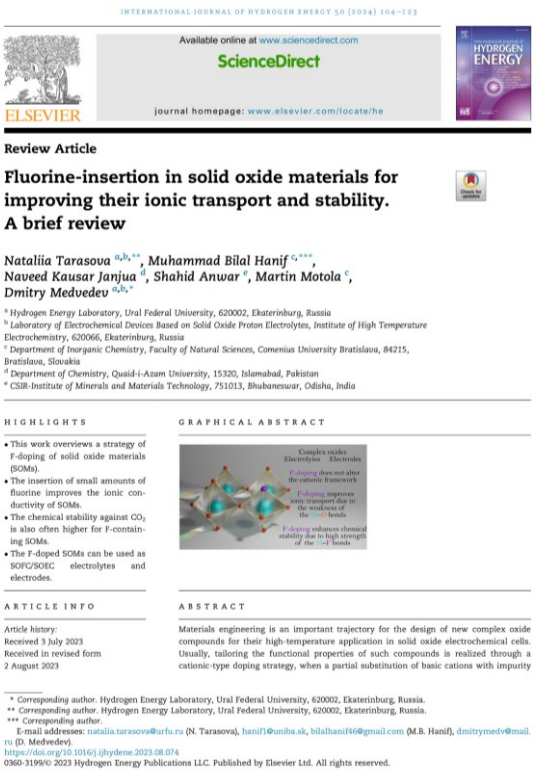
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Fluorine-insertion in solid oxide materials for improving their ionic transport and stability. A brief review.

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- *M.B. Hanif*
- *N.K. Janjua*
- *S. Anwar*
- *M. Motola*
- *D. Medvedev*

- *SOFCs*
- *SOECs*
- *Electrolyte*
- *Electrode*
- *Fluorione*
- *F-doping*
- *F-insertion*

Materials engineering is an important trajectory for the design of new complex oxide compounds for their high-temperature application in solid oxide electrochemical cells. Usually, tailoring the functional properties of such compounds is realized through a cationic-type doping strategy, when a partial substitution of basic cations with impurity ions is performed. Typically, such a doping improves some properties, but deteriorates others due to significant changes in the cationic framework of a crystal. Anionic-type doping is an alternative way to leave the cationic sites unchanged, which may be suitable for achieving a compromise between a variety of properties. In this brief review, we summarize the existing data devoted to the F-doping (or F-insertion) of solid oxide electrolyte and electrode materials. In most cases, the F-doping improves the chemical stability of compounds and their ionic transport properties. Possible reasons responsible for this improvement are briefly discussed. In addition to highlighting these advantages, possible drawbacks are also listed to stimulate further research activities on this problem.



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Review Article

Fluorine-insertion in solid oxide materials for improving their ionic transport and stability. A brief review

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HIGHLIGHTS

- This work overviews a strategy of F-doping of solid oxide materials (SOMs).
- The insertion of small amounts of fluorine improves the ionic conductivity of SOMs.
- The chemical stability against CO_2 is also often higher for F-containing SOMs.
- The F-doped SOMs can be used as SOFC/SOEC electrolytes and electrodes.

GRAPHICAL ABSTRACT

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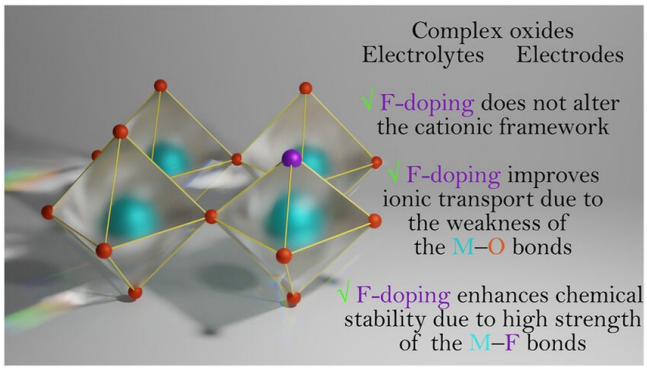
ABSTRACT

Materials engineering is an important trajectory for the design of new complex oxide compounds for their high-temperature application in solid oxide electrochemical cells. Usually, tailoring the functional properties of such compounds is realized through a cationic-type doping strategy, when a partial substitution of basic cations with impurity

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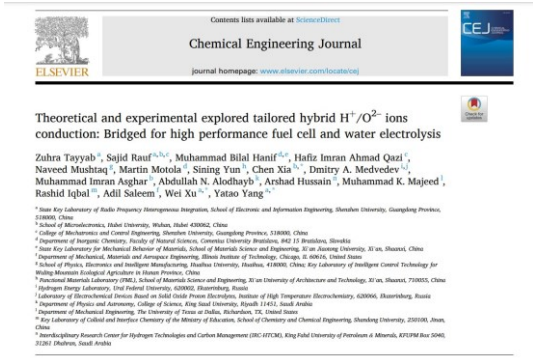
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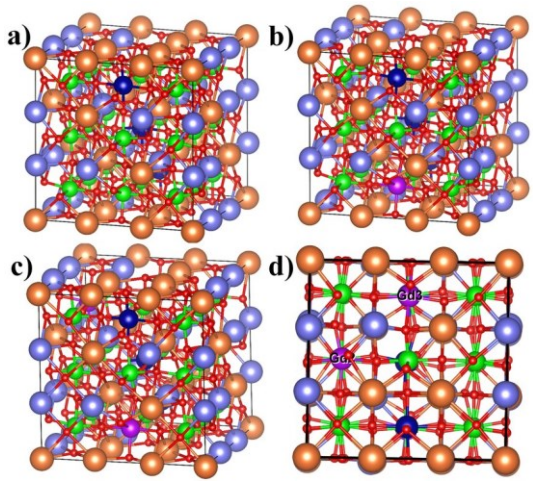
2024

Theoretical and experimental explored tailored hybrid H^+/O^{2-} ions conduction: Bridged for high performance fuel cell and water electrolysis

- Z. Tayyab
- S. Rauf
- M.B. Hanif
- HI. A. Qazi
- N. Mushtaq
- M. Motola
- S. Yun
- C. Xia
- D.A. Medvedev
- M. I. Asghar
- A. Alodhab
- A. Hussain
- MK. Majeed
- R. Iqbal
- A. Saleem
- W. Xu
- Y. Yang

- *SOFCs*
- *SOECs*
- *Electrolyte*
- *Electrode*
- *Fluorione*
- *F-doping*
- *F-insertion*





A hybrid proton and oxide ion (H+/O2–) conducting electrolyte transports ions in multiple ways can operate at lower operating temperatures than a pure oxide ion conductor in solid oxide fuel cells (SOFCs). Here, a novel hybrid H+/O2– conductor is developed based on Ba0.5Sr0.5Zr0.9Y0.1O3-δ (BSZY) by Gd3+ doping. The Ba0.5Sr0.5Zr0.9-xGdxY0.1O3-δ (x = 0, 0.05, 0.1) electrolytes are modeled to construct crystal structures by density functional theory (DFT) calculations and subsequently synthesized, followed by physicochemical characterizations. The corresponding BSZGdxY electrolyte-based SOFCs are fabricated and investigated in terms of I-V characteristics, electrochemical impedance spectra, and durable operation. It is found Gd3+doping significantly enriches the oxygen vacancies and enhance the ionic conductivity of BSZGdxY. The DFT calculations provide evidence of high oxygen vacancies formation with the optimal doping of Gd with x = 0.1. Among the three samples, the Ba0.5Sr0.5Zr0.8Gd0.1Y0.1O3-δ (BSZGd0.1Y) electrolyte exhibits the highest fuel cell power density of 805 mW cm−2, hybrid H+/O2– conductivity of 0.17 S cm−1, and stable operation for 67 h at 520 °C. Further study finds that the BSZGd0.1Y electrolyte-based fuel cell can be operated under water electrolysis mode, revealing a high current density of 2.37 A cm−2 under 1.5 V at 520 °C. Moreover, the impact of Gd doping is studied in terms of electronic structure and energy bands investigated with the help of DFT calculations and the Schottky junction effect of the cell for electron blocking is investigated. This work demonstrates an efficient way to explore hybrid H+/O2– conduction in BSZY for high-performance SOFC and water electrolysis.

Z. Tayyab, S. Rauf, M.B. Hanif, HI. A. Qazi, N. Mushtaq, M. Motola, S. Yun, C. Xia, D.A. Medvedev, M. I. Asghar, A. Alodhab, A. Hussain, MK. Majeed, R. Iqbal, A. Saleem, W. Xu, Y. Yang. Theoretical and experimental explored tailored hybrid H^+/O^{2-} ions conduction: Bridged for high performance fuel cell and water electrolysis. Chemical Engineering Journal. 2023. V. 482. Art. 148750. 10.1016/j.cej.2024.148750

DOI Q1 IF 13.3 CS 21.7 RG CoLab

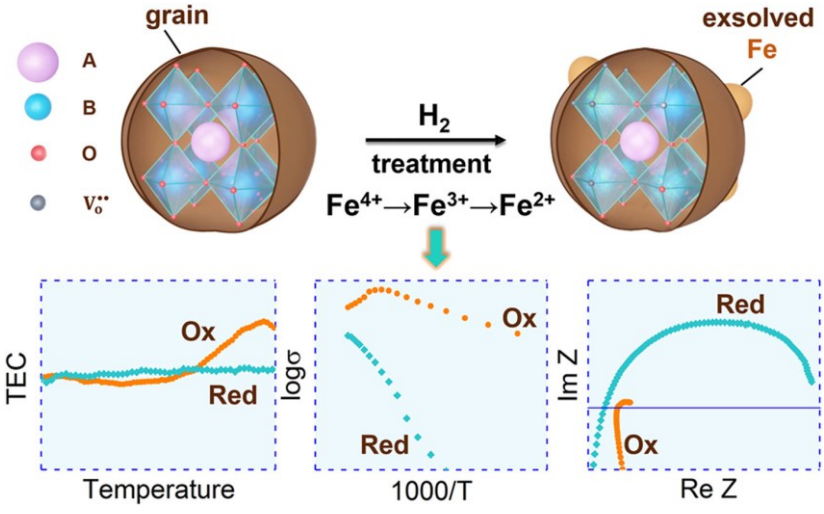
2024

Ba-containing ferrites, $Pr_{1-x}Ba_xFeO_{3-\delta}$, as symmetrical electrodes and their functional properties in both oxidizing and reducing atmospheres.

M.A. Gordeeva, A.P. Tarutin, G.K. Vdovin, D.E. Matkin, G.N. Starostin, D.A. Medvedev.

- $Pr_{1-x}Ba_xFeO_{3-\delta}$ (PBxF, x = 0.4, 0.5, 0.6) materials were synthesized and characterized.
- Functional properties of PBxF were analyzed under oxidizing and reducing conditions.
- PB0.4F exhibits the highest redox stability and lowest TEC values.
- However, the PB0.6F electrodes show the highest electrochemical activity.
- A trade-off between the functional properties is needed for real PBxF applications.

Searching for suitable materials for symmetrical solid oxide fuel cells is an essential direction in modern high-temperature electrochemistry. One promising option for symmetrical electrode materials is a family of Fe-based complex oxides, which have high mixed ionic and electronic conductivity. This study focuses on the synthesis and thorough evaluation of the $Pr_{1-x}Ba_xFeO_{3-\delta}$ (x = 0.4, 0.5, 0.6) materials as symmetrical electrodes for proton ceramic electrochemical cells. The functional properties of these phases, both in powder and ceramic forms, are investigated for the first time under oxidizing and reducing conditions. The obtained results indicate that a low Ba-content is preferable for achieving high redox stability, low thermal expansion, and high conductivity of ferrite-based perovskites. However, Ba-enriched samples exhibit the lowest polarization resistance, particularly in reducing atmospheres. This may be due to the easier exsolution of Fe-metallic particles with high electrocatalytic activity. Therefore, a certain compromise needs to be achieved considering the obtained experimental data in a complex form. This work provides a basis for designing symmetrical electrodes by offering comprehensive information on the functional properties of ferrites in both oxidizing and reducing conditions.



M.A. Gordeeva, A.P. Tarutin, G.K. Vdovin, D.E. Matkin, G.N. Starostin, D.A. Medvedev. Ba-containing ferrites, Pr1–xBaxFeO3–δ, as symmetrical electrodes and their functional properties in both oxidizing and reducing atmospheres. Ceramics International. 2024. V. 50. № 20C. P. 40417–40428. 10.1016/j.ceramint.2024.02.067

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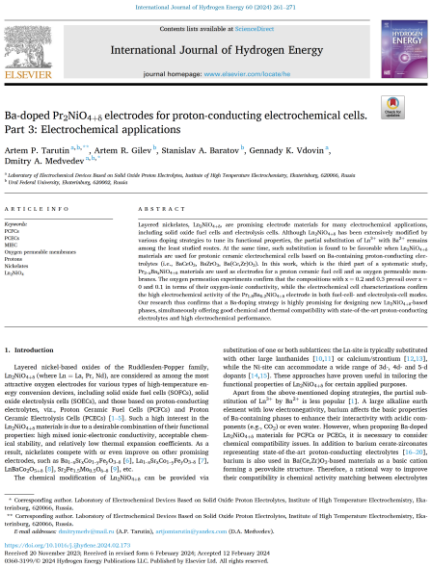
2024

Ba-doped Pr2NiO4+δ electrodes for proton-conducting electrochemical cells. Part 3: electrochemical applications.

- A.P. Tarutin
- A.R. Gilev
- S.A. Baratov
- G.K. Vdovin
- D.A. Medvedev

- $Pr_{2-x}Ba_xNiO_{4+\delta}$ (PBNx, $0 \le x \le 0.3$) materials were electrochemically characterized.
- PBNx were used as components of protonic ceramic cells and oxygen permeable membranes.
- The obtained results indicate that Ba-doping improves the ionic transport of PBNx.
- PBN0.2 and BPN0.3 can be considered as promising functional materials.

Layered nickelates, $Ln_2NiO_{4+\delta}$, are promising electrode materials for many electrochemical applications, including solid oxide fuel cells and electrolysis cells. Although $Ln_2NiO_{4+\delta}$ has been extensively modified by various doping strategies to tune its functional properties, the partial substitution of Ln^{3+} with Ba^{2+} remains among the least studied routes. At the same time, such substitution is found to be favorable when $Ln_2NiO_{4+\delta}$ materials are used for protonic ceramic electrochemical cells based on Ba-containing proton-conducting electrolytes (i.e., $BaCeO_3$, $BaZrO_3$, $Ba(Ce,Zr)O_3$). In this work, which is the third part of a systematic study, $Pr_{2-x}Ba_xNiO_{4+\delta}$ materials are used as electrodes for a proton ceramic fuel cell and as oxygen permeable membranes. The oxygen permeation experiments confirm that the compositions with x = 0.2 and 0.3 prevail over x = 0 and 0.1 in terms of their oxygen-ionic conductivity, while the electrochemical cell characterizations confirm the high electrochemical activity of the $Pr_{1.8}Ba_{0.2}NiO_{4+\delta}$ electrode in both fuel-cell- and electrolysis-cell modes. Our research thus confirms that a Ba-doping strategy is highly promising for designing new $Ln_2NiO_{4+\delta}$-based phases, simultaneously offering good chemical and thermal compatibility with state-of-the-art proton-conducting electrolytes and high electrochemical performance.


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Ba-doped $Pr_2NiO_{4+\delta}$ electrodes for proton-conducting electrochemical cells. Part 3: Electrochemical applications

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ABSTRACT

Layered nickelates, $Ln_2NiO_{4+\delta}$, are promising electrode materials for many electrochemical applications, including solid oxide fuel cells and electrolysis cells. Although $Ln_2NiO_{4+\delta}$ has been extensively modified by various doping strategies to tune its functional properties, the partial substitution of Ln^{3+} with Ba^{2+} remains among the least studied routes. At the same time, such substitution is found to be favorable when $Ln_2NiO_{4+\delta}$ materials are used for protonic ceramic electrochemical cells based on Ba-containing proton-conducting electrolytes (i.e., $BaCeO_3$, $BaZrO_3$, $Ba(Ce,Zr)O_3$). In this work, which is the third part of a systematic study, $Pr_{2-x}Ba_xNiO_{4+\delta}$ materials are used as electrodes for a proton ceramic fuel cell and as oxygen permeable membranes. The oxygen permeation experiments confirm that the compositions with x = 0.2 and 0.3 prevail over x = 0 and 0.1 in terms of their oxygen-ionic conductivity, while the electrochemical cell characterizations confirm the high electrochemical activity of the $Pr_{1.8}Ba_{0.2}NiO_{4+\delta}$ electrode in both fuel-cell- and electrolysis-cell modes. Our research thus confirms that a Ba-doping strategy is highly promising for designing new $Ln_2NiO_{4+\delta}$-based phases, simultaneously offering good chemical and thermal compatibility with state-of-the-art proton-conducting electrolytes and high electrochemical performance.

1. Introduction

Layered nickel-based oxides of the Ruddlesden-Popper family, $Ln_{n+1}Ni_nO_{3n+1}$ (where Ln = La, Pr, Nd), are considered as among the most attractive oxygen electrodes for various types of high-temperature energy conversion devices, including solid oxide fuel cells (SOFCs), solid oxide electrolysis cells (SOECs), and those based on proton-conducting electrolytes, viz., Proton Ceramic Fuel Cells (PCFCs) and Proton Ceramic Electrolysis Cells (PCECs) [1–3]. Such a high interest in the $Ln_2NiO_{4+\delta}$ materials is due to a desirable combination of their functional properties: high mixed ionic-electronic conductivity, acceptable chemical stability, and relatively low thermal expansion coefficients. As a result, nickelates compete with or even improve on other promising electrodes, such as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [4], $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [5], $LaBaCo_2O_{5+\delta}$ [6], $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [7], etc.

The chemical modification of $Ln_2NiO_{4+\delta}$ can be provided via substitution of one or both sublattices: the Ln-site is typically substituted with other large lanthanides [10,11] or calcium/strontium [12,13], while the Ni-site can accommodate a wide range of 3d-, 4d- and 5-d dopants [14,15]. These approaches have proven useful in tailoring the functional properties of $Ln_2NiO_{4+\delta}$ for certain applied purposes.

Apart from the above-mentioned doping strategies, the partial substitution of Ln^{3+} by Ba^{2+} is less popular [1]. A large alkaline earth element with low electronegativity, barium affects the basic properties of Ba-containing phases to enhance their interactivity with acidic components (e.g., CO_2) or even water. However, when preparing Ba-doped $Ln_2NiO_{4+\delta}$ materials for PCFCs or PCECs, it is necessary to consider chemical compatibility issues. In addition to barium cerate-zirconates representing state-of-the-art proton-conducting electrolytes [16–20], barium is also used in $Ba(Ce,Zr)O_3$-based materials as a basic cation forming a perovskite structure. Therefore, a rational way to improve their compatibility is chemical activity matching between electrolytes

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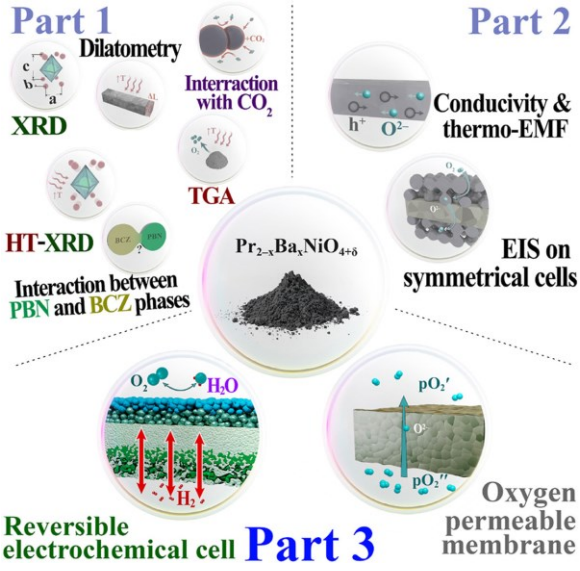
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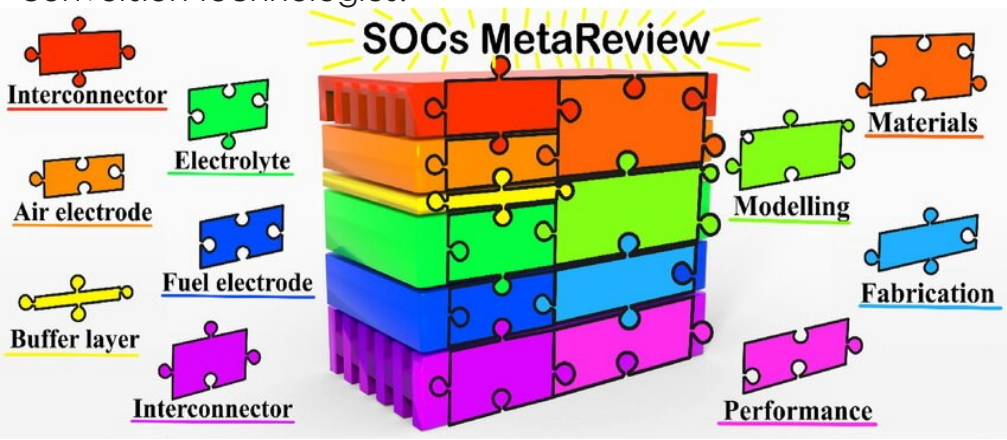
2024

Current and further trajectories in designing functional materials for solid oxide electrochemical cells: a review of other reviews

- S. Baratov
- E. Filonova
- A. Ivanova
- M.B. Hanif
- M. Irshad
- M.Z. Khan
- M. Motola
- S. Rauf
- D. Medvedev

- *SOFCs*
- *SOECs*
- *PCFCs*
- *Electrochemistry*
- *Energy conversion*
- *Hydrogen energy*
- *Carbon neutrality*

Complex oxides are an important class of materials with enormous potential for electrochemical applications. Depending on their composition and structure, such complex oxides can exhibit either a single conductivity (oxygen-ionic or protonic, or n-type, or p-type electronic) or a combination thereof generating distinct dual-conducting or even triple-conducting materials. These properties enable their use as diverse functional materials for solid oxide fuel cells, solid oxide electrolysis cells, permeable membranes and gas sensors. The literature review shows that the field of solid oxide materials and related electrochemical cells has a significant level of research engagement, with over 8,000 publications published since 2020. The manual analysis of such a large volume of material is challenging. However, by examining the review articles, it is possible to identify key patterns, recent achievements, prospects, and remaining obstacles. To perform such an analysis, the present article provides, for the first time, a comprehensive summary of previous review publications that have been published since 2020, with a special focus on solid oxide materials and electrochemical systems. Thus, this study provides an important reference for researchers specializing in the fields of solid state ionics, high-temperature electrochemistry, and energy conversion technologies.




Journal of Energy Chemistry

Current and further trajectories in designing functional materials for solid oxide electrochemical cells: A review of other reviews

S. Baratov, E. Filonova, A. Ivanova, M.B. Hanif, M. Irshad, M.Z. Khan, M. Motola, S. Rauf, D. Medvedev. Current and further trajectories in designing functional materials for solid oxide electrochemical cells: a review of other reviews. Journal of Energy Chemistry. 2024. V. 94. P. 302–331. 10.1016/j.jechem.2024.02.047

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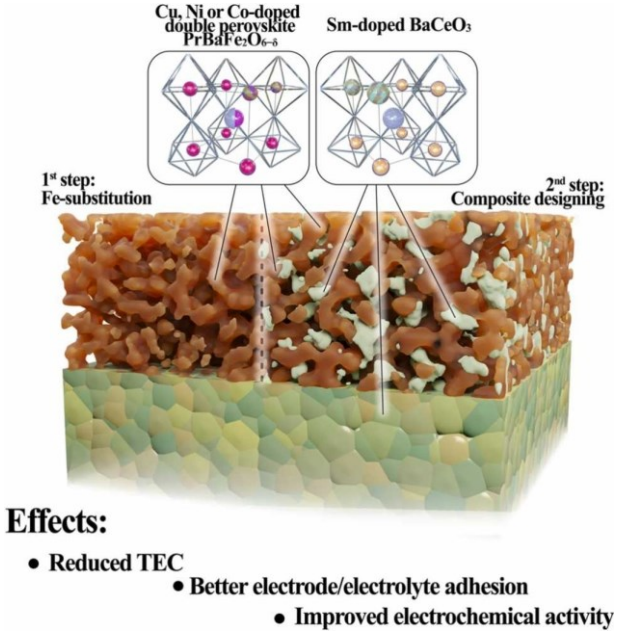
2024

PrBaFe2O6–δ-based composites as promising electrode materials for protonic ceramic electrochemical cells

- D.E. Matkin
- M.A. Gordeeva
- A.P. Tarutin
- D.A. Medvedev

- *Homogeneous and heterogeneous doping strategies were used for PrBaFe2O6–δ (PBF).*
- *A partial substitution of iron-ions in PBF with nickel, cobalt or copper is made.*
- *The Cu- and Ni-containing PBF samples exhibit better conductivity and reduced TECs.*
- *Further modification of doped PBF is performed to create composite materials.*
- *The as-prepared composites show acceptable polarization resistance values.*

$PrBaFe_2O_{6-\delta}$ (PBF) is considered as a promising material for mixed ionic-electronic conductors used in high-temperature applications. In the present work, PBF was used as a basis for two chemical modification approaches, including doping with cobalt, nickel and copper, as well as composite design with the addition of a $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ phase. The single-phase and composite materials were successfully prepared and characterized in terms of their functional properties. The two approaches were found to synergistically affect the functional properties of PBF, allowing a trade-off between thermomechanical and transport properties to be achieved. As a result, the prepared 70 wt% $PrBaFe_{1.9}M_{0.1}O_{6-\delta}$ (M = Co, Ni, Cu) + 30 wt% $BaCe_{0.8}Sm_{0.2}O_{3-\delta}$ composites exhibit acceptable electrochemical activity in the intermediate-temperature range. The best electrochemical activity was found for the sample with M = Cu, whose polarization resistance at 700 °C reaches 1.7 Ω cm^2. Therefore, the designed PBF-based composites can be considered as promising electrode materials for solid oxide fuel cell applications.



D.E. Matkin, M.A. Gordeeva, A.P. Tarutin, D.A. Medvedev. PrBaFe2O6–δ-based composites as promising electrode materials for protonic ceramic electrochemical cells. Journal of the European Ceramic Society. 2024. V. 44. № 10. P. 5782–5793. 10.1016/j.jeurceramsoc.2024.03.052

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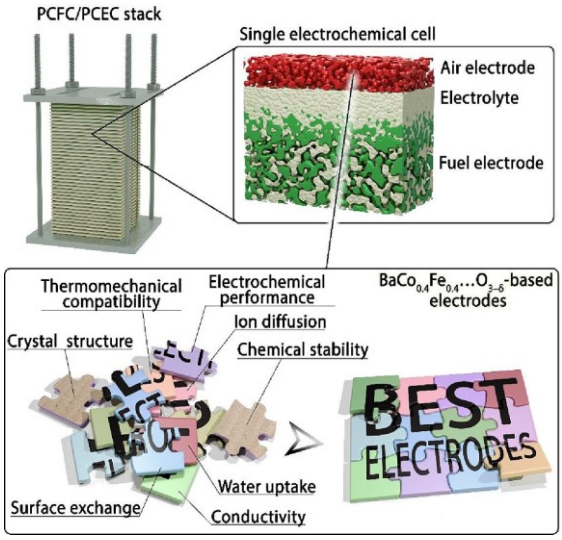
2024

Why do $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$-derived complex oxides become one of the most promising electrodes for protonic ceramic electrochemical cells? An explanatory review.

- L.R. Tarutina
- M.A. Gordeeva
- D.E. Matkin
- M.T. Akopian
- G.N. Starostin
- A.V. Kasyanova
- A.P. Tarutin
- N.A. Danilov
- I.A. Starostina
- D.A. Medvedev
- Z. Shao.

- *This review focuses on BaCe0.4Fe0.4Zr0.1Y0.1O3–δ (BCFZY) and its doped materials.*
- *BCFZY represents a basis for designing high-performance ORR and OER electrodes.*
- *Origin and doped BCFZY electrodes can be used in SOFCs, SOECs, PCFCs, and PCECs.*
- *Owing to triple-conducting nature, BCFZY is promising for protonic ceramic cells.*

Efficient energy conversion through the use of fuel and electrolysis cells is crucial for addressing the challenges posed by hydrogen energy and carbon neutrality initiatives. Solid oxide electrochemical cells, which are based on proton-conducting electrolytes (known as protonic ceramic fuel cells (PCFCs) and electrolysis cells (PCECs)), are a viable solution due to their ability to achieve high performance and efficiency at reduced operating temperatures, below 600 °C. However, electrode kinetics become sluggish at low- and intermediate-temperature ranges, necessitating the search for new electrode materials with high electrochemical and electrocatalytic activity towards oxygen reduction and oxygen evolution reactions. While a wide range of single-phase and composite materials have been proposed as PCFC/PCEC electrodes, determining the optimal composition is often challenging due to the complex interplay of functional properties. $BaCo_{0.4}Fe_{0.4}Zr_{0.2}O_{3-\delta}$ (BCFZ), $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$ (BCFZY), along with their derived compositions, are considered as highly promising oxygen electrodes for electrochemical cells with proton-conducting electrolytes. These materials offer unique advantages over widely studied materials, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (labeled as LSCF), $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (BSCF), $PrBa_{1.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{6-\delta}$ (PBSCF), and $Ln_2NiO_{4+\delta}$ (LNO). The present review discusses why BCFZ, BCFZY, and their doped compositions have garnered increased attention from both fundamental and applied perspectives.



L.R. Tarutina, M.A. Gordeeva, D.E. Matkin, M.T. Akopian, G.N. Starostin, A.V. Kasyanova, A.P. Tarutin, N.A. Danilov, I.A. Starostina, D.A. Medvedev, Z. Shao. Why do $BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-\delta}$-derived complex oxides become one of the most promising electrodes for protonic ceramic electrochemical cells? An explanatory review. Chemical Engineering Journal. 2024. V. 490. Art. 151615. 10.1016/j.cej.2024.151615

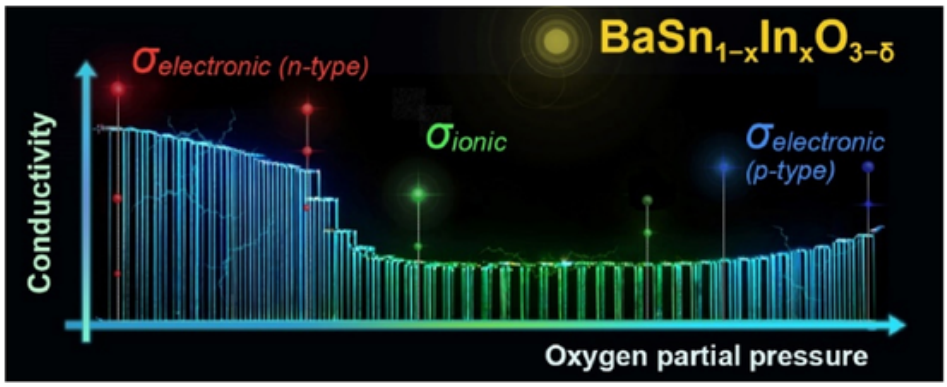
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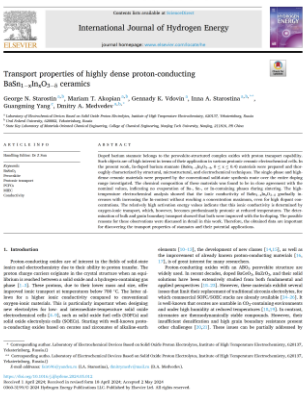
2024

Transport properties of highly dense proton-conducting $BaSn_{1-x}In_xO_{3-\delta}$ ceramics.

- G.N. Starostin
- M.T. Akopian
- G.K. Vdovin
- I.A. Starostina
- G. Yang
- D.A. Medvedev

- *In-doped BaSnO3 materials (BaSn1−xInxO3−δ, 0 ≤ x ≤ 0.4) were successfully prepared.*
- *Single-phase and high-dense ceramics were prepared for all In-concentration.*
- *Electrical properties of BaSn1−xInxO3−δ were comprehensively studied at 200–900 °C.*
- *Ionic conductivity of BaSn1−xInxO3−δ continuously increases with In-doping.*
- *BaSn1−xInxO3−δ are MIEC materials in both oxidizing and reducing atmospheres.*





Doped barium stannate belongs to the perovskite-structured complex oxides with proton transport capability. Such objects are of high interest in terms of their application in various protonic ceramic electrochemical cells. In the present work, In-doped barium stannate ($BaSn_{1-x}In_xO_{3-\delta}$, $0 \le x \le 0.4$) materials were prepared and thoroughly characterized by structural, microstructural, and electrochemical techniques. The single-phase and high-dense ceramic materials were prepared by the conventional solid-state synthesis route over the entire doping range investigated. The chemical composition of these materials was found to be in close agreement with the nominal values, indicating no evaporation of Ba-, Sn-, or In-containing phases during sintering. The high-temperature electrochemical analysis showed that the ionic conductivity of $BaSn_{1-x}In_xO_{3-\delta}$ gradually increases with increasing the In-content without reaching a concentration maximum, even for high dopant concentrations. The relatively high activation energy values indicate that this ionic conductivity is determined by oxygen-ionic transport, which, however, becomes predominantly protonic at reduced temperatures. The determination of bulk and grain boundary transport showed that both were improved with the In-doping. The possible reasons for these observations were discussed in detail in this work. Therefore, the obtained data are important for discovering the transport properties of stannates and their potential applications.

G.N. Starostin, M.T. Akopian, G.K. Vdovin, I.A. Starostina, G. Yang, D.A. Medvedev. Transport properties of highly dense proton-conducting $BaSn_{1-x}In_xO_{3-\delta}$ ceramics. International Journal of Hydrogen Energy. 2024. V. 69. P. 306–316. 10.1016/j.ijhydene.2024.05.012

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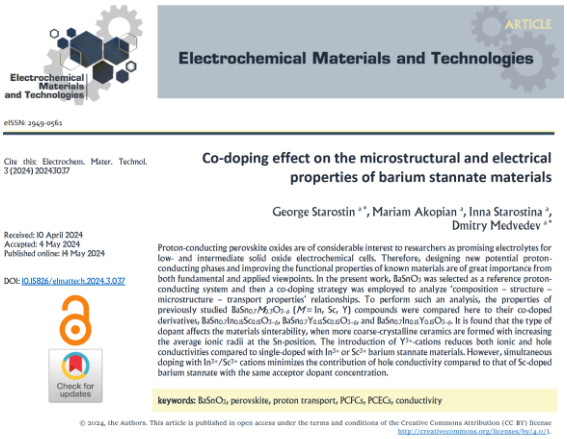
2024

Co-doping effect on the microstructural and electrical properties of barium stannate materials

- G.N. Starostin
- M.T. Akopian
- I.A. Starostina
- D.A. Medvedev

- *BaSnO3*
- *perovskite*
- *proton transport*
- *PCFCs*
- *PCECs*
- *conductivity*

Proton-conducting perovskite oxides are of considerable interest to researchers as promising electrolytes for low- and intermediate solid oxide electrochemical cells. Therefore, designing new potential proton-conducting phases and improving the functional properties of known materials are of great importance from both fundamental and applied viewpoints. In the present work, $BaSnO_3$ was selected as a reference proton-conducting system and then a co-doping strategy was employed to analyze 'composition – structure – microstructure – transport properties' relationships. To perform such an analysis, the properties of previously studied $BaSn_{0.7}M_{0.3}O_{3-\delta}$ (M = In, Sc, Y) compounds were compared here to their co-doped derivatives, $BaSn_{0.7}In_{0.15}Sc_{0.15}O_{3-\delta}$, $BaSn_{0.7}Y_{0.15}Sc_{0.15}O_{3-\delta}$, and $BaSn_{0.7}In_{0.15}Y_{0.15}O_{3-\delta}$. It is found that the type of dopant affects the materials sinterability, when more coarse-crystalline ceramics are formed with increasing the average ionic radii at the Sn-position. The introduction of Y^{3+}-cations reduces both ionic and hole conductivities compared to single-doped with In^{3+} or Sc^{3+} barium stannate materials. However, simultaneous doping with In^{3+}/Sc^{3+} cations minimizes the contribution of hole conductivity compared to that of Sc-doped barium stannate with the same acceptor dopant concentration.



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Co-doping effect on the microstructural and electrical properties of barium stannate materials

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Proton-conducting perovskite oxides are of considerable interest to researchers as promising electrolytes for low- and intermediate solid oxide electrochemical cells. Therefore, designing new potential proton-conducting phases and improving the functional properties of known materials are of great importance from both fundamental and applied viewpoints. In the present work, $BaSnO_3$ was selected as a reference proton-conducting system and then a co-doping strategy was employed to analyze 'composition – structure – microstructure – transport properties' relationships. To perform such an analysis, the properties of previously studied $BaSn_{0.7}M_{0.3}O_{3-\delta}$ (M = In, Sc, Y) compounds were compared here to their co-doped derivatives, $BaSn_{0.7}In_{0.15}Sc_{0.15}O_{3-\delta}$, $BaSn_{0.7}Y_{0.15}Sc_{0.15}O_{3-\delta}$, and $BaSn_{0.7}In_{0.15}Y_{0.15}O_{3-\delta}$. It is found that the type of dopant affects the materials sinterability, when more coarse-crystalline ceramics are formed with increasing the average ionic radii at the Sn-position. The introduction of Y^{3+}-cations reduces both ionic and hole conductivities compared to single-doped with In^{3+} or Sc^{3+} barium stannate materials. However, simultaneous doping with In^{3+}/Sc^{3+} cations minimizes the contribution of hole conductivity compared to that of Sc-doped barium stannate with the same acceptor dopant concentration.

keywords: $BaSnO_3$, perovskite, proton transport, $PCFC_s$, $PCEC_s$, conductivity

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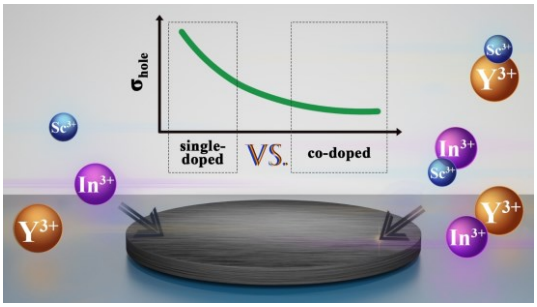
I. Introduction

Hydrogen energy is a promising direction in the development of alternative energy sources that meets the requirements of environmental friendliness and renewability [1, 2]. One of the key devices for hydrogen energy solutions are solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs). These are electrochemical devices for direct conversion of chemical energy of fuel into electricity and vice versa, being attractive for a wide range of applications, including stationary and mobile power supplies [3, 4]. In addition, SOECs are utilized to produce hydrogen by electrochemical splitting of water into oxygen and hydrogen when an electrical current is applied. The improvement of efficiency, operation time, and reliability of these devices can be achieved by varying the properties of their constitute functional materials, including electrolyte, cathode, anode, interconnector, and glass sealant [5, 6]. In particular, the SOFC/SOEC operating temperatures can be significantly reduced by utilizing proton-conducting electrolyte materials instead of conventional oxygen-ionic electrolytes. Proton transport has been found for many complex oxides, including perovskites, fergusonites/scheelites, braunmillerites, fluorites, apatites, mayenites, etc. [7, 8].

$BaSnO_3$-based materials are of interest due to their perovskite structure and proton conductivity [9]. Such stannates belong to a family of perovskite-related proton-conducting oxides, which is extensively studied. This family includes materials based on alkaline-earth cerates ($SrCeO_3$, $BaCeO_3$), zirconates ($CaZrO_3$, $SrZrO_3$, $BaZrO_3$), hafnates ($CaHfO_3$, $SrHfO_3$, $BaHfO_3$), and some others [10, 11]. Literature analysis reveals that the co-doping strategy is widely employed in the mentioned systems, until the design of high- or medium-entropy oxide systems [12, 13]. This is due to the fact that single-doping is often

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2024

Fundamental and technological aspects of thermochemical expansion of proton-conducting oxides: a case study of $BaSn_{1-x}Sc_xO_{3-\delta}$.

- G. Starostin
- D.S. Tsvetkov
- I.A. Starostina
- V.V. Sereda
- M. Akopyan
- D.A. Malyshkin
- I.L. Ivanov
- A. Murashkina
- A. Zuev
- D. Medvedev

This work provides insight into the thermal and chemical expansion behaviors of proton-conducting oxides, using Sc-doped BaSnO3 materials as examples. Both fundamental and applied aspects related to thermo-chemical expansion are thoroughly discussed.

Proton-conducting electrolytes (PCEs) are extensively researched materials utilized in solid oxide electrochemical cells with various operating principles. The high ionic (protonic) transport of PCEs offers superior performance of such cells at reduced temperatures (400–600 °C). However, chemical-related deformations (strains) caused by the materials' hydration/dehydration pose serious technological challenges for fabricating multilayered (cer-cer, cer-met, and cer-glass) assemblies. Therefore, studying both thermal and chemical expansions of PCEs is crucial. This work presents in-depth high-temperature characterization of Sc-doped BaSnO3 compounds (BaSn1−xScxO3−δ) in terms of their thermochemical expansion behavior. This characterization includes high-temperature X-ray diffraction and dilatometry analyses under various measuring conditions. On one hand, the collected data can serve as technological characteristics for the selection of appropriate functional materials. On the other hand, the thermochemical expansion data can be used to evaluate the thermodynamic parameters (enthalpy and entropy of hydration) and transport parameters (water chemical diffusion coefficient and chemical surface exchange constant) of PCEs. The latter was shown in the present work for the first time. This paves a new way to reveal the relationships between the composition, structure, thermochemical response, and transport properties of complex oxides capable of reversible water uptake.



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Supplementary information

Fundamental and technological aspects of thermochemical expansion of proton-conducting oxides: a case study of $BaSn_{1-x}Sc_xO_{3-\delta}$

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3 Figures

S–1

G. Starostin, D.S. Tsvetkov, I.A. Starostina, V.V. Sereda, M. Akopyan, D.A. Malyshkin, I. L. Ivanov, A. Murashkina, A. Zuev, D. Medvedev. Fundamental and technological aspects of thermochemical expansion of proton-conducting oxides: a case study of $BaSn_{1-x}Sc_xO_{3-\delta}$. Journal of Materials Chemistry A. 2024. V. 12. № 23. P. 14022–14034. 10.1039/D4TA02402H

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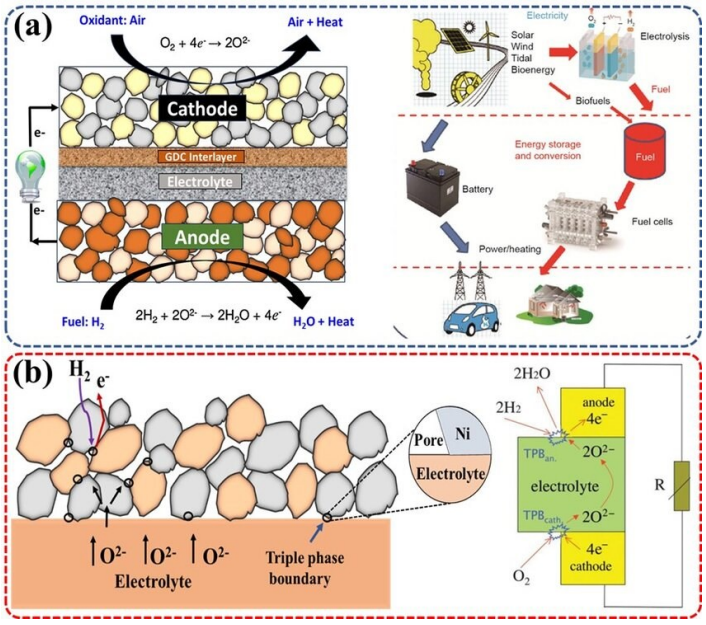
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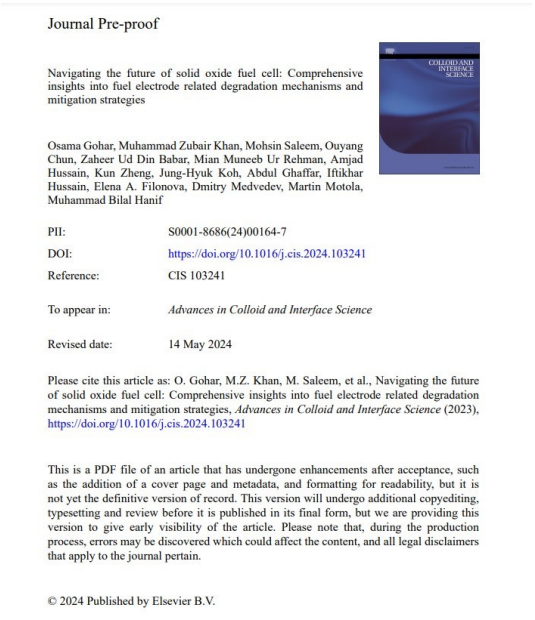
Navigating the future of solid oxide fuel cell: Comprehensive insights into fuel electrode related degradation mechanisms and mitigation strategies.

- O. Gohar
- M.Z. Khan
- M. Saleem
- O. Chun
- Z.U.D. Babar
- M.M.U. Rehman
- A. Hussain
- K. Zheng
- J.-H. Koh
- A. Ghaffar
- I. Hussain
- E. Filonova
- D. Medvedev
- M. Motola
- M.B. Hanif.

- *Anode*
- *Degradation*
- *Ni–YSZ*
- *Solid oxide fuel cell*
- *Triple phase boundaries*

Solid Oxide Fuel Cells (SOFCs) have proven to be highly efficient and one of the cleanest electrochemical energy conversion devices. However, the commercialization of this technology is hampered by issues related to electrode performance degradation. This article provides a comprehensive review of the various degradation mechanisms that affect the performance and long-term stability of the SOFC anode caused by the interplay of physical, chemical, and electrochemical processes. In SOFCs, the most used anode material is nickel-yttria stabilized zirconia (Ni–YSZ) due to its advantages of high electronic conductivity and high catalytic activity for H2 fuel. However, various factors affecting the long-term stability of the Ni–YSZ anode, such as redox cycling, carbon coking, sulfur poisoning, and the reduction of the triple phase boundary length due to Ni particle coarsening, are thoroughly investigated. In response, the article summarizes the state-of-the-art diagnostic tools and mitigation strategies aimed at improving the long-term stability of the Ni–YSZ anode.





Journal Pre-proof

Navigating the future of solid oxide fuel cell: Comprehensive insights into fuel electrode related degradation mechanisms and mitigation strategies

Osama Gohar, Muhammad Zubair Khan, Mohsin Saleem, Ouyang Chun, Zaheer Ud Din Babar, Mian Muneeb Ur Rehman, Amjad Hussain, Kun Zheng, Jung-Hyuk Koh, Abdul Ghaffar, Iftikhar Hussain, Elena A. Filonova, Dmitry Medvedev, Martin Motola, Muhammad Bilal Hanif

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2024

High-temperature gas sensors based on proton-conducting ceramic oxides.

- G. Starostin
- A.N. Volkov
- A.S. Kalyakin
- D.A. Medvedev

This review focuses on solid-state gas sensors based on proton-conducting oxides.
Potential electrolytes and sensor operating principles are presented.
Recent achievements in the use of such sensors are discussed.
Protonic ceramic sensors can be used for various electroanalytical purposes.

Proton-conducting ceramic oxides represent a promising class of materials for a range of high-temperature applications. Their excellent proton transport capabilities rival those of classical oxygen-ionic conductors, offering a basis for the design of protonic ceramic fuel cells (PCFCs) and protonic ceramic electrolysis cells (PCECs) with high performance and efficiency at temperatures ranging from 400 to 700 °C. Nevertheless, proton-conducting ceramic oxides can also be employed as electrolytes for solid-state gas sensors, which are utilized for a variety of analytical purposes, including electrochemical analysis of hydrogen-, ammonia-, oxygen-, or even carbon dioxide-containing gas mixtures. In this review, we present the recent (ten-year) achievements in the R&D field of electrochemical solid-state sensors based on proton-conducting ceramic electrolytes. Along with discussion of their operation principles, the specific functions (sensitivity, response time, selectivity) are analyzed in detail. This work therefore represents a concise overview of the application of proton-conducting electrolyte materials for *in-situ* electrochemical analysis provided at elevated temperatures.

G. Starostin, A.N. Volkov, A.S. Kalyakin, D.A. Medvedev. High-temperature gas sensors based on proton-conducting ceramic oxides. A brief review. Ceramics International. 2024. V. 50, № 20A. P. 37449–37459. 10.1016/j.ceramint.2024.07.134

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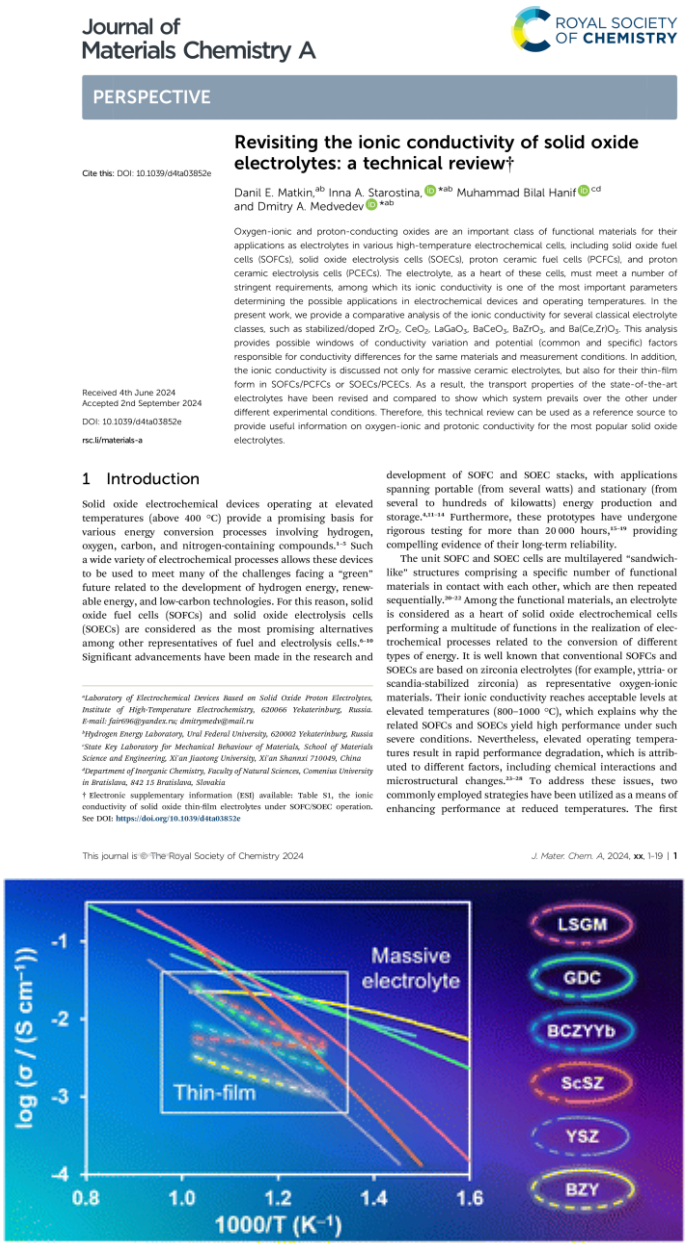
2024

Revisiting the ionic conductivity of solid oxide electrolytes: A technical review.

- D.E. Matkin
- I.A. Starostina
- M.B. Hanif
- D.A. Medvedev.

- *The present perspective revises the ionic conductivity of highly studied fluorite- and perovskite-based electrolytes for their applications in solid oxide fuel cells (SOFCs) and electrolysis cells (SOECs).*

Oxygen-ionic and proton-conducting oxides are an important class of functional materials for their applications as electrolytes in various high-temperature electrochemical cells, including solid oxide fuel cells (SOFCs), solid oxide electrolysis cells (SOECs), proton ceramic fuel cells (PCFCs), and proton ceramic electrolysis cells (PCECs). The electrolyte, as a heart of these cells, must meet a number of stringent requirements, among which its ionic conductivity is one of the most important parameters determining the possible applications in electrochemical devices and operating temperatures. In the present work, we provide a comparative analysis of the ionic conductivity for several classical electrolyte classes, such as stabilized/doped ZrO2, CeO2, LaGaO3, BaCeO3, BaZrO3, and Ba(Ce,Zr)O3. This analysis provides possible windows of conductivity variation and potential (common and specific) factors responsible for conductivity differences for the same materials and measurement conditions. In addition, the ionic conductivity is discussed not only for massive ceramic electrolytes, but also for their thin-film form in SOFCs/PCFCs or SOECs/PCECs. As a result, the transport properties of the state-of-the-art electrolytes have been revised and compared to show which system prevails over the other under different experimental conditions. Therefore, this technical review can be used as a reference source to provide useful information on oxygen-ionic and protonic conductivity for the most popular solid oxide electrolytes.



Journal of Materials Chemistry A

ROYAL SOCIETY OF CHEMISTRY

PERSPECTIVE

Revisiting the ionic conductivity of solid oxide electrolytes: a technical review†

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Danil E. Matkin,[ab] Inna A. Starostina,[ab] *Muhammad Bilal Hanif[cd] and Dmitry A. Medvedev[ab]*

Oxygen-ionic and proton-conducting oxides are an important class of functional materials for their applications as electrolytes in various high-temperature electrochemical cells, including solid oxide fuel cells (SOFCs), solid oxide electrolysis cells (SOECs), proton ceramic fuel cells (PCFCs), and proton ceramic electrolysis cells (PCECs). The electrolyte, as a heart of these cells, must meet a number of stringent requirements, among which its ionic conductivity is one of the most important parameters determining the possible applications in electrochemical devices and operating temperatures. In the present work, we provide a comparative analysis of the ionic conductivity for several classical electrolyte classes, such as stabilized/doped ZrO_2, CeO_2, $LaGaO_3$, $BaCeO_3$, $BaZrO_3$, and $Ba(Ce,Zr)O_3$. This analysis provides possible windows of conductivity variation and potential (common and specific) factors responsible for conductivity differences for the same materials and measurement conditions. In addition, the ionic conductivity is discussed not only for massive ceramic electrolytes, but also for their thin-film form in SOFCs/PCFCs or SOECs/PCECs. As a result, the transport properties of the state-of-the-art electrolytes have been revised and compared to show which system prevails over the other under different experimental conditions. Therefore, this technical review can be used as a reference source to provide useful information on oxygen-ionic and protonic conductivity for the most popular solid oxide electrolytes.

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1 Introduction

Solid oxide electrochemical devices operating at elevated temperatures (above 400 °C) provide a promising basis for various energy conversion processes involving hydrogen, oxygen, carbon, and nitrogen-containing compounds.[1–3] Such a wide variety of electrochemical processes allows these devices to be used to meet many of the challenges facing a "green" future related to the development of hydrogen energy, renewable energy, and low-carbon technologies. For this reason, solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) are considered as the most promising alternatives among other representatives of fuel and electrolysis cells.[4–10] Significant advancements have been made in the research and development of SOFC and SOEC stacks, with applications spanning portable (from several watts) and stationary (from several to hundreds of kilowatts) energy production and storage.[4,11–14] Furthermore, these prototypes have undergone rigorous testing for more than 20 000 hours,[15–19] providing compelling evidence of their long-term reliability.

The unit SOFC and SOEC cells are multilayered "sandwich-like" structures comprising a specific number of functional materials in contact with each other, which are then repeated sequentially.[20–22] Among the functional materials, an electrolyte is considered as a heart of solid oxide electrochemical cells performing a multitude of functions in the realization of electrochemical processes related to the conversion of different types of energy. It is well known that conventional SOFCs and SOECs are based on zirconia electrolytes (for example, yttria- or scandia-stabilized zirconia) as representative oxygen-ionic materials. Their ionic conductivity reaches acceptable levels at elevated temperatures (800–1000 °C), which explains why the related SOFCs and SOECs yield high performance under such severe conditions. Nevertheless, elevated operating temperatures result in rapid performance degradation, which is attributed to different factors, including chemical interactions and microstructural changes.[23–28] To address these issues, two commonly employed strategies have been utilized as a means of enhancing performance at reduced temperatures. The first

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† Electronic supplementary information (ESI) available: Table S1, the ionic conductivity of solid oxide thin-film electrolytes under SOFC/SOEC operation. See DOI: https://doi.org/10.1039/d4ta03852e

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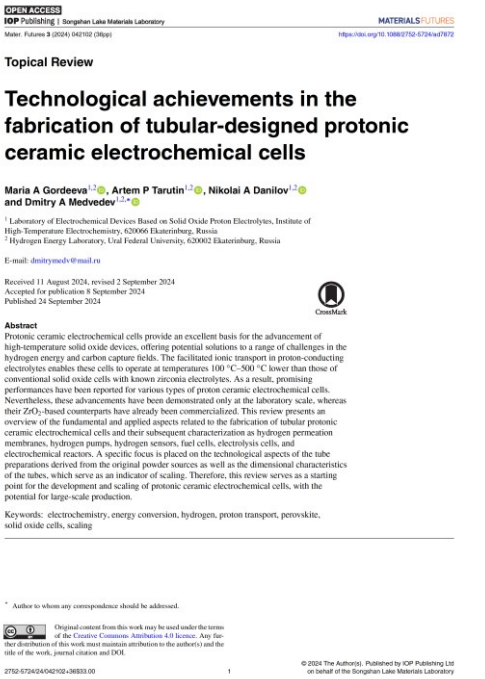
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2024

Technological achievements in the fabrication of tubular-designed protonic ceramic electrochemical cells.

- M.A. Gordeeva
- A.P. Tarutin
- N.A. Danilov
- D.A. Medvedev.

Protonic ceramic electrochemical cells provide an excellent basis for the advancement of high-temperature solid oxide devices, offering potential solutions to a range of challenges in the hydrogen energy and carbon capture fields. The facilitated ionic transport in proton-conducting electrolytes enables these cells to operate at temperatures 100 °C–500 °C lower than those of conventional solid oxide cells with known zirconia electrolytes. As a result, promising performances have been reported for various types of proton ceramic electrochemical cells. Nevertheless, these advancements have been demonstrated only at the laboratory scale, whereas their ZrO_2-based counterparts have already been commercialized. This review presents an overview of the fundamental and applied aspects related to the fabrication of tubular protonic ceramic electrochemical cells and their subsequent characterization as hydrogen permeation membranes, hydrogen pumps, hydrogen sensors, fuel cells, electrolysis cells, and electrochemical reactors. A specific focus is placed on the technological aspects of the tube preparations derived from the original powder sources as well as the dimensional characteristics of the tubes, which serve as an indicator of scaling. Therefore, this review serves as a starting point for the development and scaling of protonic ceramic electrochemical cells, with the potential for large-scale production.



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Topical Review

Technological achievements in the fabrication of tubular-designed protonic ceramic electrochemical cells

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Abstract

Protonic ceramic electrochemical cells provide an excellent basis for the advancement of high-temperature solid oxide devices, offering potential solutions to a range of challenges in the hydrogen energy and carbon capture fields. The facilitated ionic transport in proton-conducting electrolytes enables these cells to operate at temperatures 100 °C–500 °C lower than those of conventional solid oxide cells with known zirconia electrolytes. As a result, promising performances have been reported for various types of proton ceramic electrochemical cells. Nevertheless, these advancements have been demonstrated only at the laboratory scale, whereas their ZrO_2-based counterparts have already been commercialized. This review presents an overview of the fundamental and applied aspects related to the fabrication of tubular protonic ceramic electrochemical cells and their subsequent characterization as hydrogen permeation membranes, hydrogen pumps, hydrogen sensors, fuel cells, electrolysis cells, and electrochemical reactors. A specific focus is placed on the technological aspects of the tube preparations derived from the original powder sources as well as the dimensional characteristics of the tubes, which serve as an indicator of scaling. Therefore, this review serves as a starting point for the development and scaling of protonic ceramic electrochemical cells, with the potential for large-scale production.

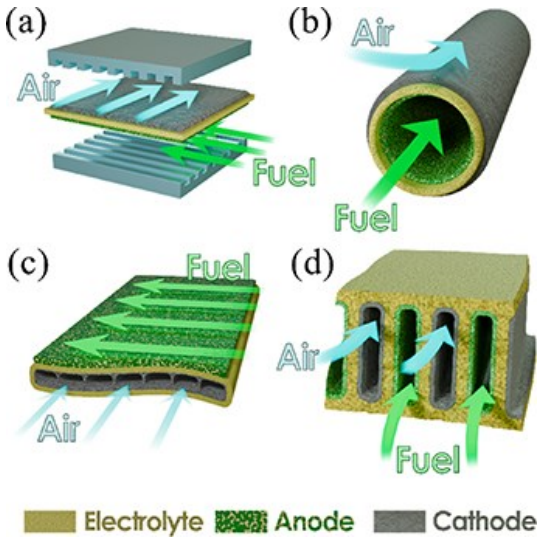
Keywords: electrochemistry, energy conversion, hydrogen, proton transport, perovskite, solid oxide cells, scaling

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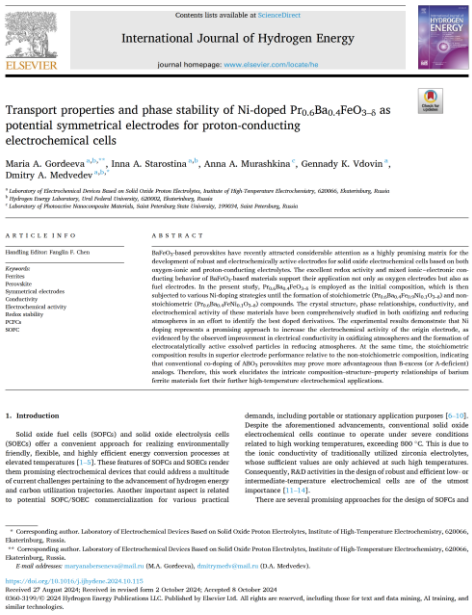
2024

Transport properties and phase stability of Ni-doped $Pr_{0.6}Ba_{0.4}FeO_{3-\delta}$ as potential symmetrical electrodes for proton-conducting electrochemical cells.

- M.A. Gordeeva
- I.A. Starostina
- A.A. Murashkina
- G.K. Vdovin
- D.A. Medvedev

- Ferrites
- Perovskite
- Symmetrical electrodes
- Conductivity
- Electrochemical activity
- Redox stability
- PCFCs
- SOFC

$BaFeO_3$-based perovskites have recently attracted considerable attention as a highly promising matrix for the development of robust and electrochemically active electrodes for solid oxide electrochemical cells based on both oxygen-ionic and proton-conducting electrolytes. The excellent redox activity and mixed ionic–electronic conducting behavior of $BaFeO_3$-based materials support their application not only as oxygen electrodes but also as fuel electrodes. In the present study, $Pr_{0.6}Ba_{0.4}FeO_{3-\delta}$ is employed as the initial composition, which is then subjected to various Ni-doping strategies until the formation of stoichiometric ($Pr_{0.6}Ba_{0.4}Fe_{0.9}Ni_{0.1}O_{3-\delta}$) and non-stoichiometric ($Pr_{0.6}Ba_{0.4}FeNi_{0.1}O_{3-\delta}$) compounds. The crystal structure, phase relationships, conductivity, and electrochemical activity of these materials have been comprehensively studied in both oxidizing and reducing atmospheres in an effort to identify the best doped derivatives. The experimental results demonstrate that Ni doping represents a promising approach to increase the electrochemical activity of the origin electrode, as evidenced by the observed improvement in electrical conductivity in oxidizing atmospheres and the formation of electrocatalytically active exsolved particles in reducing atmospheres. At the same time, the stoichiometric composition results in superior electrode performance relative to the non-stoichiometric composition, indicating that conventional co-doping of ABO_3 perovskites may prove more advantageous than B-excess (or A-deficient) analogs. Therefore, this work elucidates the intricate composition–structure–property relationships of barium ferrite materials fort their further high-temperature electrochemical applications.



International Journal of Hydrogen Energy

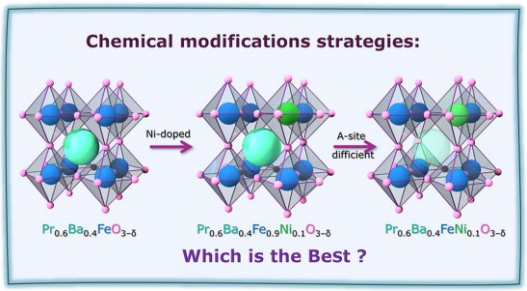
Transport properties and phase stability of Ni-doped $Pr_{0.6}Ba_{0.4}FeO_{3-\delta}$ as potential symmetrical electrodes for proton-conducting electrochemical cells

Maria A. Gordeeva, Inna A. Starostina, Anna A. Murashkina, Gennady K. Vdovin, Dmitry A. Medvedev

ARTICLE INFO

ABSTRACT

1. Introduction



M.A. Gordeeva, I.A. Starostina, A.A. Murashkina, G.K. Vdovin, D.A. Medvedev. Transport properties and phase stability of Ni-doped $Pr_{0.6}Ba_{0.4}FeO_{3-\delta}$ as potential symmetrical electrodes for proton-conducting electrochemical cells. International Journal of Hydrogen Energy. 2024. V. 91. P. 16–28. 10.1016/j.ijhydene.2024.10.115

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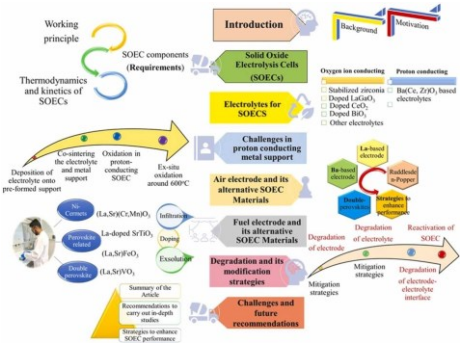
2024

Innovative advances and challenges in solid oxide electrolysis cells: Exploring surface segregation dynamics in perovskite electrodes.

- M.B. Hanif
- S. Rauf
- M.Z. Khan
- Z.U.D. Babar
- O. Gohar
- M. Saleem
- K. Zheng
- I. Hussain
- B. Lin
- D. Medvedev
- C.-X. Li
- M. Motola

- *Solid oxide fuel cell*
- Perovskite

Hydrogen generation by means of environmentally friendly approaches is of paramount importance in the field of contemporary science and technology. Solid oxide electrolysis cells (SOECs) represent a high-temperature trajectory of H_2 production, offering highly efficient electrical-to-chemical energy conversion at 400–800 °C. SOECs exhibit numerous advantages over low-temperature electrolysis technologies, including a wide potential performance range, high conversion efficiency, excellent selectivity, and the ability to provide co-electrolysis of H_2O and CO_2, supporting hydrogen energy strategies and carbon emission reduction programs. However, SOECs suffer from unsatisfactory long-term stability, which is caused by a number of microstructurally, chemically, and electrically related factors. In order to address these issues, we present the current review article, which provides a detailed description of the chemical and electrochemical phenomena that occur in SOECs during their real operation, in relation to both internal factors (the composition of functional materials) and external aspects (gas compositions, temperature, and applied potential). An in-depth analysis of these interrelationships enables the rational selection of materials and optimization of SOEC operating conditions. Various strategies for the optimal functioning of fuel electrodes, such as doping, in-situ exsolution, and catalytic advancements, are explored. For oxygen electrodes, performance optimization strategies including the development of novel perovskite materials with tailored surface properties and the incorporation of mixed ionic-electronic conductors to facilitate enhanced oxygen ion transport and electrochemical activity, are comprehensively summarized. Moreover, a particular focus of this review is on the surface segregation behavior of perovskite electrodes, a critical aspect influencing SOEC performance and stability. Recent innovations in SOECs development aimed at mitigating surface segregation, such as doping strategies, surface treatments, and the development of novel perovskite compositions with enhanced stability, are discussed in detail for the first time. Consequently, this work is regarded as a valuable reference in the field of SOECs, particularly in relation to energy materials, degradation processes, solid state ionics, and electrochemistry. By employing these innovative strategies, the long-term stability and efficiency of SOECs can be significantly enhanced, making them more viable for large-scale hydrogen production and carbon reduction initiatives.





M.B. Hanif, S. Rauf, M.Z. Khan, Z.U.D. Babar, O. Gohar, M. Saleem, K. Zheng, I. Hussain, B. Lin, D. Medvedev, C.-X. Li, M. Motola. Innovative advances and challenges in solid oxide electrolysis cells: Exploring surface segregation dynamics in perovskite electrodes. Materials Science and Engineering: R: Reports. 2024. V. 161. Art. 100864. 10.1016/j.mser.2024.100864

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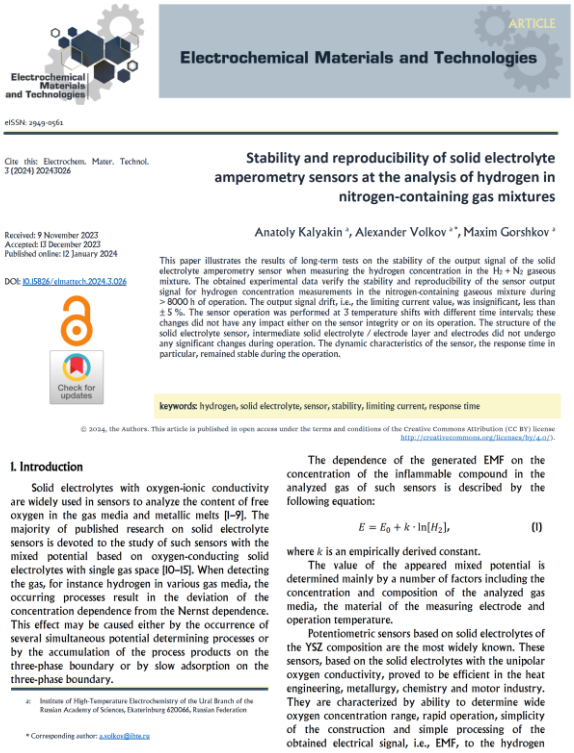
2024

Stability and reproducibility of solid electrolyte amperometry sensors at the analysis of hydrogen in nitrogen-containing gas mixtures.

- A.S. Kalyakin
- A.N. Volkov
- M.Yu. Gorshkov

- Hydrogen
- Solid electrolyte
- Sensor
- Stability
- Limiting current
- Response time

This paper illustrates the results of long-term tests on the stability of the output signal of the solid electrolyte amperometry sensor when measuring the hydrogen concentration in the H2 + N2 gaseous mixture. The obtained experimental data verify the stability and reproducibility of the sensor output signal for hydrogen concentration measurements in the nitrogen-containing gaseous mixture during > 8000 h of operation. The output signal drift, i.e., the limiting current value, was insignificant, less than ± 5 %. The sensor operation was performed at 3 temperature shifts with different time intervals; these changes did not have any impact either on the sensor integrity or on its operation. The structure of the solid electrolyte sensor, intermediate solid electrolyte / electrode layer and electrodes did not undergo any significant changes during operation. The dynamic characteristics of the sensor, the response time in particular, remained stable during the operation



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Stability and reproducibility of solid electrolyte amperometry sensors at the analysis of hydrogen in nitrogen-containing gas mixtures

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This paper illustrates the results of long-term tests on the stability of the output signal of the solid electrolyte amperometry sensor when measuring the hydrogen concentration in the $H_2 + N_2$ gaseous mixture. The obtained experimental data verify the stability and reproducibility of the sensor output signal for hydrogen concentration measurements in the nitrogen-containing gaseous mixture during > 8000 h of operation. The output signal drift, i.e., the limiting current value, was insignificant, less than ± 5 %. The sensor operation was performed at 3 temperature shifts with different time intervals; these changes did not have any impact either on the sensor integrity or on its operation. The structure of the solid electrolyte sensor, intermediate solid electrolyte / electrode layer and electrodes did not undergo any significant changes during operation. The dynamic characteristics of the sensor, the response time in particular, remained stable during the operation.

keywords: hydrogen, solid electrolyte, sensor, stability, limiting current, response time

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I. Introduction

Solid electrolytes with oxygen-ionic conductivity are widely used in sensors to analyze the content of free oxygen in the gas media and metallic melts [1–9]. The majority of published research on solid electrolyte sensors is devoted to the study of such sensors with the mixed potential based on oxygen-conducting solid electrolytes with single gas space [10–15]. When detecting the gas, for instance hydrogen in various gas media, the occurring processes result in the deviation of the concentration dependence from the Nernst dependence. This effect may be caused either by the occurrence of several simultaneous potential determining processes or by the accumulation of the process products on the three-phase boundary or by slow adsorption on the three-phase boundary.

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The dependence of the generated EMF on the concentration of the inflammable compound in the analyzed gas of such sensors is described by the following equation:

$$E = E_0 + k \cdot \ln[H_2], \quad (1)$$

where k is an empirically derived constant.

The value of the appeared mixed potential is determined mainly by a number of factors including the concentration and composition of the analyzed gas media, the material of the measuring electrode and operation temperature.

Potentiometric sensors based on solid electrolytes of the YSZ composition are the most widely known. These sensors, based on the solid electrolytes with the unipolar oxygen conductivity, proved to be efficient in the heat engineering, metallurgy, chemistry and motor industry. They are characterized by ability to determine wide oxygen concentration range, rapid operation, simplicity of the construction and simple processing of the obtained electrical signal, i.e., EMF, to the hydrogen

A.S. Kalyakin, A.N. Volkov, M.Yu. Gorshkov. Stability and reproducibility of solid electrolyte amperometry sensors at the analysis of hydrogen in nitrogen-containing gas mixtures. Electrochemical Materials and Technologies, [S.l.]. 2024. V. 3, №1, p. 20243026, jan. 2024. 10.15826/elmattech.2024.3.026

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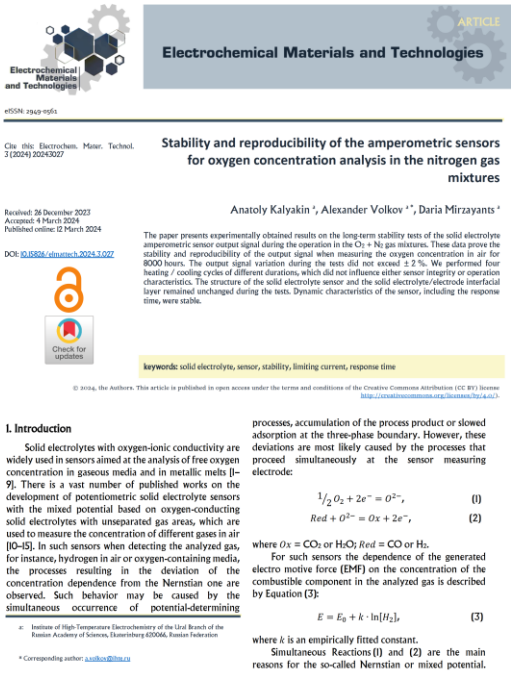
2024

Stability and reproducibility of the amperometric sensors for oxygen concentration analysis in the nitrogen gas mixtures

- A.S. Kalyakin
- A.N. Volkov
- D.P. Mirzayants

- solid electrolyte
- sensor
- stability
- limiting current
- response time

The paper presents experimentally obtained results on the long-term stability tests of the solid electrolyte amperometric sensor output signal during the operation in the O2 + N2 gas mixtures. These data prove the stability and reproducibility of the output signal when measuring the oxygen concentration in air for 8000 hours. The output signal variation during the tests did not exceed ± 2 %. We performed four heating / cooling cycles of different durations, which did not influence either sensor integrity or operation characteristics. The structure of the solid electrolyte sensor and the solid electrolyte/electrode interfacial layer remained unchanged during the tests. Dynamic characteristics of the sensor, including the response time, were stable.



Electrochemical Materials and Technologies

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Stability and reproducibility of the amperometric sensors for oxygen concentration analysis in the nitrogen gas mixtures

Anatoly Kalyakin [a], Alexander Volkov [a,*], Daria Mirzayants [a]

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The paper presents experimentally obtained results on the long-term stability tests of the solid electrolyte amperometric sensor output signal during the operation in the $O_2 + N_2$ gas mixtures. These data prove the stability and reproducibility of the output signal when measuring the oxygen concentration in air for 8000 hours. The output signal variation during the tests did not exceed ± 2 %. We performed four heating / cooling cycles of different durations, which did not influence either sensor integrity or operation characteristics. The structure of the solid electrolyte sensor and the solid electrolyte/electrode interfacial layer remained unchanged during the tests. Dynamic characteristics of the sensor, including the response time, were stable.

keywords: solid electrolyte, sensor, stability, limiting current, response time

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1. Introduction

Solid electrolytes with oxygen-ionic conductivity are widely used in sensors aimed at the analysis of free oxygen concentration in gaseous media and in metallic melts [1–9]. There is a vast number of published works on the development of potentiometric solid electrolyte sensors with the mixed potential based on oxygen-conducting solid electrolytes with unseparated gas areas, which are used to measure the concentration of different gases in air [10–15]. In such sensors when detecting the analyzed gas, for instance, hydrogen in air or oxygen-containing media, the processes resulting in the deviation of the concentration dependence from the Nernstian one are observed. Such behavior may be caused by the simultaneous occurrence of potential-determining processes, accumulation of the process product or slowed adsorption at the three-phase boundary. However, these deviations are most likely caused by the processes that proceed simultaneously at the sensor measuring electrode:

$$^1/_2 O_2 + 2e^- = O^{2-}, \quad (1)$$

$$Red + O^{2-} = Ox + 2e^-, \quad (2)$$

where Ox = CO_2 or H_2O; Red = CO or H_2.

For such sensors the dependence of the generated electro motive force (EMF) on the concentration of the combustible component in the analyzed gas is described by Equation (3):

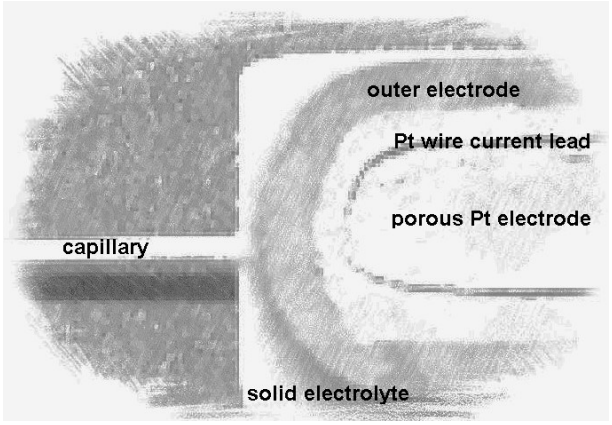
$$E = E_0 + k \cdot \ln[H_2], \quad (3)$$

where k is an empirically fitted constant.

Simultaneous Reactions (1) and (2) are the main reasons for the so-called Nernstian or mixed potential.

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A.S. Kalyakin, A.N. Volkov, D.P. Mirzayants. Stability and reproducibility of the amperometric sensors for oxygen concentration analysis in the nitrogen gas mixtures. Electrochemical Materials and Technologies, [S.l.], V. 3, № 1, p. 20243027. https://doi.org/10.15826/elmattech.2024.3.027

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IF N/A

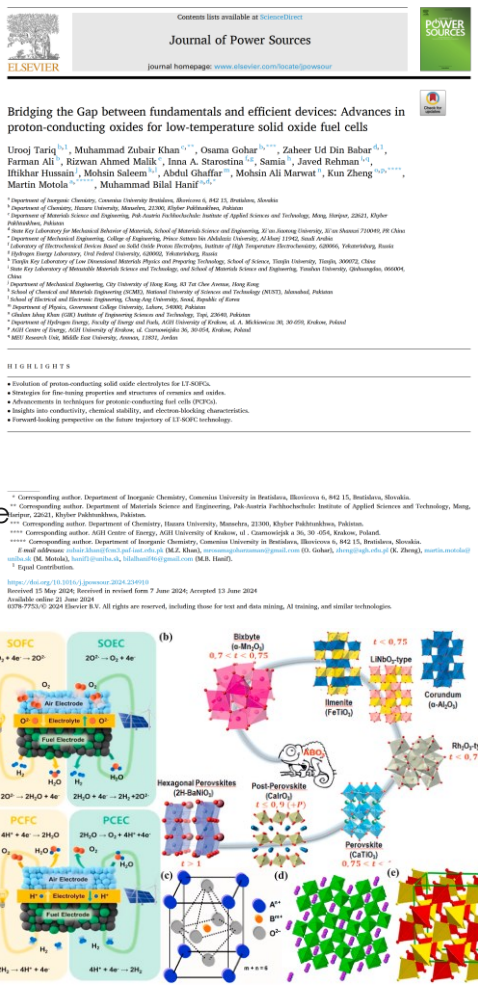
CS N/A

2024

Innovative advances and challenges in solid oxide electrolysis cells: Exploring surface segregation dynamics in perovskite electrodes.

- Tariq U.
- Khan M.Z.
- Gohar O.
- Babar Z.U.D.
- Ali F.
- Malik R.A.
- Starostina I.A.
- Samia
- Rehman J.
- Hussain I.
- Saleem M.
- Ghaffar A.
- Marwat M.A.
- Zheng K.
- Motola M.
- Hanif M.B.

- *Evolution of proton-conducting solid oxide electrolytes for LT-SOFCs.*
- *Strategies for fine-tuning properties and structures of ceramics and oxides.*
- *Advancements in techniques for protonic-conducting fuel cells (PCFCs).*
- *Insights into conductivity, chemical stability, and electron-blocking characteristics.*
- *Forward-looking perspective on the future trajectory of LT-SOFC technology.*


Journal of Power Sources

Bridging the Gap between fundamentals and efficient devices: Advances in proton-conducting oxides for low-temperature solid oxide fuel cells

Low-temperature solid oxide fuel cells (LT-SOFCs) represent a cutting-edge solution in the domain of clean energy, poised to revolutionize electricity generation for both stationary and mobile applications. At the core of LT-SOFCs lies the proton-conducting solid oxide electrolyte, a subject of extensive exploration and advancement. This comprehensive review investigates the evolution of proton-conducting solid oxide electrolytes for LT-SOFCs, exploring the landscape from fundamental materials to diverse device architectures. The review meticulously examines three pivotal dimensions: 1) strategies for fine-tuning the properties and structures of ceramics and proton-conducting oxides, 2) advancements in techniques for protonic-conducting fuel cells (PCFCs), and 3) an exploration of the opportunities and challenges intrinsic to the progression of electrolyte-based PCFCs. By elucidating the advancements made in optimizing conductivity, chemical stability, sinterability, and electron-blocking characteristics of proton-conducting electrolytes, this review offers invaluable insights into the state-of-the-art for LT-SOFC technology. Furthermore, it casts a forward-looking perspective, envisioning the future trajectory of proton-conducting electrolyte research and its potential to reshape the landscape of LT-SOFC technology. By providing a comprehensive overview of past achievements and future prospects, this review serves as a valuable resource for researchers, engineers, and stakeholders, guiding them towards the realization of efficient and sustainable energy solutions.

Tariq U., Khan M.Z., Gohar O., Babar Z.U.D., Ali F., Malik R.A., Starostina I.A., Samia, Rehman J., Hussain I., Saleem M., Ghaffar A., Marwat M.A.,Zheng K., Motola M., Hanif M.B. Bridging the Gap between fundamentals and efficient devices: Advances in proton-conducting oxides for low-temperature solid oxide fuel cells // Journal of Power Sources, 2024, 613, p. 234910. 10.1016/j.jpowsour.2024.234910

DOI Q1 IF 8.1 CS 16.4 RG CoLab

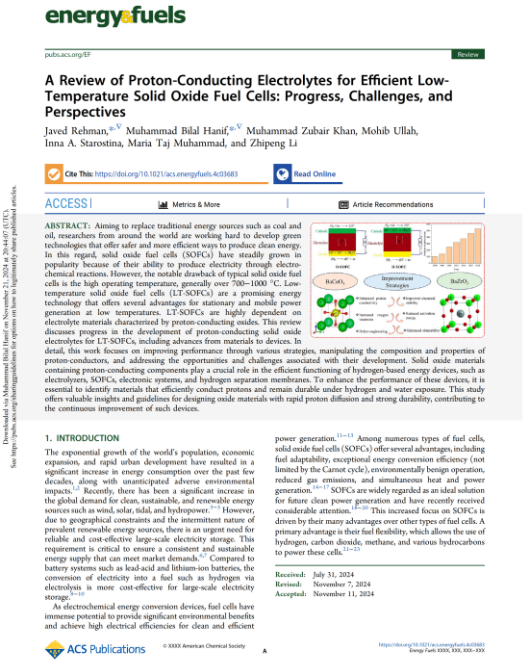
2024

A Review of Proton-Conducting Electrolytes for Efficient Low-Temperature Solid Oxide Fuel Cells: Progress, Challenges, and Perspectives

- J. Rehman
- M.B. Hanif
- M.Z. Khan
- M. Ullah
- I.A. Starostina
- M.T. Muhammad
- Z. Li.

- *Electrolytes*
- *Fuel cells*
- *Materials*
- *Oxygen*
- *Stability*

Aiming to replace traditional energy sources such as coal and oil, researchers from around the world are working hard to develop green technologies that offer safer and more efficient ways to produce clean energy. In this regard, solid oxide fuel cells (SOFCs) have steadily grown in popularity because of their ability to produce electricity through electrochemical reactions. However, the notable drawback of typical solid oxide fuel cells is the high operating temperature, generally over 700–1000 °C. Low-temperature solid oxide fuel cells (LT-SOFCs) are a promising energy technology that offers several advantages for stationary and mobile power generation at low temperatures. LT-SOFCs are highly dependent on electrolyte materials characterized by proton-conducting oxides. This review discusses progress in the development of proton-conducting solid oxide electrolytes for LT-SOFCs, including advances from materials to devices. In detail, this work focuses on improving performance through various strategies, manipulating the composition and properties of proton-conductors, and addressing the opportunities and challenges associated with their development. Solid oxide materials containing proton-conducting components play a crucial role in the efficient functioning of hydrogen-based energy devices, such as electrolyzers, SOFCs, electronic systems, and hydrogen separation membranes. To enhance the performance of these devices, it is essential to identify materials that efficiently conduct protons and remain durable under hydrogen and water exposure. This study offers valuable insights and guidelines for designing oxide materials with rapid proton diffusion and strong durability, contributing to the continuous improvement of such devices.


energy&fuels

A Review of Proton-Conducting Electrolytes for Efficient Low-Temperature Solid Oxide Fuel Cells: Progress, Challenges, and Perspectives

Javed Rehman, Muhammad Bilal Hanif, Muhammad Zubair Khan, Mohib Ullah, Inna A. Starostina, Maria Taj Muhammad, and Zhipeng Li

ACS Publications

J. Rehman, M.B. Hanif, M.Z. Khan, M. Ullah, I.A. Starostina, M.T. Muhammad, Z. Li. A Review of Proton-Conducting Electrolytes for Efficient Low-Temperature Solid Oxide Fuel Cells: Progress, Challenges, and Perspectives // Energy & Fuels 2024 38 (23), 22637-22665. 10.1021/acs.energyfuels.4c03683

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Exhaustive Study of Electrical Conductivity in the $MNb_{2-x}Ti_xO_6$–0.5_x (M = Mg, Ca, Zn; x = 0, 0.1, 0.2) Columbites

- Ye.A. Morkhova
- M.S. Koroleva
- A.V. Egorova
- A.G. Krasnov
- I.A. Starostina
- A.A. Kabanov

The $CaNb_2O_6$ and $ZnNb_2O_6$ columbites (Sp.gr. *Pbcn*) were studied as oxygen ion conductors both theoretically and experimentally. A theoretical approach included geometrical-topological analysis, bond valence site energy (BVSE) and density functional theory (DFT) calculations. The BVSE approach showed the possibility of pure oxygen ions diffusion with migration energies less than 0.45 eV in both compounds. However, DFT calculations indicated the possibility of diffusion of both anions and cations. The single-phases columbites were synthesized by the Pechini method for accurately determine charge carriers type and investigated by impedance spectroscopy, by the Tubandt method, which confirmed the absence of cationic conductivity, and measured the electrical conductivity as a function of oxygen partial pressures. The $CaNb_2O_6$ sample was characterized by the pure oxygen-ionic conductivity ~2×10^{-6} S cm^{-1} at 800 °C (E_a = 0.82 eV), while the $ZnNb_2O_6$ had a similar conductivity value due to mixed ionic-electronic contribution (E_a = 0.83 eV). The electromotive force method also showed the predominance of the ionic type of conductivity in $CaNb_2O_6$, while $ZnNb_2O_6$ has a mixed conductivity with ion transport number of about 0.4. Additionally, we synthesized Ti-doped samples $MNb_{2-x}Ti_xO_{6-0.5x}$ (M = Mg, Ca; x = 0.1, 0.2) to study the doping effect on conducting properties.


ECS Advances, 2024 3 024504

Exhaustive Study of Electrical Conductivity in the $MNb_{2-x}Ti_xO_{6-0.5x}$ (M = Mg, Ca, Zn; x = 0, 0.1, 0.2) Columbites

Yelizaveta A. Morkhova, Mariia S. Koroleva, Anastasia V. Egorova, Aleksei G. Krasnov, Inna A. Starostina, and Artem A. Kabanov

Ye.A. Morkhova, M.S. Koroleva, A.V. Egorova, A.G. Krasnov, I.A. Starostina, A.A. Kabanov. Exhaustive Study of Electrical Conductivity in the $MNb_{2-x}Ti_xO_6$–0.5_x (M = Mg, Ca, Zn; x = 0, 0.1, 0.2) Columbites // ECS Advances, volume 3, issue 2, p. 24504. 10.1149/2754-2734/ad3f31

DOI Q3 IF N/A CS 1.1 RG CoLab

2024

Novel layered perovskite $BaLa_{0.9}Fe_{0.1}InO_{4-\delta}$ with triple conductivity

- Tarasova N.
- Abakumova E.
- Kuznetsova T.
- Bedarkova A.
- Pryakhina V.
- Cherepanova V.
- Tarutin A.
- Danilov N.
- Starostin G.
- Starostina I.
- Animitsa I.

- *Evolution of proton-conducting solid oxide electrolytes for LT-SOFCs.*
- *Strategies for fine-tuning properties and structures of ceramics and oxides.*
- *Advancements in techniques for protonic-conducting fuel cells (PCFCs).*
- *Insights into conductivity, chemical stability, and electron-blocking characteristics.*
- *Forward-looking perspective on the future trajectory of LT-SOFC technology.*

The search for novel functional ceramic materials with targeted properties is currently very important. Complex oxides with perovskite or perovskite-related structure are being considered for the production of electrochemical devices for the hydrogen energy ecosystem. Layered perovskites including based on $BaLaInO_4$ are promising materials for proton-conducting electrolyte of solid oxide fuel cells. The idea of this work is to create a triple conductivity material based on $BaLaInO_4$. In this work, the doping of the lanthanum sublattice with iron ions was carried out for the first time. The effect of doping on the structure, water uptake and electrical conductivity was investigated. It was shown that the introduction of iron ions into lanthanum sublattice changes the crystal lattice from orthorhombic to tetragonal structure. The water uptake is very small and it is 0.02 mol H_2O per formula unit for $BaLa_{0.9}Fe_{0.1}InO_{4-\delta}$ composition. Studies of the electrical properties have shown that the nature of conductivity is mixed hole/oxygen ionic at dry air and hole/oxygen ionic/protonic and wet air. The Fe-doped-composition can be considered as triple conducting materials and it is prospective as the electrode materials comparable with protonic electrolyte $Ba_{1.1}La_{0.9}InO_{3.95}$.

Tarasova N., Abakumova E., Kuznetsova T., Bedarkova A., Pryakhina V., Cherepanova V., Tarutin A., Danilov N., Starostin G.,Starostina I., Animitsa I. Novel layered perovskite $BaLa_{0.9}Fe_{0.1}InO_{4-\delta}$ with triple conductivity // Ceramics International, 2024, 50 (20), Part C, pp. 40445-40452. 10.1016/j.ceramint.2024.06.190

DOI Q1 IF 5.1 CS 9.4 RG CoLab

Математические подходы к решению химических задач.

- нестандартные задачи
- межпредметные связи
- олимпиады по химии
- методология решения

В данной статье рассмотрены возможные подходы к решению химических задач на выпадение кристаллогидратов из насыщенных растворов. Показана широкая вариативность решения таких задач с применением математического аппарата.

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