H/D isotope effects in the electrical conductivity of LaScO₃-based solid state proton-conducting electrolyte
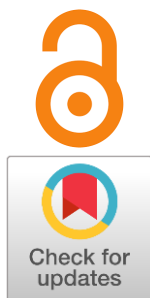
Ekaterina Antonova [a] [*]

Electrical conductivity of a solid proton-conducting electrolyte with the composition of $La_{0.9}Sr_{0.1}ScO_3$ is studied depending on temperature and oxygen partial pressure in the atmospheres, humidified with H_2O and D_2O. Isotope H/D effect in the electrical conductivity is observed at the temperatures below 700 °C in air conditions. For reductive atmosphere, the isotope effect is pronounced for the whole investigated temperature range. Based on the pO_2-dependencies of electrical conductivity, the transport numbers of ions and electron holes are determined. The ionic transport numbers in the H_2O-containing atmosphere are found to be higher than the corresponding values for the D_2O-containing atmosphere for all investigated conditions. The possible role of protons (deuterons) in the oxygen ion transport is pointed out. The kinetic isotope effect is found to be predominant in the conditions under study.

1. Introduction

In recent decades, perovskite-structured oxides have attracted the attention of the researchers due to various possible applications, such as ferroelectricity, luminescence, photocatalysis, fuel cells [1–3]. Among them, energy applications, for example the creation of solid oxide fuel cells (SOFCs), are of great interest in view of the increasing demand in the electricity and environmental issues [4, 5]. SOFCs are electrochemical devices, which can directly convert energy of chemical reaction to electricity. The heart of the device is a combination of a solid electrolyte and electrodes. Oxygen-ion conducting electrolytes are usually applied in conventional SOFCs (O^{2-}-SOFCs). However, some acceptor-doped ABO_3 oxides are known to dissolve water in their structure in water/hydrogen-containing atmospheres and thus to exhibit proton conductivity according to

$$H_2O + V_O^{\bullet\bullet} + O_O^\times \leftrightarrow 2OH_O^\bullet. \qquad (1)$$

These materials are considered as solid proton conducting electrolytes for applications in solid oxide fuel cells, electrolysis, hydrogen sensors, etc. [6–8]. SOFCs based on solid state proton conductors (H^+-SOFCs) have a number of advantages over O^{2-}-SOFCs, such as a lower operating temperature and the absence of fuel dilution. Currently, a wide row of perovskite-structured oxides is known to exhibit proton conductivity, e.g. solid solutions based on cerates and zirconates of alkaline-earth elements [9–15]. $LaScO_3$ based oxides are also typical representatives of this class of materials, combining a sufficient level of ionic conductivity with the chemical stability in the H_2O/CO_2-containing atmosphere, making them promising materials for practical application [16–18]. To date, various doping in A- and B-sublattices in $LaScO_3$ has already been studied, and it was found that the $LaScO_3$ doped with strontium in A-sublattice has the best

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characteristics, in particular, 10 % of strontium was found to be the best level of doping [19–21].

As was mentioned above, protons appear in the crystal structure as a result of the interaction with water. Since hydrogen has a stable isotope with twice the mass - deuterium, it is possible to substitute hydrogen with deuterium in the proton-conducting oxide thus affecting its physicochemical properties, in particular, electrical conductivity [22–24]. This phenomenon is known as H/D isotope effect. Usually, the conductivity of proton conductors in the D_2O-containing atmosphere is lower than in the H_2O-containing atmosphere due to the lower mobility of deuterons than of protons (the so-called kinetic isotope effect) [25]. However, the solubility of deuterons in the oxides is shown to be higher than the solubility of protons, leading to higher concentrations of charge careers in the first case. This effect is called the thermodynamic isotope effect and is usually more pronounced at low temperatures, when the full saturation of the oxides occurs [26, 27]. Investigation of isotope effects can be used as the verification of the proton conduction as well as give information on the mechanisms of proton conductivity [28, 29].

This paper is focused on the study of electrical conductivity of Sr-doped $LaScO_3$ from the point of possible H/D isotope effects.

2. Experimental

$La_{0.9}Sr_{0.1}ScO_3$ oxide (hereinafter LSS) was prepared by coprecipitation of the lanthanum and scandium hydroxides with further addition of strontium carbonate. $La(NO_3) \cdot 6H_2O$, $Sc(NO_3)_3 \cdot 4H_2O$, $SrCO_3$ were used as starting reagents. Details of the synthesis procedure can be find elsewhere [30]. Phase purity of the resulting ceramics was confirmed by X-ray diffraction method (D/MAX-2200 RIGAKU conventional diffractometer in Cu K_α - radiation ($\lambda(K_{\alpha_1} = 1.54$ Å). The obtained LSS oxide was found to be single-phase, crystallizing in the perovskite structure with orthorhombic distortions, space group *Pnma*, see Figure 1. Relative density of the resulting ceramics estimated from geometrical parameters was of about 92 %.

For electrical measurements, Pt electrodes were applied on the electrolyte disk with subsequent heat treatment at 950 °C for 2 h. Electrical conductivity was measured by means of impedance spectroscopy using the IM6 (Zahner) in the temperature range of 400–800 °C in the atmosphere, humidified with H_2O or D_2O. For humidification, the gas circulating in the experimental setup was bubbled through distilled water at room temperature. Before replacing H_2O with D_2O, the gas was
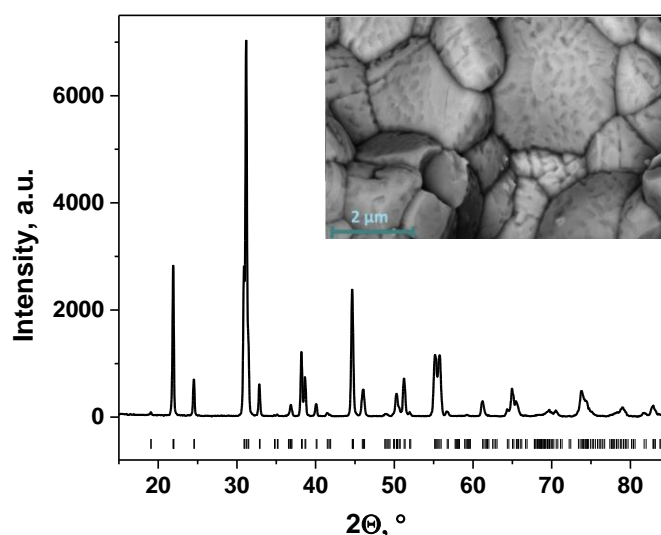

Figure 1 XRD pattern for LSS sample. On the insert – SEM image of LSS ceramics.

dried by passing through zeolites. Additionally, pO_2-dependenicies of electrical conductivity were measured in the temperature range 500–800 °C in the oxygen partial pressure range 0.21–10^{-20} atm in the D_2O-containing atmosphere. Regulation of oxygen partial pressure in the experimental setup was performed using a Zirconia 318 universal controller (Russia). Impedance spectra were collected in the frequency range of 1–10^5 Hz at the AC amplitude of 20 mV.

3. Results and discussion

Figure 2 presents temperature dependencies of electrical conductivity for LSS in air and reductive conditions, humidified with H_2O or D_2O. One can see that in air conditions the conductivity values at high temperature are almost the same for both atmospheres at the temperatures 700–800 °C, while at lower temperatures the conductivity values in H_2O-containing atmosphere exceed corresponding values in D_2O-containing one. The ratio of $\sigma(H_2O)/\sigma(D_2O)$ can be found in Table 1. The difference increases with the temperature decrease. The dependencies in air are linear, activation energy values were found to be 51 ± 3 and 57 ± 1 kJ/mol for H_2O- and D_2O-humidified air respectively. In air conditions, LSS is known to exhibit mixed ionic-electron hole conductivity, whereas under reductive conditions it is a pure ionic conductor [16, 30]. Thus, the great contribution of electron hole conductivity at high temperatures may be the reason why the isotope effect is not observed at high temperatures. Additionally, the ratio of ionic conductivities in H_2O- and D_2O-containing atmosphere ($\sigma_{ion}(H_2O)/\sigma_{ion}(D_2O)$) can be calculated. The obtained values are presented in Table 1. Basbus et al. [31] previously distinguished the electrical conductivity
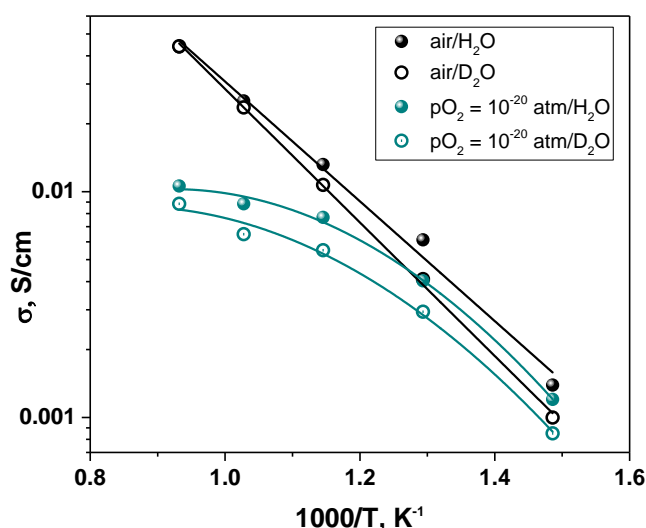
Figure 2 Temperature dependencies of electrical conductivity for LSS in air and reductive atmospheres, humidified with H_2O and D_2O.

Table 1 – Ratio of electrical conductivity values for LSS in air and under reductive conditions, humidified with H_2O and D_2O.

T, °C	$\sigma(H_2O)/\sigma(D_2O)$	$\sigma_{ion}(H_2O)/\sigma_{ion}(D_2O)$
800	0.99	1.2
700	1.07	1.36
600	1.23	1.39
500	1.35	1.37
400	1.39	1.41

regions for $BaCe_{0.4}Zr_{0.4}Y_{0.2}O_{3-\delta}$ based on the ratio $\sigma(H_2O)/\sigma(D_2O)$ as follows:

1) $1.4 < \sigma_{ion}(H_2O)/\sigma_{ion}(D_2O) < 1.8$. The oxygen vacancies are fully hydrated and the electrical transfer is almost pure protonic.

2) $1.2 < \sigma_{ion}(H_2O)/\sigma_{ion}(D_2O) < 1.4$. Mixed oxygen-ionic and protonic conduction is realized.

3) $\sigma_{ion}(H_2O) \approx \sigma_{ion}(D_2O)$. Electric conduction is dominated by oxygen vacancies.

If we apply this for the case of LSS, we can suppose that at the temperatures 500–800 °C the mixed conduction is realized, where the oxygen ionic conductivity is more pronounced at 800 °C, while at temperatures below 600 °C LSS is almost pure proton conductor. However, the clear difference in the ionic conductivity values is observed in the entire temperature range. Therefore, we can suppose that the presence of protons (deuterons) can affect the oxygen ionic conductivity as well. Previously, the possible role of protons in oxygen ionic transport in $LaScO_3$-based oxides was discussed in [32]. The dependencies in the reductive atmosphere have a nonlinear form and a clear H/D isotope effect is observed over the entire temperature range investigated. The non-linearity of the dependencies

under reductive conditions was previously observed and explained in terms of the mixed conductive nature of LSS and a consequence of the mutual superposition of oxygen and proton conductivities [16]. Moreover, the decrease in the proton concentration with the temperature increase may take place, as it was shown in [33]. Supposing the predominantly ionic conductivity at low pO_2, the electron hole conductivity can be determined as the difference between the conductivity values in air and under reductive conditions. From the obtained dependencies (Figure 3) it can be seen that the electron hole conductivity is almost the same in the temperature range 600–800 °C and slightly decreases in D_2O-humidified atmosphere at the temperatures below 600 °C. The activation energy values of electron hole conductivity were found to be 77 ± 3 and 83 ± 3 kJ/mol for air humidified with H_2O and D_2O respectively.

For more detailed distinguishing of electron hole and ion contributions to the total conductivity, the dependencies of the electrical conductivity on the oxygen partial pressure were measured. The results obtained are presented in Figure 4. Similar to the previously reported dependencies in H_2O-containing atmospheres [30], the electrical conductivity decreases with decreasing oxygen partial pressure and is almost independent of pO_2 at $pO_2 < 10^{-15}$ atm. Thus, the dependencies were fitted according to

$$\sigma_{tot} = \sigma_i + \sigma_p^0 \cdot pO_2^{0.25}, \qquad (2)$$

where σ_{tot} is total conductivity, σ_i is ionic conductivity, and σ_p^0 is a value of electron hole conductivity at an oxygen partial pressure of 1 atm.

Using the obtained values of ionic conductivity, transport numbers of ions and electron holes were calculated. Obtained results were compared with previously published values for H_2O-containig atmosphere and are summarized in Figure 5 and Table 2. It can be seen that for all the temperatures the ionic transport numbers in H_2O-containing atmosphere are higher than corresponding values in D_2O-containing one, even at 800 °C, thus confirming the idea of proton influence on oxygen ionic conductivity. With a temperature decrease, this difference increases due to the increasing contribution of proton (deuteron) conductivity. The difference is also observed for different pO_2 values (see Figure 5). Electron hole transport numbers are higher for all the temperatures for a D_2O-containing atmosphere than the corresponding values in a H_2O-containing atmosphere.

Table 2 summarizes the data on transport numbers in air atmospheres, humidified with H_2O and D_2O, available

for other proton-conducting oxides. A similar trend was previously observed for $BaCe_{0.7}Zr_{0.1}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCZYYb) [34]. This phenomenon is a consequence of the kinetic isotope effect: due to the lower mobility of deuterons the contribution of ionic conductivity decreases, and the contribution of electron hole conductivity increases. For $BaZr_{0.9}Y_{0.1}O_{3-\delta}$ (BZY10) the opposite trend was observed – the ionic transport

numbers increased and electron hole transport numbers decreased in D_2O containing atmosphere [27]. This was explained by the contribution of a thermodynamic isotope effect. Thus, we can conclude that for LSS under the investigated conditions, the contribution of the thermodynamic isotope effect is not observable and the kinetic isotope effect is responsible for the experimental dependencies, obtained during the study.

Table 2 – Transport numbers of ions and electron holes for LSS in air, humidified with H_2O and D_2O, and available literary data on other proton conducting oxides.

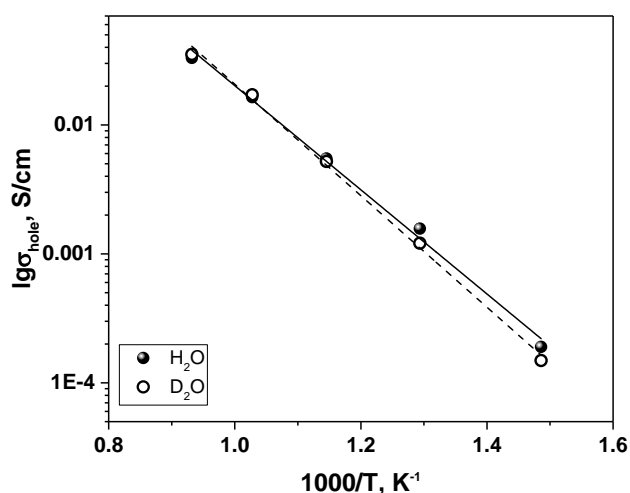| Composition	T, °C	$t_i(H_2O)$	$t_{hole}(H_2O)$	$t_i(D_2O)$	$t_{hole}(D_2O)$	Source
LSS	800	0.24	0.76	0.20	0.80	This study and [30]
LSS	700	0.34	0.66	0.28	0.72	This study and [30]
LSS	600	0.62	0.38	0.51	0.49	This study and [30]
LSS	500	0.89	0.11	0.76	0.24	This study and [30]
BZY10	600	0.38	0.62	0.54	0.46	[27]
BCZYYb	800	0.6	0.4	0.56	0.44	[34]
BCZYYb	600	0.89	0.11	0.82	0.18	[34]

Figure 3 Temperature dependencies of electron hole conductivity for LSS in air, humidified with H_2O and D_2O.
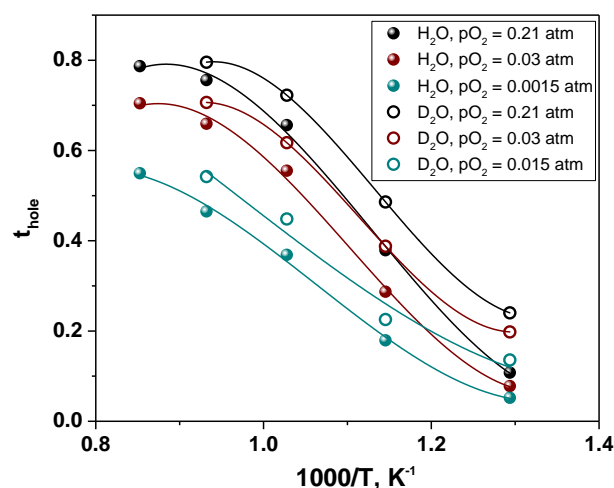

Figure 5 Temperature dependencies of electron hole transport numbers at different pO_2 values. Data for H_2O-containig atmospheres were taken from [30].
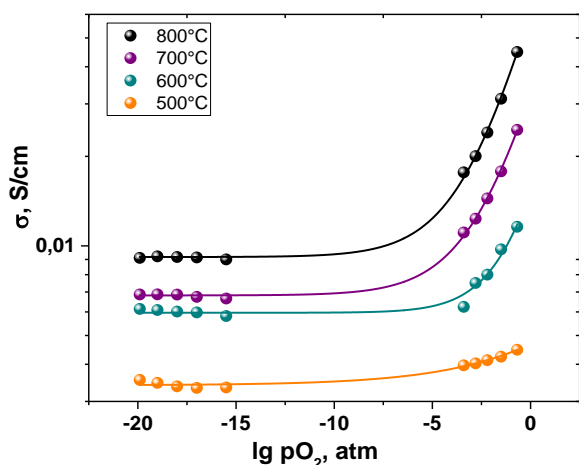
4. Conclusions

During the study, the electrical conductivity of Sr-doped $LaScO_3$ solid state proton-conducting oxide was investigated by impedance spectroscopy in the atmospheres, humidified with H_2O and D_2O in the temperature range of 400–800 °C and oxygen partial pressure range $10^{-20} < pO_2 < 0.21$ atm. It was found that under air conditions, replacing H_2O with D_2O did not affect the electrical conductivity at the temperatures 700–800 °C, and led to a decrease in the conductivity at lower temperatures. However, the ionic conductivity values in the D_2O-containing atmosphere were found to be lower than the corresponding values in the H_2O-

Figure 4 Electrical conductivity of LSS as a function of pO_2 in D_2O-containing atmosphere.

containing atmosphere in the entire investigated temperature range, thus, it was suggested that protons (deuterons) influence on the oxygen ionic transport in the investigated oxide. Based on the conductivity dependencies on oxygen partial pressure, the ionic and electron hole contributions to the electrical conductivity were distinguished and corresponding transport numbers were calculated. The kinetic isotope effect, caused by difference in proton and deuteron mobility, was found to be determinative for all investigated conditions: transport numbers of ions decreased with the substitution of H_2O with D_2O, while the electron hole conductivity contribution remained the same.

Supplementary materials

No supplementary materials are available.

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Author contributions

Ekaterina Antonova: Conceptualization; Investigation; Methodology; Writing – Original draft; Writing – Review & Editing; Visualization.

Conflict of interest

The authors declare no conflict of interest.

Additional information

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