Chimica Techno Acta

Transparent peer-review report

Structural and transport properties of La tungstate and its composite with nickel (II) and copper (II) oxides

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Contents

1st peer-review round

Reviewer #1 | minor revision

The work is devoted to the synthesis of lanthanum tungstate $La_{27}W_5O_{55.5}$ and a composite based on it, important materials for hydrogen energy, from mechanically activated oxides. Samples obtained by two methods are compared: traditional furnace sintering and radiation-thermal sintering. The effect of the synthesis method on the transport properties of the samples is considered. The work certainly deserves publication after clarification the following points:

1) Powder synthesis and final sintering of the ceramics were carried out at 1100 °C. "The impurity presence in LWO and LWORT samples is probably associated with relatively low sintering temperature since single-phase sample with ratio La:W = 5.4 can be obtained at the temperature of at least 1300 °C [26]" The authors note that the formation of the La_2O_3 impurity during synthesis at such a low temperature is not surprising. But what was the reason for choosing the annealing temperature of the samples at 1100 °C instead of 1300 °C?

2) Why did LWORT contain $La_6W_2O_{15}$ impurities and not La_2O_3? $La_6W_2O_{15}$ is formed at low La:W ratios or high synthesis temperatures. Since the cation ratios for the two samples LWO and LWORT were initially the same, could RTS have led to local overheating of the sample? Was the structure of the LWORT samples investigated after RTS treatment but before sintering? Is the sintering step even necessary for LWORT?

3) What is the error in the determination of the La/W cation ratio (Table 1)? The value of 4.41 for LWO seems to be too small; according to the data given in [26], compounds with such a structure can only exist at La/W>5.

4) In Figures 2 and 3, for CLWO, different symbols are used to denote the $LaNi_{0.8}W_{0.2}O_3$ phase when labelling the phase peaks, which makes it difficult to understand.

5) Has the phase ratio in CLWO and CLWORT been quantitatively estimated (at least approximately)? CLWO is further described as a $Ni_{0.5}Cu_{0.5}O$-$La_{27}W_5O_{55.5}$ composite, but the $La_{27}W_5O_{55.5}$ phase itself does not appear to be present in this composite according to the XRD data. It appears that the main phase determining the

properties of the composite is the perovskite $LaNi_{0.8}W_{0.2}O_3$ and not $La_{27}W_5O_{55.5}$. This probably explains why CLWOreox was not comparable to LWO even after removing the supposed blocking factor of CuO and NiO nanoparticles.

6) The captions to Figures 11 and 12 do not correspond to the content.

Reviewer #2 | minor revision

The manuscript, entitled 'Structural and transport properties of La tungstate and its composite with nickel (II) - copper (II) oxide', is devoted to studies of composite materials with triple conductivity. This field is a popular area of research, and these materials have the potential for practical use. The research topics and the manuscript meet the requirements of the CTA journal, and the manuscript can be considered for publication after revision.

- In the experimental part, describe in more detail or provide references to published papers concerning the methodology of research in the atmosphere of labelled carbon dioxide.
- The appearance of the C16O18o is not obvious. Describe in detail the recombination process.
- Since a mixture of $C_{16}O_2$ + $C_{18}O_2$ was used specify the concentration of $C_{18}O_2$ in this mixture.
- Specify the methodology for the preparation of $Ni_{0.5}Cu_{0.5}O$.
- For what reason there is no HR TEM data for the composite material? The most interesting is the phase boundary in the composite material.
- Compare diffusion coefficients with data for popular proton conducting materials.
- As it can be seen from SEM the samples have significant porosity. How correct it is to carry out studies of the kinetics of exchange with gas phase on porous samples and how further porosity was taken into account when analyzing the data.
- How stable are LWO and CLWO in a carbon dioxide atmosphere at experimental temperatures?
- The influence of redox is poorly described. Why do not you consider the possibility of changing the microstructure, namely porosity, which will also lead to a change in the exchange rate.
- There are no unambiguous conclusions about the positive or negative effect of NCO addition on LWO transport properties
- consider citing works:

on the use of proton-conducting oxide for hydrogen separation
https://doi.org/10.1016/j.jechem.2022.02.019

table data on proton and oxygen diffusion coefficients https://doi.org/10.1016/j.ijhydene.2024.06.266

Editor's decision

Major revision.

Responses to the comments of Reviewer #1

We are thankful to the honored Editor and Reviewers for the helpful comments. The respective corrections have been made and highlighted yellow. The responses are given below.

Response to Editor's and Reviewer's comments:

Reviewer 1:

The work is devoted to the synthesis of lanthanum tungstate La27W5O55.5 and a composite based on it, important materials for hydrogen energy, from mechanically activated oxides. Samples obtained by two methods are compared: traditional furnace sintering and radiation-thermal sintering. The effect of the synthesis method on the transport properties of the samples is considered. The work certainly deserves publication after clarification the following points:

1) Powder synthesis and final sintering of the ceramics were carried out at 1100 °C. "The impurity presence in LWO and LWORT samples is probably associated with relatively low sintering temperature since single-phase sample with ratio La:W = 5.4 can be obtained at the temperature of at least 1300 °C [26]" The authors note that the formation of the La_2O_3 *impurity during synthesis at such a low temperature is not surprising. But what was the reason for choosing the annealing temperature of the samples at 1100 °C instead of 1300 °C?*

Reply:

The materials are supposed to be used as components of asymmetric supported hydrogen separation membranes. We typically fabricate such membranes using the sintering temperature of 1100 °C for each layer (except for catalytic one which is typically sintered at 900 °C) in order to avoid deformation of metallic foam substrate of the membrane. Procedure of membrane fabrication can be found in the authors' previous works:

Bespalko Y, Sadykov V, Eremeev N, Skryabin P, Krieger T, Sadovskaya E, Bobrova L, Uvarov N, Lukashevich A, Krasnov A, Fedorova Y. Synthesis of tungstates/$Ni_{0.5}Cu_{0.5}O$

nanocomposite materials for hydrogen separation cermet membranes. Compos Struct. 2018;202:1263–74. doi:10.1016/j.compstruct.2018.06.004

Sadykov VA, Krasnov AV, Fedorova YuE, Lukashevich AI, Bespalko YuN, Eremeev NF, Skriabin PI, Valeev KR, Smorygo OL. Novel nanocomposite materials for oxygen and hydrogen separation membranes. Int J Hydrog Energy. 2020;45(25):13575-85. doi:10.1016/j.ijhydene.2018.02.182

Sadykov VA, Eremeev NF, Fedorova YuE, Krasnov AV, Bobrova LN, Bespalko YuN, Lukashevich AI, Skriabin PI, Smorygo OL, Van Veen AC. Design and performance of asymmetric supported membranes for oxygen and hydrogen separation. Int J Hydrog Energy. 2021;46(38):20222–39. doi 10.1016/j.ijhydene.2020.01.106

2) Why did LWORT contain $La_6W_2O_{15}$ *impurities and not* La_2O_3*?* $La_6W_2O_{15}$ *is formed at low La:W ratios or high synthesis temperatures. Since the cation ratios for the two samples LWO and LWORT were initially the same, could RTS have led to local overheating of the sample? Was the structure of the LWORT samples investigated after RTS treatment but before sintering? Is the sintering step even necessary for LWORT?*

Reply:

Sintering takes place during the electron beam bombardment. This is radiation thermal sintering (RTS). Hence, the studies after RTS but before sintering cannot be carried out. For the samples after synthesis via mechanical activation but before sintering (conventional or RTS), authors' previous study demonstrated that the unsintered samples are defective fluorite and can contain admixtures of simple oxides:

Bespalko Y, Eremeev N, Skryabin P, Krieger T, Chesalov Y, Lapina O, Khabibulin D, Ulihin A, Uvarov N, Sadykov V. Structural and transport properties of neodymium tungstates prepared via mechanochemical activation. Ceram Int. 2019;45(7B):9529–36. doi:10.1016/j.ceramint.2018.09.277

In the present study, for the RTS sample, the $La_6W_2O_{15}$ admixture is formed. We agree that this phase is formed at higher synthesis temperatures. We believe that the reason of such a phase formation is shifting phase transition towards lower temperatures during RTS compared to conventional sintering. The related statement has been added. Such a feature of RTS is mentioned in the introduction.

3) What is the error in the determination of the La/W cation ratio (Table 1)? The value of 4.41 for LWO seems to be too small; according to the data given in [26], compounds with such a structure can only exist at La/W>5.

Reply:

This can be a large error in estimation since the occupancy of the sites correlates with temperature factors. These temperature factor values were set equal for both LWO and LWO_{RT} samples, and the occupancies were calculated for these values. This resulted in provided La:W ratios. La:W ratio of the LWO sample is lower compared to the LWO_{RT} one which agrees with that fact that the LWO sample contains La_2O_3 admixture.

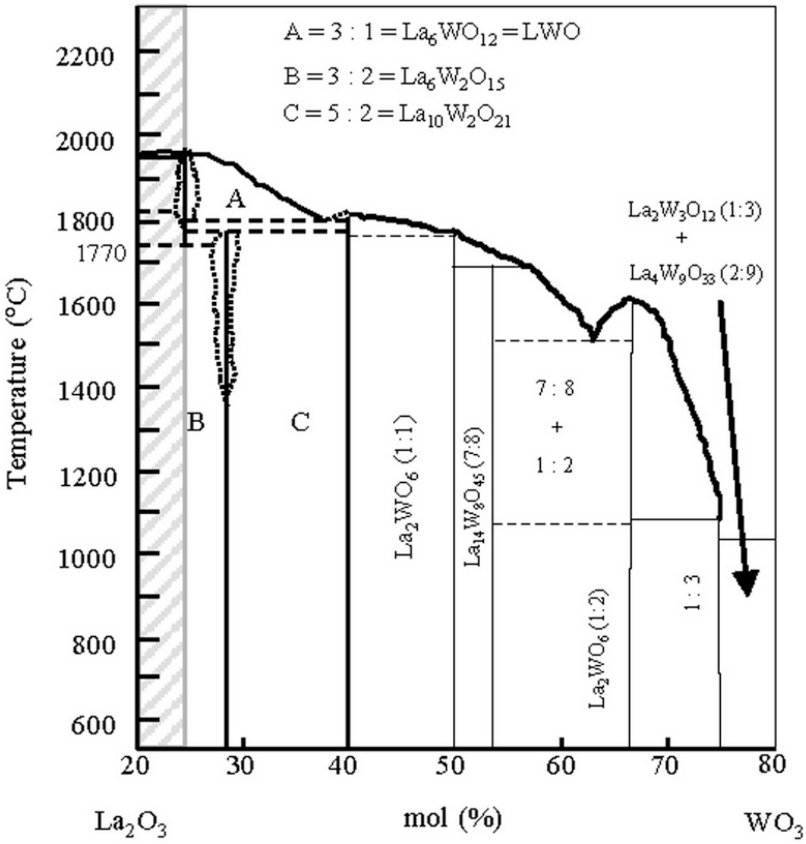
According to the phase diagrams provided in the works:

Kojo G, Shono Y, Ushiyama H, Oshima Y, Otomo J. Influence of La/W ratio on electrical conductivity of lanthanum tungstate with high La/W ratio. J Solid State Chem. 2017;248:1–8. doi:10.1016/j.jssc.2017.01.011

Magrasó A, Haugsrud R. Effects of the La/W ratio and doping on the structure, defect structure, stability and functional properties of proton-conducting lanthanum tungstate $La_{28-x}W_{4+x}O_{54+\delta}$. A review. J Mater Chem A. 2014;2(32):12630–41. doi:10.1039/C4TA00546E

Seeger J, Ivanova ME, Meulenberg WA, Sebold D, Stöver D, Scherb T, Schumacher G, Escolástico S, Solís C, Serra JM. Synthesis and characterization of nonsubstituted and substituted proton-conducting $La_{6-x}WO_{12-y}$. Inorg Chem. 2013;52(18):10375–86. doi:10.1021/ic401104m

e.g.,



for La:W ratios below 5 there should be also fluorite-derived $La_{10}W_2O_{21}$-like phase which possesses a good level of oxygen mobility (oxide-ionic conductivity of $6.4 \cdot 10^{-4}$ S/cm at 700 °C) (or its mixture with $La_6W_2O_{15}$).

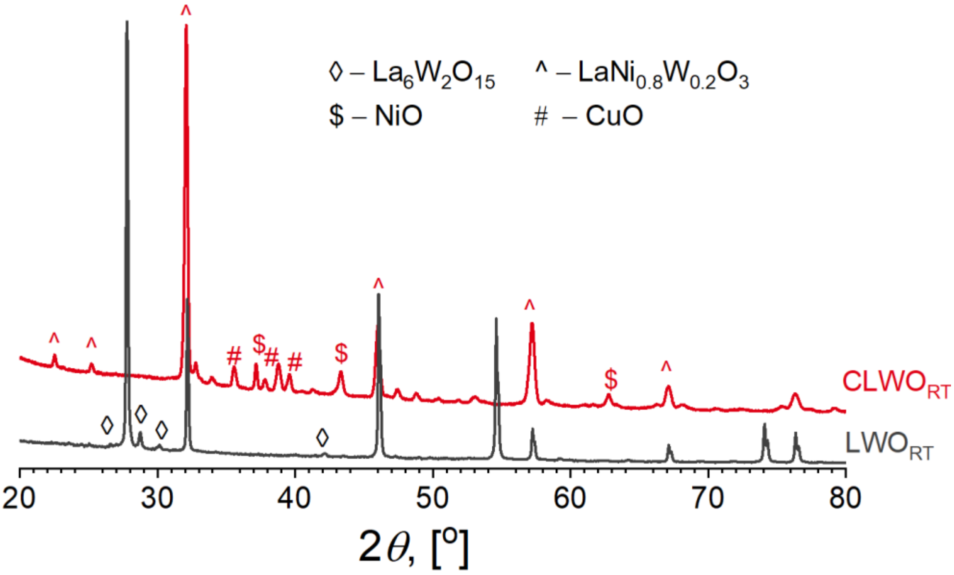
Chambrier M-H, Le Bail A, Giovannelli F, Redjaïmia A, Florian P, Massiot D, Suard E, Goutenoire F. $La_{10}W_2O_{21}$: An anion-deficient fluorite-related superstructure with oxide ion conduction. Inorg Chem. 2014;53(1):147–59. doi:10.1021/ic401801u

It is more likely that La:W ratio for the LWO sample is really lower compared to the LWO_{RT} sample, however, it is closer to 5.

4) In Figures 2 and 3, for CLWO, different symbols are used to denote the LaNi0.8W0.2O3 phase when labelling the phase peaks, which makes it difficult to understand.

Reply:

The symbols for this phase have been corrected to be the same as in Fig. 2:



5) Has the phase ratio in CLWO and CLWORT been quantitatively estimated (at least approximately)? CLWO is further described as a Ni0.5Cu0.5O-La27W5O55.5 composite, but the La27W5O55.5 phase itself does not appear to be present in this composite according to the XRD data. It appears that the main phase determining the properties of the composite is the perovskite LaNi0.8W0.2O3 and not La27W5O55.5. This probably explains why CLWOreox was not comparable to LWO even after removing the supposed blocking factor of CuO and NiO nanoparticles.

Reply:

The composites CLWO and $CLWO_{RT}$ possess different phase composition. In the case of $CLWO_{RT}$ the main phase is $LaNi_{0.8}W_{0.2}O_3$, while in the case of CLWO along with $LaNi_{0.8}W_{0.2}O_3$ there is a cubic phase La_6WO_{12} (the estimation of these phases ratio is ~1:1).

Unfortunately, the information on the oxygen transport properties of the perovskite $LaNi_{0.8}W_{0.2}O_3$ is still not available in the literature, only total conductivity data exists:

Alvarez I, Martínez JL, Veiga ML, Pico C. Synthesis, structural characterization, and electronic properties of the $LaNi_{1-x}W_xO_3$ ($0 \le x \le 0.25$) perovskite-like system. J Solid State Chem. 1996;125(1):47–53. doi:10.1006/jssc.1996.0263

$LaNiO_3$-based perovskites are assumed to be a good mixed ionic-electronic conductors:

Che W, Wei M, Sang Z, Ou Y, Liu Y, Liu J. Perovskite $LaNiO_{3-\delta}$ oxide as an anion-intercalated pseudocapacitor electrode. J Alloys Compd. 2018;731:381–8. doi:10.1016/j.jallcom.2017.10.027

Lu Y, Akbar M, Xia C, Mi Y, Ma L, Wang B, Zhu B. Catalytic membrane with high ion–electron conduction made of strongly correlated perovskite $LaNiO_3$ and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ for fuel cells. J Catal. 2020;386:117–25. doi:10.1016/j.jcat.2020.04.004

However, up to now, no one published or even studied the effect of W doping on the oxygen transport properties of Ni perovskites. If such a doping deteriorates oxygen mobility, this, along with the other mentioned reasons, can explain why $CLWO_{reox}$ was not comparable to LWO even after removing the supposed blocking factor of CuO and NiO nanoparticles.

6) The captions to Figures 11 and 12 do not correspond to the content.

Reply:

Corrected as follows:

“Schematic illustration of the model of oxygen isotope exchange between $C^{18}O_2$ and oxide.”

“Arrhenius plots for oxygen incorporation coefficient (a) and tracer diffusion coefficient (b) acquired for the $La_{27}W_5O_{55.5-\delta}$ samples sintered in furnace (LWO) and by RTS (LWO_{RT}) from the TPIE $C^{18}O_2$ data.”

Responses to the comments of Reviewer #2

We are thankful to the honored Editor and Reviewers for the helpful comments. The respective corrections have been made and highlighted yellow. The responses are given below.

Reviewer 2:

The manuscript, entitled 'Structural and transport properties of La tungstate and its composite with nickel (II) - copper (II) oxide', is devoted to studies of composite materials with triple conductivity. This field is a popular area of research, and these materials have the potential for practical use. The research topics and the manuscript meet the requirements of the CTA journal, and the manuscript can be considered for publication after revision.

- In the experimental part, describe in more detail or provide references to published papers concerning the methodology of research in the atmosphere of labelled carbon dioxide.

Reply:

The following references concerning the methodology have been provided:

> Sadykov V, Sadovskaya E, Bobin A, Kharlamova T, Uvarov N, Ulikhin A, Argirusis C, Sourkouni G, Stathopoulos V. Temperature-programmed $C^{18}O_2$ SSITKA for powders of fast oxide-ion conductors: estimation of oxygen self-diffusion coefficients. Solid State Ionics. 2015;271:69–72. doi:10.1016/j.ssi.2014.11.004
>
> Sadykov VA, Sadovskaya EM, Uvarov NF. Methods of isotopic relaxations for estimation of oxygen diffusion coefficients in solid electrolytes and materials with mixed ionic-electronic conductivity. Russ J Electrochem. 2015;51(5):458–67. doi:10.1134/S1023193515050109
>
> Sadykov VA, Sadovskaya EM, Eremeev NF, Skriabin PI, Krasnov AV, Bespalko YuN, Pavlova SN, Fedorova YuE, Pikalova EYu, Shlyakhtina AV. Oxygen mobility in the materials for solid oxide fuel cells and catalytic membranes (Review). Russ J Electrochem. 2019;55(8):701–18. doi:10.1134/S1023193519080147

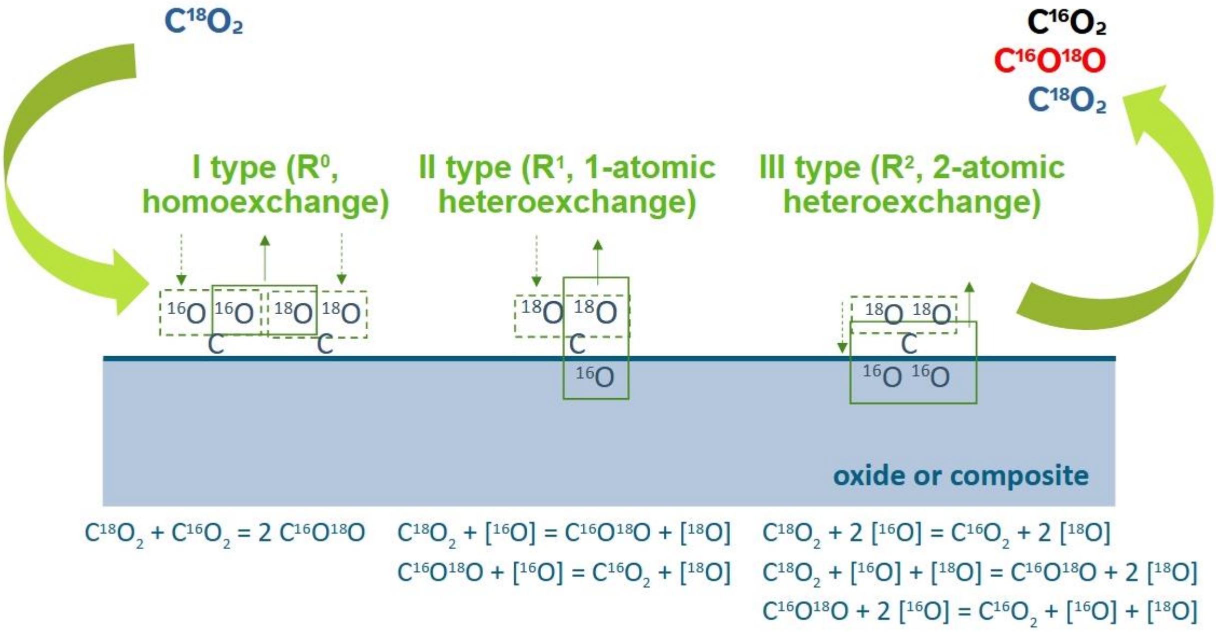
- The appearance of the c16o18o is not obvious. Describe in detail the recombination process.

Reply:

Routes of the recombination process are various and can be grouped into three types of the exchange mechanism according to the Muzykantov’s classification as given in the classical works including the following:

> Muzykantov VS, Popovski VV, Boreskov GK. Kinetika izotopnogo obmena v sisteme molekulyarnyi kislorod - tvyodyi okisel [Kinetics of isotope exchange in molecular oxygen - solid oxide system]. Kinet Katal. 1964;5(4):624–9. Russian.

The following image describing isotope exchange processes has been added to the Supplementary materials:



- *Since a mixture of C16O2 + C18O2 was used specify the concentration of C18O2 in this mixture.*

Reply:

Various mixtures (containing 0.9–1.0 vol. % CO_2 total) were prepared, since various isotope exchange experiments were divided by some periods of time. The content of $C^{16}O_2$, $C^{16}O^{18}O$ and $C^{18}O_2$ depend on the purveyor selling the original $C^{18}O_2$. Such a little variation should not affect the calculated diffusion coefficient values. E.g., the mixture used for LWO sample contains 0.03 vol. % $C^{16}O_2$, 0.17 vol. % $C^{16}O^{18}O$ and 0.70 vol. % $C^{18}O_2$ as depicted in Figure 1.

- *Specify the methodology for the preparation of Ni0.5Cu0.5O.*

Reply:

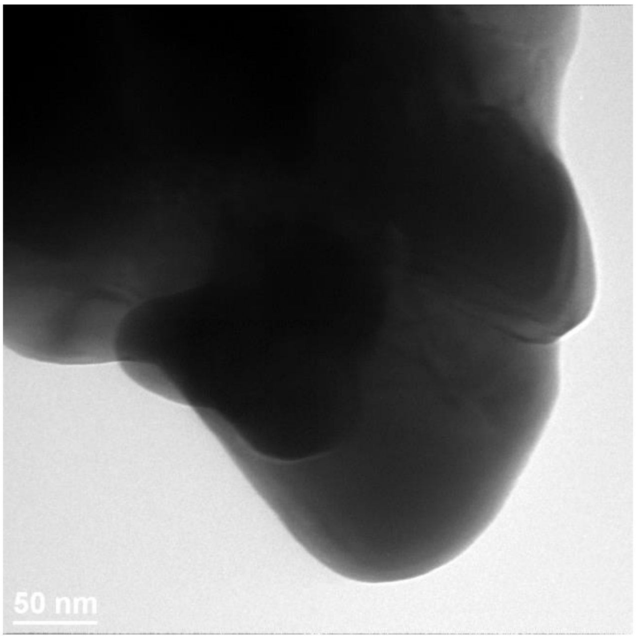
Pure $Ni_{0.5}Cu_{0.5}O$ has been not prepared itself. Only the composites with designed composition of 30 wt. % $Ni_{0.5}Cu_{0.5}O$ + LWO were prepared via mechanical activation of the LWO, NiO and CuO powders. The synthesis process is identical to the one described in authors' previous work:

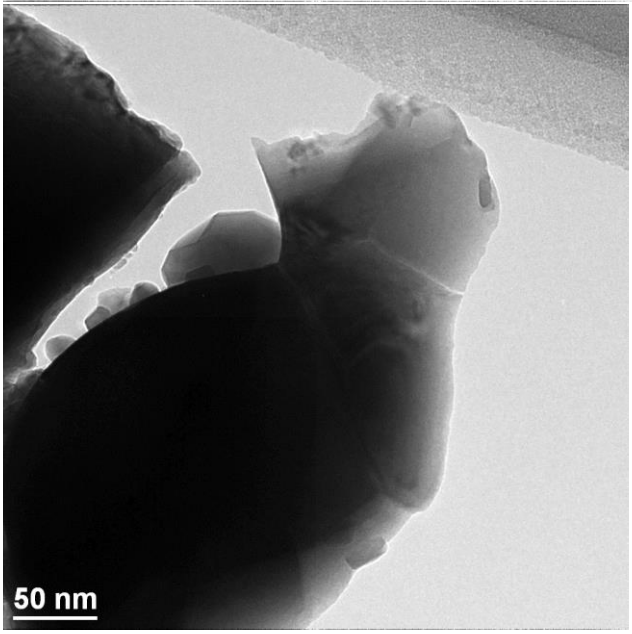
> Eremeev NF, Bespalko YuN, Sadovskaya EM, Skriabin PI, Krieger TA, Ishchenko AV, Sadykov VA. Structural and transport properties of Nd tungstates and their composites with $Ni_{0.5}Cu_{0.5}O$ obtained by mechanical activation. Dalton Trans. 2022;51(19):7705–14. doi:10.1039/d2dt00498d

- For what reason there is no HR TEM data for the composite material? The most interesting is the phase boundary in the composite material.

Reply:

HR TEM data for the composite have been provided. Example images:





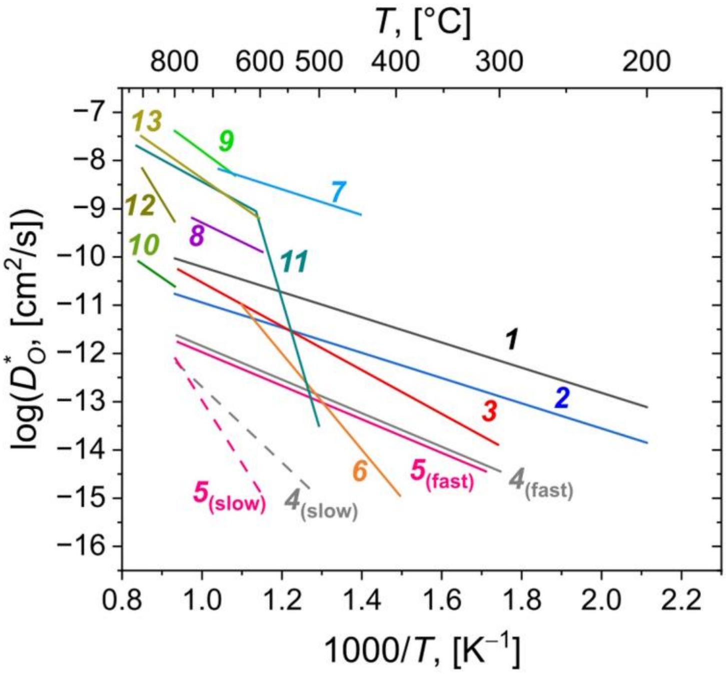
According to the HR TEM data, the composite sample possesses the extended defect features similar to those of the LWO sample including the presence of grain boundaries and other extended defects.

- Compare diffusion coefficients with data for popular proton conducting materials.

Reply:

The comparison has been added to the Supplementary materials:

Oxygen tracer diffusion coefficients:



1 – LWO (this work), *2* – LWO_{RT} (this work),

3 – $Er_{5.5}MoO_{11.25-\delta}$ [Shlyakhtina AV, Lyskov NV, Šalkus T, Kežionis A, Patrakeev MV, Leonidov IA, Shcherbakova LG, Chernyak SA, Shefer KI, Sadovskaya EM, Eremeev NF, Sadykov VA. Conductivity and oxygen diffusion in bixbyites and fluorites $Ln_{6-x}MoO_{12-\delta}$ (Ln = Er, Tm; x = 0, 0.5). Int J Hydrog Energy. 2021;46(32):16965–76. doi:10.1016/j.ijhydene.2021.02.029]

4 – $La_{0.99}Ca_{0.01}NbO_4$, *5* – $La_{0.99}Ca_{0.01}NbO_4$–$LaNb_3O_9$ [Sadykov VA, Bespalko YuN, Krasnov AV, Skriabin PI, Lukashevich AI, Fedorova YuE, Sadovskaya EM, Eremeev NF, Krieger TA, Ishchenko AV, Belyaev VD, Uvarov NF, Ulihin AS, Skovorodin IN. Novel proton-conducting nanocomposites for hydrogen separation membranes. Solid State Ionics. 2018;322:69–78. doi:10.1016/j.ssi.2018.05.003]

6 – $Sm_{1.9}Ca_{0.1}ScTaO_{7-\delta}$ [Shlyakhtina AV, Pigalskiy KS, Belov DA, Lyskov NV, Kharitonova EP, Kolbanev IV, Borunova AB, Karyagina OK, Sadovskaya EM, Sadykov VA, Eremeev NF. Proton and oxygen ion conductivity in the pyrochlore/fluorite family of $Ln_{2-x}Ca_xScMO_{7-\delta}$ (Ln = La, Sm, Ho, Yb; M = Nb, Ta; x = 0, 0.05, 0.1) niobates and tantalates. Dalton Trans. 2018;47(7):2376–92. doi:10.1039/c7dt03912c]

7 – $La_{9.83}Si_5Al_{0.75}Fe_{0.25}O_{26.5}$ [Sadykov VA, Sadovskaya EM, Eremeev NF, Skriabin PI, Krasnov AV, Bespalko YuN, Pavlova SN, Fedorova YuE, Pikalova EYu, Shlyakhtina AV. Oxygen mobility in the materials for solid oxide fuel cells and catalytic membranes (Review). Russ J Electrochem. 2019;55(8):701–18. doi:10.1134/S1023193519080147]

8 – $Ca_3Co_4O_{9\pm\delta}$ [Thoréton V, Hu Y, Pirovano C, Capoen E, Nuns N, Mamede AS, Dezanneau G, Yoo CY, Bouwmeester HJM, Vannier RN. Oxygen transport kinetics of the misfit layered oxide $Ca_3Co_4O_{9+\delta}$. J Mater Chem A. 2014;2(46):19717–25. doi:10.1039/C4TA02198C]

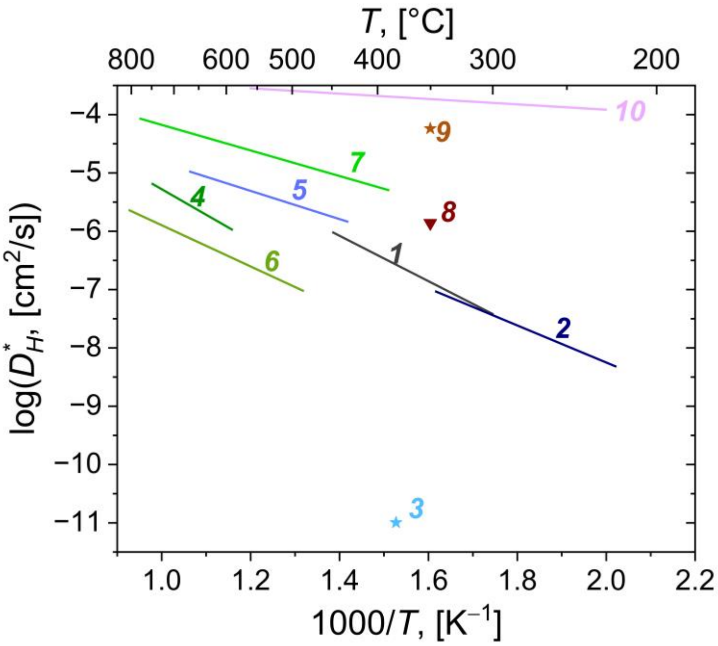
9 – $Sr_{1.95}Fe_{1.4}Ni_{0.1}Mo_{0.5}O_{6-\delta}$ [Porotnikova NM, Khodimchuk AV, Zakharov DM, Bogdanovich NM, Osinkin DA. Enhancement of surface exchange and oxygen diffusion of $Sr_{1.95}Fe_{1.4}Ni_{0.1}Mo_{0.5}O_{6-\delta}$ oxide determined by two independent isotope exchange methods. Appl Surf Sci. 2023;613:156015. doi:10.1016/j.apsusc.2022.156015]

10 – $BaZr_{0.80}Y_{0.20}O_{3-\delta}$ [Farlenkov AS, Ananyev MV, Eremin VA, Porotnikova NM, Kurumchin EKh, Melekh B-T. Oxygen isotope exchange in doped calcium and barium zirconates. Solid State Ionics. 2016;290:108–15. doi:10.1016/j.ssi.2016.04.015]

11 – $BaCe_{0.9}La_{0.1}O_{3-\delta}$ [De Souza RA, Kilner JA, Jeynes C. The application of secondary ion mass spectrometry (SIMS) to the study of high temperature proton conductors (HTPC). Solid State Ionics. 1997;97(1–4):409–19. doi:10.1016/S0167-2738(97)00038-6]

12 – $LaScO_{3-\delta}$, *13* – $La_{0.91}Sr_{0.09}ScO_{3-\delta}$ [Farlenkov AS, Khodimchuk AV, Shevyrev NA, Stroeva AYu, Fetisov AV, Ananyev MV. Oxygen isotope exchange in proton-conducting oxides based on lanthanum scandates. Int J Hydrog Energy. 2019;44(48):26577–88. doi:10.1016/j.ijhydene.2019.08.088]

Hydrogen tracer diffusion coefficients:



1 – $La_{27.15}W_{4.85}O_{55-\delta}$ [Hancke R, Li Z, Haugsrud R. Thermogravimetric relaxation study of the proton conductor lanthanum tungstate, $La_{28-x}W_{4+x}O_{54+\delta}v_{2-\delta}$, $x = 0.85$. Int J Hydrog Energy. 2012;37(9):8043–50. doi:10.1016/j.ijhydene.2011.11.050]

2 – $La_{27.15}W_{4.85}O_{55-\delta}$ [Hancke R, Fearn S, Kilner JA, Haugsrud R. Determination of proton- and oxide ion tracer diffusion in lanthanum tungstate (La/W = 5.6) by means of ToF-SIMS. Phys Chem Chem Phys. 2012;14(40):13971–8. doi:10.1039/c2cp42278f]

3 – $Nd_{5.5}WO_{11.25-\delta}$ [Sadykov VA, Bespalko YuN, Pavlova SN, Skriabin PI, Krasnov AV, Eremeev NF, Krieger TA, Sadovskaya EM, Belyaev VD, Vinokurov ZS. Protonic mobility of neodymium tungstate. J Electrochem En Conv Stor. 2017;14(4):044501. doi:10.1115/1.4037957]

4 – $Sr_{1.95}Fe_{1.5}Mo_{0.5}O_{6-\delta}$ [Osinkin DA. Electrochemical behaviour of redox-robust electrode in contact with protonic electrolyte: Case of double-layered $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ - $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ composite. Int J Hydrog Energy. 2024;77:1066–73. doi:10.1016/j.ijhydene.2024.06.266, Ren R, Sun J, Wang G, Xu C, Qiao J, Sun W, Wang Z, Sun K. Rational design of $Sr_2Fe_{1.5}Mo_{0.4}Y_{0.1}O_{6-\delta}$ oxygen electrode with triple conduction for hydrogen production in protonic ceramic electrolysis cell. Sep Purif Technol. 2022;299:121780. doi:10.1016/j.seppur.2022.121780]

5 – $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ [Osinkin DA. Electrochemical behaviour of redox-robust electrode in contact with protonic electrolyte: Case of double-layered $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ - $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ composite. Int J Hydrog Energy. 2024;77:1066–73. doi:10.1016/j.ijhydene.2024.06.266, Kreuer KD. Aspects of the formation and mobility of protonic charge carriers and the stability of perovskite-type oxides. Solid State Ionics. 1999;125 (1–4):285–302. doi:10.1016/S0167-2738(99)00188-5]

6 – $La_{0.91}Sr_{0.09}ScO_{3-\delta}$ [Farlenkov AS, Vlasov MI, Porotnikova NM, Bobrikov IA, Khodimchuk AV, Ananyev MV. Hydrogen diffusivity in the Sr-doped $LaScO_3$ proton-conducting oxides. Int J Hydrog Energy. 2020;45(43):23455–6810. doi:10.1016/j.ijhydene.2020.06.148]

7 – Ni [Osinkin DA. Electrochemical behaviour of redox-robust electrode in contact with protonic electrolyte: Case of double-layered $Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$ - $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ composite. Int J Hydrog Energy. 2024;77:1066–73. doi:10.1016/j.ijhydene.2024.06.266, Edwards AG. Measurement of the diffusion rate of hydrogen in nickel. Br J Appl Phys. 1958;8(10):406–10. doi:10.1088/0508-3443/8/10/306]

8 – $Cu_{0.447}Pd_{0.553}$, *9* – $Cu_{0.554}Pd_{0.446}$ [Piper J. Diffusion of hydrogen in copper-palladium alloys. J Appl Phys. 1966;37(2):715–21. doi:10.1063/1.1708243]

10 – V [Huang F, Li X, Shan X, Guo J, Gallucci F. Annaland MVS, Liu D. Hydrogen transport through the V-Cr-Al Alloys: Hydrogen solution, permeation and thermal-stability. Sep Purif Technol 2020;240:116654. do:10.1016/j.seppur.2020.116654]

- As it can be seen from SEM the samples have significant porosity. How correct it is to carry out studies of the kinetics of exchange with gas phase on porous samples and how further porosity was taken into account when analyzing the data.

Reply:

The isotope exchange experiments are carried out in plug flow reactor for the samples in the form of 0.25 – 0.5 mm fraction having large pores and voids (references to the methodology are provided above). This should exclude the effect of gas-phase diffusion limitation and retardation. This problem is discussed in details in the Supplement C of the Supplementary materials of the authors' previous work:

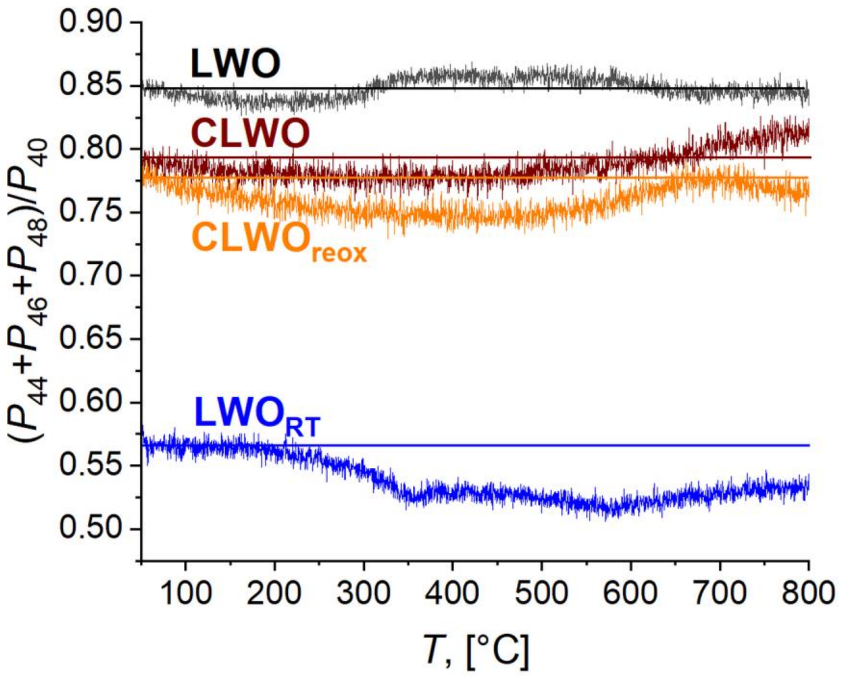
Sadykov VA, Shlyakhtina AV, Lyskov NV, Sadovskaya EM, Cherepanova SV, Eremeev NF, Skazka VV, Goncharov VB, Kharitonova EP. Oxygen diffusion in Mg-doped Sm and Gd zirconates with pyrochlore structure. Ionics. 2020;26(9):4621–33. doi:10.1007/s11581-020-03614-5

In this work, for the LWO samples, the oxygen incorporation coefficient (K) has been introduced in order to describe the limiting process at low temperatures (at higher temperatures, bulk diffusion is limiting). K can be a net parameter of mass exchange between gas and solid phases which can include gas-phase diffusion of CO_2 molecules in the sample pores, the surface heteroexchange rate and the sample surface layer permeability with respect to the oxide anions (as discussed in the Section 3.4 and illustrated in Figure 11). The RTS sample possesses lower K values compared to the conventionally sintered one which is probably due to the effect of less porosity. For the composite samples, bulk oxygen diffusion is limiting, so the porosity effect cannot be estimated.

- How stable are LWO and CLWO in a carbon dioxide atmosphere at experimental temperatures?

Reply:

The stability under the CO_2 atmosphere has not been studied yet, since there are little amounts of samples used for the isotope exchange studies (50 mg) which is not enough for XRD studies. Undirect information on the stability can be acquired from the dependencies of total CO_2 content showing absence or presence of adsorption/desorption of CO_2 during TPIE run. This can be given from the sum of partial pressures of $C^{16}O_2$, $C^{16}O^{18}O$ and $C^{18}O_2$ divided by partial pressure of Ar (which concentration remains constant) in the mass-spectrometer chamber:



As follows from the Figure above, there are some deviations from the linear behavior which can make evidence that CO_2 can be adsorbed and desorbed at some temperatures in a small amounts which apparently results in formation of surface carbonates.

- The influence of redox is poorly described. Why do not you consider the possibility of changing the microstructure, namely porosity, which will also lead to a change in the exchange rate.

Reply:

The redox properties of materials can affect the oxygen mobility in the following way. W^{6+} is a reducible cation, and its reduction to lower valency can result in generating more oxygen vacancies and, hence higher oxygen mobility. Less W content can result in decreasing the oxygen mobility for this reason as well. This is in agreement with TGA, TPR H_2 and TPD O_2 data for La tungstates with different La:W ratio presented in the work:

> Chen Y, Wei Y, Xie H, Zhuang L, Wang H. Effect of the La/W ratio in lanthanum tungstate on the structure, stability and hydrogen permeation properties. J Memb Sci. 2017;542:300–6. doi:10.1016/j.memsci.2017.08.031

as well as electrical conductivity behavior analysis:

> Seeger J, Ivanova ME, Meulenberg WA, Sebold D, Stöver D, Scherb T, Schumacher G, Escolástico S, Solís C, Serra JM. Synthesis and characterization of nonsubstituted and substituted proton-conducting $La_{6-x}WO_{12-y}$. Inorg Chem. 2013;52(18):10375–86. doi:10.1021/ic401104m

According to the XPS data for La tungstates, depending on La:W ratio and synthesis techniques, W can be presented only in the form of W^{6+}:

Vøllestad E, Gorzkowska-Sobas A, Haugsrud R. Fabrication, structural and electrical characterization of lanthanum tungstate films by pulsed laser deposition. Thin Solid Films. 2012;520(21):6531–4. doi:10.1016/j.tsf.2012.06.060

Kojo G, Shono Y, Ushiyama H, Oshima Y, Otomo J. Influence of La/W ratio on electrical conductivity of lanthanum tungstate with high La/W ratio. J Solid State Chem. 2017;248:1–8. doi:10.1016/j.jssc.2017.01.011

or in the forms of W^{6+} + W^{5+} + W^{4+}:

Escolástico S, Balaguer M, Solís C, Toldra-Reig F, Somacescu S, Gerhards U, Aguadero A, Haas-Santo K, Dittmeyer R, Serra JM. Promotion of mixed protonic–electronic transport in $La_{5.4}WO_{11.1-\delta}$ membranes under H_2S atmospheres. J Mater Chem A. 2023;11(32):17246–56. doi:10.1039/d3ta01827j

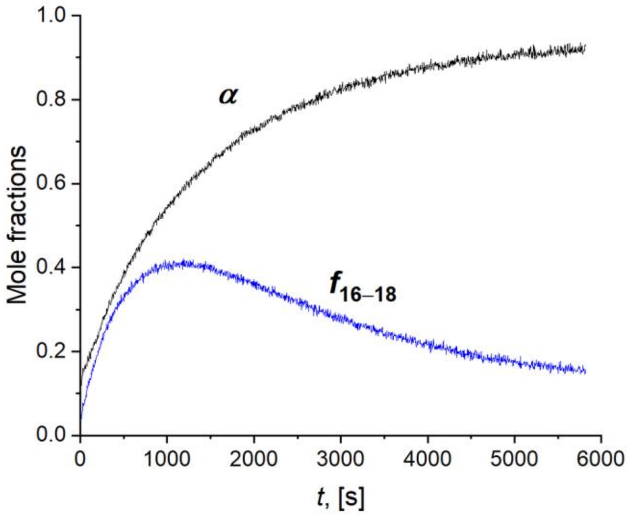
For the composites, the contain different La tungstate phases compared to the LWO samples, and their redox properties can differ from the LWO as well.

The related statements have been added into the Section 3.4.

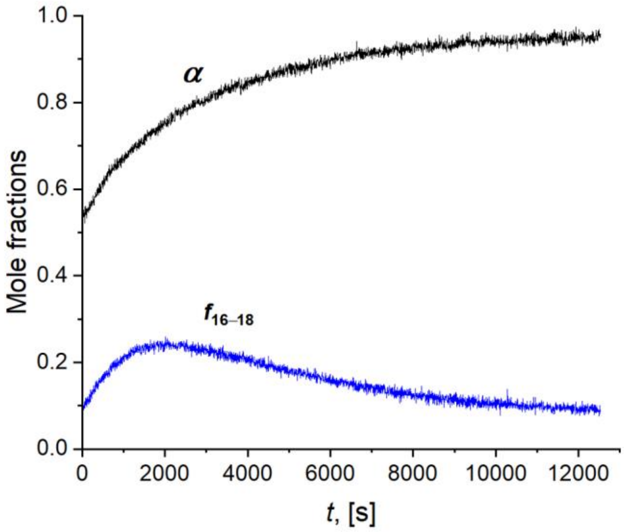
We do consider the effect of porosity on the oxygen incorporation coefficient (K), the effective parameter mentioned above. It may include the surface exchange rate, however, the experiments with $^{18}O_2$ are required for accurate estimation of the surface exchange rate.

Isothermal isotope exchange (IIE) with $^{18}O_2$ experiments for La tungstate samples were carried out at 800 °C in order to show the difference in oxygen heteroexchange rate:

LWO:



LWO_{RT}:



Indeed, the conventionally sintered LWO sample demonstrated higher heteroexchange rate
($1.6\cdot10^{-4}$ mol/(m² s)) compared to the e-beam sintered one ($5.1\cdot10^{-5}$ mol/(m² s)) which can be associated, in particular, with the difference in microstructure including the porosity.

For the composite samples, such experiments have not been carried out since they possess much lower oxygen transport properties and can be insensitive to the exchange with $^{18}O_2$ at the temperature range that we are able to carry out such experiments. Unfortunately, our equipment does not allow us to carry out the isotope exchange experiments at the temperatures above 800 °C.

The IIE $^{18}O_2$ data have been added to the Supplementary materials.

- There are no unambiguous conclusions about the positive or negative effect of NCO addition on LWO transport properties

Reply:

The main positive effect of NCO addition is increasing electronic conductivity which is relatively low for pure LWO. Mixed protonic-electronic conductivity is required for fine operation of hydrogen separation membrane to avoid limiting the hydrogen permeability by coupled electron transport. In reducing conditions, NCO transforms into NiCu alloy which possess a high protonic conductivity as well.

The negative effect is related to the phase composition, hydrogen and oxygen transport properties which is discussed in this work. Moreover, the hydrogen and oxygen transport properties of the main phase in the composites, the $LaNi_{0.8}W_{0.2}O_{3-\delta}$ perovskite, have not been studied yet. Without this information missing in the literature, there is a complicated task to predict its performance as hydrogen separation membrane component.

- consider citing works:

on the use of proton-conducting oxide for hydrogen separation

https://doi.org/10.1016/j.jechem.2022.02.019

table data on proton and oxygen diffusion coefficients

https://doi.org/10.1016/j.ijhydene.2024.06.266

Reply:

We thank the Reviewer for providing very useful links. The articles have been cited.

2nd peer-review round

Reviewer #1 | acceptance

The authors responded to the comments and made appropriate changes to the manuscript. The article may be accepted for publication.

Reviewer #2 | acceptance

I have reviewed the revised manuscript, and I believe it has been significantly improved. The authors have added necessary corrections, new points, and detailed answers to the reviewers' comments. I believe that the manuscript can be considered for publication without further improvements.

Final Editor's decision

Accept.