



## Novel proton-conducting nanocomposites for hydrogen separation membranes



V.A. Sadykov<sup>a,b</sup>, Yu.N. Bepalko<sup>a</sup>, A.V. Krasnov<sup>a</sup>, P.I. Skriabin<sup>a</sup>, A.I. Lukashevich<sup>a</sup>,  
Yu.E. Fedorova<sup>a</sup>, E.M. Sadovskaya<sup>a,b</sup>, N.F. Ereemeev<sup>a,\*</sup>, T.A. Krieger<sup>a,b</sup>, A.V. Ishchenko<sup>a,b</sup>,  
V.D. Belyaev<sup>a</sup>, N.F. Uvarov<sup>c,d</sup>, A.S. Ulihin<sup>c</sup>, I.N. Skovorodin<sup>e</sup>

<sup>a</sup> Borekov Institute of Catalysis SB RAS, pr. Akad. Lavrentieva 5, Novosibirsk 630090, Russia

<sup>b</sup> Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia

<sup>c</sup> Institute of Solid State Chemistry and Mechanochemistry SB RAS, Kutateladze str. 18, Novosibirsk 630128, Russia

<sup>d</sup> Novosibirsk State Technical University, pr. Karla Marksa 20, Novosibirsk 630073, Russia

<sup>e</sup> Institute of Automation and Electrometry SB RAS, Academician Koptyug ave. 1, Novosibirsk 630090, Russia

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### ABSTRACT

Design of oxide and nanocomposite materials with high mixed protonic-electronic conductivity such as lanthanide niobates and tungstates is encouraging approach in developing hydrogen separation membranes. This work aims at elucidating the relation of structure, oxygen and protonic mobility of such materials.  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ ,  $\text{LaNb}_3\text{O}_9$  and  $\text{Nd}_{5.5}\text{WO}_{11.25-8}$  were synthesized by Pechini and citrate route. Nanocomposites with  $\text{LaNb}_3\text{O}_9$  and  $\text{Ni} + \text{Cu}$  were prepared by ultrasonic dispersion or mechanical treatment in a high energy mill and wet impregnation, then sintered using conventional thermal sintering and hot pressing. All obtained materials were characterized using XRD, SEM, TEM with EDX analysis, IR and Raman spectroscopy. The oxygen and proton mobility were studied by isotope exchange, unit cell volume and weight relaxation techniques. The proton conductivity was studied by Van der Pauw technique. The main phases were scheelite for  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ , perovskite for  $\text{LaNb}_3\text{O}_9$  and fluorite for  $\text{Nd}_{5.5}\text{WO}_{11.25-8}$ , extended defects were observed agreeing with IR and Raman spectroscopy data. The oxygen mobility studies revealed two types of bulk oxygen related to two phases in samples.  $\text{D}_2\text{O}$  exchange studies demonstrated very fast protonic transport in samples.  $\text{H}_2\text{O}$  desorption experiments revealed the working temperature range being 300–450 °C. The protonic conductivity values ( $\sim 10^{-4} \Omega^{-1} \text{cm}^{-1}$  at 400 °C) agree with the literature data and are sufficiently high for the practical application. Proton tracer and chemical diffusion coefficients values are  $\sim 10^{-11}$  and  $\sim 10^{-3} \text{cm}^2/\text{s}$  at working temperatures, respectively. Successful test of proton conducting membrane with  $\text{Nd}_{5.5}\text{WO}_{11.25-8}$  based functional layer showing promising performance has been carried out.

### 1. Introduction

A fuel processor based on catalytic reactor with hydrogen separation membrane [1–3] is clean and sustainable technology for hydrogen production by transformation of fuels into syngas. Such device allows producing pure  $\text{H}_2$  separated from other reaction products from biofuels [4–6]. There are many studies devoted to development and performance of membranes containing homogenous gas-tight pellet [7–9] as well as silica, zeolite, polymer membranes etc. [5,6], the promising approach is also using ceramic or cermet membranes [10–13]. Asymmetric supported hydrogen separation membrane typically consists of compressed porous metallic (e.g. Ni-Al foam) or cermet substrate, porous and dense functional layers of mixed ionic (protonic) –

electronic conductors (MIEC), dense buffer nanocomposite and porous catalytic layers [13,14].

The main purpose of MIEC functional layers is to transport hydrogen from the fuel side to the permeate one, so they should have a high protonic/electronic conductivity as well as the surface reactivity to provide promising membrane performance. Design of oxide and nanocomposite materials with high mixed protonic-electronic conductivity for functional layers is encouraging approach in developing hydrogen separation membranes. The most promising materials are based on lanthanum niobates with fergusonite, scheelite or perovskite structure [15], alkaline earth metal cerates/zirconates with perovskite structure [10,16,17], lanthanide titanates with pyrochlore structure [18], molybdates and tungstates [7–9,19–25]. Such materials demonstrate a

\* Corresponding author.

E-mail addresses: [yeremeev21@gmail.com](mailto:yeremeev21@gmail.com), [yeremeev21@catalysis.ru](mailto:yeremeev21@catalysis.ru) (N.F. Ereemeev).

high protonic conductivity due to features of their defect structure.

Rare-earth ortho-niobates and ortho-tantalates such as 1% Ca-doped  $\text{LaNbO}_4$  provide a high proton conductivity ( $\sim 10^{-3}$  S/cm at 900 °C) [15,26,27].  $\text{RE}_{1-x}\text{A}_x\text{MO}_{4-\delta}$  (RE = rare-earth metals, A = acceptor dopant (e.g., Ca), M = Nb or Ta) are electronic, pure ionic or mixed ionic-electronic conductors depending on conditions. Both the low-temperature monoclinic and high-temperature tetragonal polymorphs of  $\text{RE}_{1-x}\text{A}_x\text{MO}_{4-\delta}$  demonstrate a high proton mobility [27]. While preparing  $\text{LaNbO}_4$ , admixture of  $\text{La}_3\text{NbO}_7$  or  $\text{LaNb}_3\text{O}_9$  may form [15,26].  $\text{LaNb}_3\text{O}_9$  demonstrates relatively high n-type electronic conductivity [15,28]. The other advantage of such niobates and tantalates is their high chemical stability in humid and  $\text{CO}_2$ -rich atmospheres [15,27,29]. Thus, doped  $\text{LaNbO}_4$ – $\text{La}_3\text{NbO}_7$  and  $\text{LaNbO}_4$ – $\text{LaNb}_3\text{O}_9$  nanocomposites are promising materials for the functional MIEC layers of hydrogen separation membranes.

Stable to hydrolysis and carbonization lanthanide tungstates  $\text{Ln}_6\text{WO}_{12-\delta}$  are known to have high mixed protonic-electronic conductivity [8,22,25,30,31]. Such solid solutions have  $\text{Y}_7\text{ReO}_{14}$ -like disordered fluorite superstructure with cubic (for Ln = La–Pr), tetragonal (Nd–Gd) or rhombohedral (Tb–Lu and Y) syngony [23,32–34]. More accurate “ $\text{Ln}_{6-x}\text{WO}_{12-\delta}$ ” composition notation is  $\text{Ln}_{28-x}\text{W}_4+x\text{O}_{54+1.5x}\text{V}_O\text{ }_{2-1.5x}$  ( $\text{V}_O$  is the oxygen vacancy) [24,32]. For Nd tungstates  $\text{Nd}_{6-x}\text{WO}_{12-\delta}$  consisting of cubic, tetragonal phase or their mixture depending on the method of their preparation and sintering [7,34,35],  $\text{Nd}_2\text{O}_3$  admixture is present for  $x = 0$ , the optimal  $x$  value seems to be 0.3–1 according to studies devoted to similar systems [7,24,32,33]. In the row of Ln = La, Nd, Gd, Er  $\text{Ln}_6\text{WO}_{12-\delta}$  tungstates a better conductivity (total as well as protonic) was shown for La and Nd-containing samples ( $\sim 10^{-3}$  S/cm) [30]. Ionic transport numbers were shown to be 0.9 and 0.6 at 300 and 600 °C, respectively [32].  $\text{H}^+$  and  $\text{O}^{2-}$  transport dominates amongst ionic mobility at low/intermediate and high temperatures, respectively [20].

This work aims at studying structure features, transport properties such as electrical conductivity, oxygen and protonic mobility and performance characteristics of materials based on La niobates and Nd tungstates.

## 2. Materials and methods

$\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$ ,  $\text{LaNb}_3\text{O}_9$  and  $\text{Sm}_{0.15}\text{Pr}_{0.15}\text{Ce}_{0.35}\text{Zr}_{0.3}\text{O}_{2-\delta}$  were synthesized by modified polymerized precursor (Pechini) route [36], and  $\text{Nd}_{5.5}\text{WO}_{11.25-\delta}$  - by a citrate method with microwave irradiation as described elsewhere [37]. The nanocomposites  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$  (60 wt%)– $\text{LaNb}_3\text{O}_9$  were obtained by ultrasonic dispersion in propan-2-ol using ULTRA TURRAX (IKA, Germany) homogenizer. Nanocomposites Ni + Cu/ $\text{Nd}_{5.5}\text{WO}_{11.25-\delta}$  (70 wt%) were prepared by mechanical treatment in a high energy mill AGO-2 (ZAO NOVIC, Russia) [13,38]. Pelletized samples were sintered by conventional thermal sintering in the furnace at 900–1300 °C and by hot pressing at 1100 °C and 50 MPa during 15 min in Ar in specially built setup using TST 017.010.00 RE press.

All obtained materials were characterized using XRD, TEM with EDX analysis, IR and Raman spectroscopy. X-ray diffraction (XRD) studies were performed using a D8 Advance (Bruker, Germany) diffractometer with Cu-K $\alpha$  monochromatic radiation ( $\lambda = 1.5418$  Å) in 2 $\theta$  range 20–90° with a step of 0.05°. The phase composition analysis was carried out using diffraction databases PDF-2 and ICSD. High resolution transmission electron microscopy (HR TEM) images were obtained with a JEM-2010 (Jeol, Japan) instrument (lattice resolution 1.4 Å, acceleration voltage  $2 \times 10^5$  V). ATR-FTIR spectra (4000–250  $\text{cm}^{-1}$ , 32 scans, resolution 4  $\text{cm}^{-1}$ ) were obtained using a Cary 660 FTIR spectrometer (Agilent Technologies) and a PIKE Technologies GladiATR accessory (diamond crystal). FT-Raman spectra (3600–100  $\text{cm}^{-1}$ , 300 scans, resolution 4  $\text{cm}^{-1}$ , 180° geometry) were recorded using an RFS 100/S Bruker spectrometer. Excitation of the 1064-nm line was provided by a Nd:YAG laser (100 mW power output). Thermal analysis

(DTA/TG) was carried out with a Simultaneous DTA-TG Apparatus DTG-60H SHIMADZU in the flow of air (30 ml/min) at a heating rate of 10 °C/min. The specific surface area of samples was determined from the Ar thermal desorption data by using BET method.

Oxygen mobility and surface reactivity of the ground samples were studied by using the temperature-programmed isotope exchange (TPIE) with  $\text{C}^{18}\text{O}_2$  in open and closed reactors. In the flow mode of experiments pretreatment was carried out at 700 °C in 1%  $\text{O}_2$  + He stream during 30 min, while the heteroexchange was carried out with 1%  $\text{C}^{18}\text{O}_2$  + He stream in 50–800 °C range with 5 °C/min ramp. In the static mode of exchange, samples were pretreated in air at 650 °C for 2 h, then, after degassing at the same temperature up to  $\sim 10^{-6}$ – $10^{-7}$  Torr, samples were cooled down to room temperature. After introducing  $\text{C}^{18}\text{O}_2$  into the reactor space (gas phase volume  $\sim 680$   $\text{cm}^3$ , pressure 1.4–2.1 Torr), the linear temperature ramp of 5 K/min up to 700 °C was started. The gas phase composition was analyzed by using UGA-200 mass spectrometer (Stanford Research Systems, USA) for the experiments in the open reactor and SRS QMS200 mass spectrometer (Stanford Research Systems, USA) for the experiments in the closed reactor. Time dependencies of  $\text{C}^{16}\text{O}^{18}\text{O}$  molecules fraction  $f_{16-18}(t)$  and  $^{18}\text{O}$  atoms fraction  $\alpha(t)$  (referred to as isotope kinetic curves) were analyzed by using isotope kinetic equations [39–43].

The electrical conductivity studies were carried out using two techniques. Samples of solid electrolytes not containing metals additives were investigated by impedance spectroscopy technique in two electrode cells placed in dry or humid air atmosphere using a HP-4284A Precision LCR Meter in the ac-frequency range of 20 Hz–1 MHz. Bulk conductivity values were determined from the analysis of  $Z''$ - $Z'$  plots. Protonic conductivity of composites containing metals were determined on compact samples by 4-probes Van der Pauw technique in the galvanostatic mode with 4 ion-selective probes made of proton conducting ceramics  $\text{La}_{0.99}\text{Ca}_{0.01}\text{NbO}_4$  similar to the technique described by Hebb [44]. The ionic probes completely block electronic current and are reversible electrodes for protons. Measurements were carried out in atmosphere of humid hydrogen using IPU-1 Meter (Russia) in the temperature range of 50–750 °C. Humid hydrogen atmosphere was used to avoid oxidation of metals and provide proton conductivity of ionic probes.

The protonic mobility and surface reactivity characteristics were studied by the temperature programmed desorption of  $\text{H}_2\text{O}$ , isotope exchange of the oxide bulk protons with  $\text{D}_2\text{O}$  and mass relaxation after abrupt change of humidity. The temperature programmed desorption of  $\text{H}_2\text{O}$  (TPD  $\text{H}_2\text{O}$ ) was carried out for powdered samples pretreated at 150 °C in overheated (300 °C) water steam. Pretreatment was carried out at  $T = 100$ – $450$  °C in a static reactor.

Studies of the isotope heteroexchange of the oxide bulk protons with  $\text{D}_2\text{O}$  were performed for powdered samples at 0.08 Torr pressure in closed reactor. The gas phase composition was analyzed by using a SRS QMS200 mass spectrometer (Stanford Research Systems, USA). The studies were carried out in the isothermal mode (IIE) at the optimal temperature preliminary determined by TPD  $\text{H}_2\text{O}$ . The values of proton tracer diffusion coefficient  $D_H$  were determined as described elsewhere [42,45].

Mass relaxation studies were carried out for pelletized samples using humidified 5.5%  $\text{O}_2$  +  $\text{N}_2$  gas stream. Dependencies of the sample mass  $m(t)$  were recorded after an abrupt change of the gas humidity ( $P(\text{H}_2\text{O})$  2  $\rightarrow$  10 mbar and back) using a STA 409 PC “LUX” NETZSCH machine (Netzsch, Germany). Chemical diffusion coefficients  $D_{chem}$  and exchange constants  $k_{chem}$  were estimated using the multifold model allowing distinguishing two and more transport processes as described elsewhere [46–48].

For hydrogen separation membrane building, upgraded Ni/Al foam substrates kindly provided by Powder Metallurgy Institute (Republic of Belarus) were used. For design of supported membranes disc-shaped planar Ni/Al foam substrates (average porosity  $\sim 0.6$ , mean cell size  $\sim 0.02$  mm) with diameters 26 mm and thickness 1 mm fixed in

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