



## Evaluation of lanthanum tungstates as electrolytes for proton conductors Solid Oxide Fuel Cells



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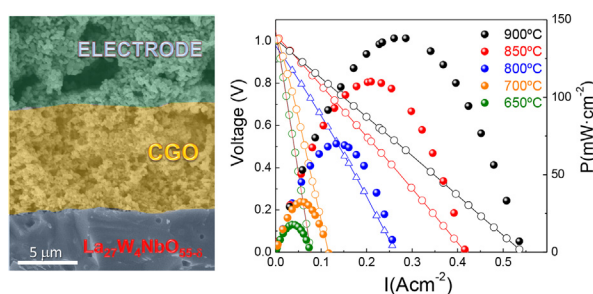
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### HIGHLIGHTS

- $\text{La}_{27}\text{W}_4\text{NbO}_{55-\delta}$  is evaluated as a proton conductor for SOFCs.
- Chemical compatibility and performance of  $\text{La}_{27}\text{W}_4\text{NbO}_{55-\delta}$  with different electrodes is investigated.
- A CGO buffer layer, deposited between the electrolyte and electrodes, improves the performance.
- A fuel cell with a 350  $\mu\text{m}$ -thick electrolyte rendered a power density of 140  $\text{mW cm}^{-2}$  at 900 °C.

### GRAPHICAL ABSTRACT



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### ABSTRACT

$\text{La}_{27}\text{W}_4\text{NbO}_{55-\delta}$  (LWNO) has been tested as electrolyte for proton conductor Solid Oxide Fuel Cells (PC-SOFCs). For this purpose, different electrodes and composite electrodes are considered, including:  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ,  $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ ,  $\text{SrFe}_{0.75}\text{Nb}_{0.25}\text{O}_{3-\delta}$  and NiO. Chemical compatibility between the cell components is investigated by X-ray powder diffraction (XRPD) and energy dispersive spectroscopy (EDS). Furthermore, area specific resistance (ASR) for the different electrodes is determined in symmetrical cells by impedance spectroscopy. XRPD and EDS analysis does not reveal significant bulk reactivity between most of these electrodes and LWNO electrolyte in the typical operating temperature range of an SOFC (600–900 °C). However, minor interdiffusion of elements at the electrolyte/electrode interface has negative effects on both the ohmic losses and electrode polarization of the cells. ASR values are significantly improved by using a porous buffer layer of  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$  (CGO), deposited between the electrolyte and electrode materials, to prevent reactivity. A single cell with a 350  $\mu\text{m}$ -thick electrolyte, NiO-CGO and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ -CGO composite as anode and cathode, respectively, generates maximum power densities of 140 and 18  $\text{mWcm}^{-2}$  at 900 and 650 °C, respectively.

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## 1. Introduction

The reduction of operating temperature of Solid Oxide Fuel Cells (SOFCs) at the range of 400–700 °C is the main challenge for this technology, which would lead to several benefits, including lower working costs, longer lifetime of the cell components and less

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expensive ferritic steels might be used as interconnector materials.

In the last few years, high temperature proton conductors have received greater attention than the corresponding oxide ion conductors because of their high ionic conductivity and potential application in SOFCs at reduced temperatures [1–4].

Most of the prior research on proton conducting electrolytes has been focused on perovskite-type materials based on BaCeO<sub>3</sub> and BaZrO<sub>3</sub> [5–8]. These systems typically display high oxide ion conductivity at elevated temperatures, while in wet atmospheres and intermediates temperatures the conductivity is enhanced through water incorporation into the oxide ion vacancies, leading to the presence of proton defects. These protonic defects account for the proton conductivity observed in these systems.

BaCeO<sub>3</sub>-based materials are the state-of-the-art proton conductors, exhibiting the highest conductivity values ( $\sim 10^{-2}$  S cm<sup>-1</sup> at 600 °C). However, these materials are susceptible to carbonation in the presence of CO<sub>2</sub> [9,10]. In contrast, proton conductors based on BaZrO<sub>3</sub> show better chemical stability against the carbonation, though they require high sintering temperatures (1700 °C) to obtain dense ceramics. Barium zirconates also exhibit lower conductivity compared to BaCeO<sub>3</sub>, mainly due to their high grain boundary resistance, which decreases the overall conductivity and performance.

Alternative proton-conducting materials have been proposed, such as those based on LaNbO<sub>4</sub> that offer high CO<sub>2</sub> tolerance [11,12]. However, the values of conductivity are one order of magnitude lower than those reported for proton conducting perovskites.

More recently, rare-earth tungstates with general composition Ln<sub>6</sub>WO<sub>12</sub> (LWO) have attracted great attention due to their relatively high mixed proton-electron conductivity [13–18]. In general, these materials show predominant proton conductivity at low temperature, while they are mixed ionic-electronic conductors at high temperatures. The chemical stability of LWO in CO<sub>2</sub> and sulphur-containing gases represents one of the main advantages of these materials over the perovskite proton conductors [13–18].

The structural analysis by neutron and synchrotron powder diffraction revealed that these materials crystallize in a cubic structure with space group *F* $\bar{4}3m$  and the composition of the these compounds can be better written as La<sub>28y</sub>W<sub>4+y</sub>O<sub>54+δ</sub>V<sub>2-δ</sub>, where tungsten partially occupies the lanthanum sites, and the oxygen vacancies is determined by the La/W ratio ( $v = 2-\delta$ ;  $\delta = 3y/2$ ) [18–20].

In order to increase the conductivity of lanthanum tungstates, several cation substitutions have been investigated. For instance, the partial substitution of W<sup>6+</sup> by Mo<sup>6+</sup>, La<sub>28-y</sub>(W<sub>1-x</sub>Mo<sub>x</sub>)<sub>4+y</sub>O<sub>54+δ</sub> ( $x = 0-1$ ,  $y = 0.923$ ), increases significantly the ambipolar conductivity, making these materials interesting as mixed electronic-proton conductors for hydrogen gas separation membrane applications [21,22]. Other substitutions, such as Nb<sup>5+</sup>, La<sub>27</sub>(W<sub>1-x</sub>Nb<sub>x</sub>)<sub>5</sub>O<sub>55.5-5x/2</sub> ( $0 \leq x \leq 0.2$ ), increase the oxygen vacancy concentration and the conductivity, i.e. 0.01 S cm<sup>-1</sup> at 800 °C for La<sub>27</sub>NbW<sub>4</sub>O<sub>55-δ</sub> compared to 0.004 S cm<sup>-1</sup> for the non-substituted material La<sub>27</sub>W<sub>5</sub>O<sub>55.5-δ</sub> [23]. These values of conductivity are much lower than those of BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> and BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.1</sub>Yb<sub>0.1</sub>O<sub>3-δ</sub>, comparable to BaZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> and significantly higher compared to La<sub>0.99</sub>Ca<sub>0.01</sub>NbO<sub>4-δ</sub> [24–28]. The conductivity of these proton conductors is compared in Fig. S1 (supplementary content).

Several works have investigated the application of these materials in hydrogen separation membranes, yielding hydrogen fluxes significantly higher than those of the state-of-the-art membranes [29–32]. In contrast, there are a few works about the application of these materials in PC-SOFCs. For instance, Quarez et al. have studied the compatibility of La<sub>6</sub>WO<sub>12-δ</sub> with standard cathode materials: La<sub>0.7</sub>Sr<sub>0.3</sub>MnO<sub>3-δ</sub> (LSM), La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3-δ</sub> (LSCM) and Ba<sub>0.5</sub>Sr<sub>0.5</sub>Co<sub>0.8</sub>Fe<sub>0.2</sub>O<sub>3-δ</sub> (BSCF) [33]. LWO resulted to be chemically

compatible with LSM and LSCM, but secondary phases were observed for BSCF. The values of area specific resistance were relatively elevated, e.g. 4.3 Ω cm<sup>2</sup> for LSM and 9.7 Ω cm<sup>2</sup> for BSCF at 750 °C. Composites of LSM and LWO were also investigated, obtaining ASRs between 3 and 10 Ω cm<sup>2</sup> at 750 °C, depending on the LWO/LSM ratio [33,34]. Quarez et al. have also examined the application of Pr<sub>2</sub>NiO<sub>4</sub> cathode with LWO, achieving ASRs of 0.46 Ω cm<sup>2</sup> at 700 °C, despite the segregation of Pr<sub>6</sub>O<sub>11</sub> [35]. Finally, La<sub>2-x</sub>Pr<sub>x</sub>Ni<sub>1-y</sub>Co<sub>y</sub>O<sub>4-δ</sub> cathodes were investigated, reaching ASRs of 0.62 Ω cm<sup>2</sup> at 750 °C [36].

On the other hand, several anode materials have also been explored with LWO electrolyte. NiO and LWO resulted to be chemically incompatible even at very low temperatures [37]. ASR of 0.47 Ω cm<sup>2</sup> at 700 °C were obtained for La<sub>0.85</sub>Sr<sub>0.15</sub>Cr<sub>0.8</sub>Ni<sub>0.2</sub>O<sub>3-δ</sub>, although Ni segregation was observed under anodic conditions [38]. Ni-infiltrated La<sub>0.75</sub>Ce<sub>0.1</sub>Sr<sub>0.15</sub>CrO<sub>3-δ</sub> anodes exhibited the lowest ASR, i.e. 0.26 Ω cm<sup>2</sup> at 750 °C [39].

Until now, only a fuel cell with Pt electrodes was prepared by Magrasó, rendering a maximum power density of 13.6 mW cm<sup>-2</sup> at 1000 °C [22]. Hence, further studies are still needed for a better characterization of these materials as potential electrolyte for PC-SOFCs on several issues, such as chemical compatibility with different electrode materials, electrochemical performance and fuel cell tests.

The aim of this work is to evaluate the potential use of La<sub>27</sub>W<sub>4</sub>NbO<sub>55-δ</sub> (LWNO) as a solid electrolyte for PC-SOFCs. This electrolyte composition was chosen because of its high ionic transport numbers and conductivity compared to the undoped compound [23]. Chemical compatibility and area-specific resistance, with different electrodes and composite electrode materials, such as La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub>, La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>1-x</sub>Fe<sub>x</sub>O<sub>3-δ</sub>, La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3-δ</sub>, SrFe<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>3-δ</sub> and NiO, are investigated by X-ray powder diffraction, energy dispersive spectroscopy and impedance spectroscopy. Doped ceria was also used as protective buffer layer between the electrolyte and electrode materials to prevent reactivity. In addition, a fuel cell is assembled with the most compatible electrodes to evaluate the performance.

## 2. Experimental

### 2.1. Synthesis

Polycrystalline powders of La<sub>27</sub>W<sub>4</sub>NbO<sub>55-δ</sub> (LWNO) electrolyte were obtained by a freeze-drying precursor method as described in details elsewhere [23]. La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>1-x</sub>Fe<sub>x</sub>O<sub>3-δ</sub> ( $x = 0.2$  and 0.8) cathodes were prepared by a sol-gel citrate precursor method, while La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3-δ</sub> and SrFe<sub>0.75</sub>Nb<sub>0.25</sub>O<sub>3-δ</sub>, used simultaneously as both cathode and anode materials, were prepared from a freeze-drying precursor route (Table 1). The starting reagents were: La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.99%), WO<sub>3</sub> (99.99%), Sr(NO<sub>3</sub>)<sub>2</sub> (99.9%), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98%), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99.99%), Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99%), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%), Nb(HC<sub>2</sub>O<sub>4</sub>)<sub>5</sub>H<sub>2</sub>C<sub>2</sub>O<sub>7</sub> (97%), citric acid and Ethylenediaminetetraacetic acid (EDTA), all of them supplied by Aldrich. The synthesis procedure was similar to that previously reported [40–42]. Commercial powders of La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3-δ</sub> cathode (LSM, Praxair) and Ce<sub>0.8</sub>Gd<sub>0.2</sub>O<sub>2-δ</sub> electrolyte (CGO, Rhodia) were also used. 60wt%NiO-CGO composite powders were prepared by adding the CGO powders into an ethanol solution of nickel nitrate. The solution was dried under stirring at room temperature and finally calcined at 900 °C for 1 h to obtain the composite material.

X-ray powder diffraction (XRPD) patterns were recorded using a PANalytical X'Pert Pro diffractometer with CuK<sub>α1</sub> radiation to determine the purity of the synthesized materials. XRPD was also performed to examine the chemical compatibility between the

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