LaNb_{0.84}W_{0.16}O_{4.08} as a novel electrolyte for solid oxide electrolysis applications

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Abstract

LaNb_{0.84}W_{0.16}O_{4.08} has been successfully synthesized and proposed as an electrolyte for high temperature fuel cell and electrolysis applications due to its remarkable ionic conductivity. A single electrolyte supported cell using standard electrodes has been fabricated and tested in both modes of operation. Due to the high activation energy of this phase, the performance of the cell at 900-950 °C could compete with that of standard zirconia electrolytes. The measured current density of a non-optimized cell (~360 μm of electrolyte thickness) at 950 °C at 0.5V (fuel cell mode) and 1.3 V (electrolysis mode) using 50%H₂O – 50% H₂ as the fuel was about -200 mA cm⁻² and about 250 mA cm⁻², respectively. The reason for the better performance in electrolysis mode is probably associated with the inherent oxygen excess of the LaNb_{0.84}W_{0.16}O_{4.08} phase.

Introduction

One of the major concerns in research related to future energy sources is the production, storage and distribution of hydrogen. The hydrogen economy will require the development of clean and efficient methods for the production of hydrogen. Probably the most advanced nowadays is the generation of hydrogen by electrolysis of water. This technology is widely developed at low temperature using alkaline electrolyzers, and it is currently under continuous research at high temperature (600-1000 °C) using Solid Oxide Electrolysis Cells (SOECs) [1]. At higher temperatures, these devices present numerous advantages in comparison with low temperature devices, as the electrical energy demand is significantly reduced [2].

Currently there are only a limited number of electrolyte materials available for both Solid Oxide Fuel Cells (SOFC) and SOEC applications, as they need to be stable in a wide pO_2 range, ensure fast ion conduction, and present no reactivity with other cell components at the operation temperatures. Even today the most common SOFC electrolyte material is YSZ (yttria stabilized zirconia), based on a simple cubic structure type with oxygen vacancies introduced through ZrO_2 substitution with Y_2O_3 . Although another family of materials such as doped- CeO_2 present higher conductivity values, YSZ is still the most used electrolyte for SOFC/SOEC applications. Despite the relatively low levels of conductivity, these materials have the major advantage of presenting considerable chemical stability as a function of oxygen partial pressure, and they suffer no degradation at a pO_2 as low as 10^{-24} atm. However, there are some further considerations when using doped- ZrO_2 as the electrolyte material, including the reactivity of the electrolyte with cathode materials, for example the formation of insulating phases such as $La_2Zr_2O_7$ [3]. Apart from the fluorites (doped- ZrO_2 and doped CeO_2), many other materials have been proposed as the solid electrolyte for SOFC

1 applications, including perovskite materials based on $\text{La}_{1-x}\text{Sr}_x\text{Ga}_y\text{Mg}_{1-y}\text{O}_{3-\delta}$ (LSGM),
2 electrolytes based on $\text{La}_2\text{Mo}_2\text{O}_9$ (LAMOX), brownmillerites such as doped- $\text{Ba}_2\text{In}_2\text{O}_5$,
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4 apatite structured oxides of general formula $\text{A}_{10}(\text{MO}_4)_6\text{O}_{2-\delta}$, or melilite structured
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6 electrolytes ($\text{LaSrGa}_3\text{O}_7$) [4,5,6,7]. However, the chemical stability of these materials
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9 needs to be improved and hence there is a need for new electrolyte alternatives.

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11 Recently, a substituted LaNbO_4 based oxide ($\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$) in which additional
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13 oxygen content is accommodated through the adoption of a superstructure leading to
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15 interstitial ion conducting pathways was presented as an alternative SOFC electrolyte
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17 [8]. The proposed material is based on the cerium niobate structure. $\text{CeNbO}_{4+\delta}$
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19 possesses high values for oxygen diffusivity at intermediate SOFC temperatures (~ 600
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21 $^\circ\text{C}$). The partial substitution of La^{3+} for lower valence cations such as Ca^{2+} has shown
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23 high values of protonic conductivity [9,10]. By doping the B-site with a W^{6+} cation,
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25 oxygen excess is incorporated into the structure imitating the structural behaviour of the
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27 $\text{CeNbO}_{4+\delta}$ superstructures. Details of the crystal structure of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$
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29 phase can be found in reference [8]. Total conductivity of the material outperforms YSZ
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31 at 1000°C and presents negligible ionic conductivity at a $p\text{O}_2$ as low as 10^{-22} atm. Initial
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33 diffusivity measurements, preliminary fuel cell testing correlated with AC impedance
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35 studies, as well as thermal expansion coefficient (TEC) and chemical compatibility
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37 studies with both anode and cathode have been recently presented [8]. In the present
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39 paper we explore the steam electrolysis behaviour of single cells using this type of
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41 materials as the electrolyte.
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53 Experimental

54 Commercial powders of La_2O_3 (Sigma-Aldrich, 99.9%), WO_3 (Sigma-Aldrich,
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56 99.9%), and NbO_2 (Merck, 98%) were stoichiometrically mixed and calcined inside of a
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1 platinum vessel at 1400 °C for 24 hours. This process was repeated several times until
2 no change was observed in the XRD pattern and the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ single phase
3 powders were formed. Sample purity was confirmed using X-ray diffraction using a
4 PANalytical X'Pert PRO diffractometer ($\text{Cu K}\alpha$, $\lambda = 1.5406\text{\AA}$) fitted with an X-
5 Celerator detector.
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11 The chemical compatibility of the potential electrolyte was studied with both fuel
12 electrode (NiO/YSZ) and oxygen electrode (LSM). For this purpose, powders of
13 $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}\text{:NiO/YSZ}$ (50:50 wt%) and $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}\text{:LSM}$ (50:50 wt%)
14 were mixed and isostatically pressed at 200 MPa. The pellets were then heated to 1000
15 °C for a period of 2 hours and finally they were reground and analysed by powder XRD.
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24 Powders were then uniaxially pressed using a 20mm die at 200 MPa followed by
25 sintering at 1550 °C for 6 hours. The dense pellets were then ground down to a
26 thickness of about 360 μm using SiC grinding media. Electrodes were deposited into the
27 electrolyte using terpeneol-based slurries (Sigma-Aldrich) of NiO/YSZ (50/50 wt%
28 from Alfa Aesar and Tosoh respectively) and $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.98}\text{MnO}_3/\text{YSZ}$ (50/50 wt%
29 LSM/YSZ from FuelCell Materials) by brush-painting on both sides of the electrolytes.
30 NiO/YSZ electrode ($\sim 30\text{ }\mu\text{m}$ thickness) was firstly sintered at 1350 °C for 1.5 hours and
31 then LSM/YSZ ($\sim 30\text{ }\mu\text{m}$ thickness) was sintered at 1150 °C for 1.5 hours.
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44 Samples were then sealed into an alumina tube using Ceramabond 503 high temperature
45 sealant (Aremco, US). The measurements were performed using four Pt wires to
46 measure voltage and current. A Pt mesh was attached to the electrodes using spring
47 loads. *j-V* and AC impedance measurements were recorded using a VSP
48 Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, US) at temperatures
49 between 850 and 950 °C using 50% steam/ 50%hydrogen at the fuel electrode ($Q_T = 100$
50 sccm) and 20% oxygen/ 80% nitrogen ($Q_T = 100$ sccm) at the oxygen electrode site. *j-V*
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measurements were recorded from OCV down to 300 mV (SOFC mode) and from OCV up to 1500 mV (SOEC mode) at a scan rate of 1 mA cm⁻² s⁻¹. AC impedance measurements were recorded in galvanostatic mode using a sinusoidal signal amplitude of 20 mA over the frequency range of 10 kHz to 0.01 Hz.

SEM analysis was carried out in fractured transverse cross-section samples using a Merlin Field Emission SEM (Carl Zeiss, Germany).

Results and Discussion

The powder XRD pattern for the single phase W-doped LaNb_{0.84}W_{0.16}O_{4.08} material is shown in Figure 1. The parent material (LaNbO₄) presents an ABO₄ fergusonite type structure [11] whereas the W-doped phase presents a phase transition undertaking a reduction in symmetry identical to that observed between CeNbO₄ and CeNbO_{4.08} [12,13]. Although the crystal structure of the LaNb_{0.84}W_{0.16}O_{4.08} material is still not fully resolved, additional structural information can be found in reference [8]. Dilatometric studies also revealed TEC values between room temperature (RT) and 1000 °C of 11.44-12.01 x 10⁻⁶ K⁻¹. Those values are similar to YSZ and as a consequence the proposed electrolyte will be thermomechanically compatible with the standard LSM (11.2 x 10⁻⁶ K⁻¹) [14] and Ni-YSZ (10.3-14.1 x 10⁻⁶ K⁻¹) [15] electrodes.

The chemical compatibility of the potential electrolyte has also been studied with both fuel electrode (NiO/YSZ) and oxygen electrode (LSM) showing no apparent reaction of the LaNb_{0.84}W_{0.16}O_{4.08} (LNWO) phase with both electrodes (confirmed by XRD) up to 1000 °C for a period of 2 hours, suggesting that the selected electrodes will be suitable for fuel cell and electrolysis applications using LaNb_{0.84}W_{0.16}O_{4.08} as the electrolyte.

The typical microstructure of the cell prior to the electrochemical studies is shown in Figure 2. Figure 2 (a) shows that the LaNb_{1-x}W_xO_{4+δ} electrolyte is fully dense,

1 containing grain sizes between 2 and 20 μm . Figures 2 (b) and (c) show the interfaces of
2 the electrolyte material with the NiO/YSZ fuel electrode and the LSM/YSZ oxygen
3 electrode, respectively. Although the porosity of the electrodes is not fully optimized
4 and functionally graded electrodes will lead to lower polarization resistances, it is
5 remarkable that clean interfaces were formed, showing no apparent reactivity during
6 sintering, as confirmed by EDS analysis.

15 Preliminary SOFC measurements over a $\sim 300 \mu\text{m}$ electrolyte thickness sample showed
16 no reactivity under operating conditions and generating a reasonable power output in
17 fuel cell mode of $>100 \text{mW cm}^2$ at 900°C and with OCV values above 1V [8]. It is also
18 noticeable that the performance of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ based cell at higher
19 temperatures ($900\text{--}950^\circ\text{C}$) becomes more remarkable due to the high activation energy
20 of the $\text{La}(\text{Nb},\text{W})\text{O}_{4+\delta}$ conductivity. In this case, the performance of a cell with $\sim 360 \mu\text{m}$
21 electrolyte thickness was explored under both fuel cell and electrolysis conditions.
22 Typical j -V curves for both SOEC and SOEC operation modes recorded using a
23 steam/hydrogen ratio of 1:1 are shown in Figure 3. A summary of the measured
24 properties, including OCV and ASR_{cell} values, and current densities at 0.5V and 1.5V as
25 a function of the temperature are also summarized in Table 1. OCV values are in good
26 agreement with those predicted from the Nernst equation assuring good sealing and, as
27 a consequence, no apparent gas leakage from the fuel chamber to the air chamber was
28 detected. SOFC performance is in concordance with previous studies [8]. Current
29 densities of $\sim 200 \text{mA cm}^{-2}$ at 950°C and 0.7 V using 97% H_2 / 3% H_2O as a fuel were
30 previously reported, whereas this time at the same temperature and voltage the
31 measured current density was $\sim 100 \text{mA cm}^{-2}$. Even though we can conclude that both
32 samples are comparable, the decrease in the current density can be explained by an
33 increase of the electrolyte thickness for the current sample ($\sim 300 \mu\text{m}$ vs. $\sim 360 \mu\text{m}$), and

also to the decrease of hydrogen content (97% vs. 50%). The performance of the cell increases significantly when increasing the temperature, due to the high activation energy of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ electrolyte. The scattering observed in the data at 950 °C, especially at high current densities was associated with contact issues.

The performance of the cell in SOEC mode, reported for the first time, is of great interest. The reversibility of the cell when swapping the cell polarization (change from SOFC to SOEC mode) is demonstrated. In addition, the cell performance is enhanced in SOEC mode, as observed in the figure and also from the obtained ASR values (Table 1). In electrolysis mode, there is an increase of $p\text{O}_2$ at the oxygen electrode/electrolyte interface due to the oxygen evolution. It has been previously reported that the hyperstoichiometry of some oxygen electrode materials such as the NNO ($\text{Nd}_2\text{NiO}_{4+\delta}$) [16] or the LSCN ($\text{La}_{1.7}\text{Sr}_{0.3}\text{Co}_{0.5}\text{Ni}_{0.5}\text{O}_{4.08}$) [17] is favourable for oxygen evolution, as the performance of these electrodes is enhanced in SOEC mode. From our knowledge, this is the first time that an oxygen hyperstoichiometric phase has been tested as an electrolyte under SOEC mode. As for the Ruddlesden-Popper electrodes [16,17], the ability of the $\text{La}(\text{Nb},\text{W})\text{O}_{4+\delta}$ structure to accommodate oxygen excess is probably the reason for the increase of performance under electrolysis mode.

AC impedance experiments (as shown in Figure 4) were also performed applying 50 mA of current load in order to analyse the SOEC regime. A summary of the AC impedance parameters are shown in Table 2. Ohmic resistance of the sample at 850 °C is rather high due to the low LWNO conductivity at this temperature. This value decreases significantly when increasing the temperature, in concordance with the j -V results. Polarization resistance due to the electrodes is also higher than the SOFC/SOEC standards as the microstructure is not optimized. However the aim of the present study

was to demonstrate the suitability of the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ as an electrolyte for high temperature electrolysis applications.

Finally, SEM studies were performed after the SOFC/SOEC experiments in order to study any possible degradation (Figure 5). Figure 5 (a) shows the clean interface between the Ni/YSZ electrode and the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ electrolyte displaying no apparent degradation. However, as marked by the arrow in Figure 5 (b), slight delamination of the LSM/YSZ electrode was observed after operation. Although this is out of the scope of the present work, delamination is one of the main problems associated with electrolysis cells due to the high $p\text{O}_2$ taking place at the electrolyte/oxygen electrode interface, as previously reported by different authors [1,18,19].

Conclusions

$\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ is presented for the first time as a novel electrolyte for SOEC applications. The material presents no apparent reactivity with standard Ni/YSZ and LSM electrodes. Preliminary SOEC results showed similar performance that standard YSZ at high temperatures (900-950 °C). It is believed to be first reported the enhancement in SOEC mode in comparison with SOFC mode. It is suggested that the reason for this effect will be the excess oxygen of the ionic conductor phase. Although much work is now required in order to fully understand this phase, the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ structure could be an interesting alternative for the traditional YSZ electrolyte.

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Figure 1. Powder XRD pattern for the single phase W-doped $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ material.

Figure 2. SEM micrographs (fractured transverse-cross sections) showing (a) the fully dense $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ electrolyte; (b) interface of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ electrolyte and the NiO/YSZ fuel electrode; and (c) interface of the $\text{LaNb}_{1-x}\text{W}_x\text{O}_{4+\delta}$ electrolyte and the LSM/YSZ oxygen electrode.

Figure 3. *j*-V curves for both SOEC and SOEC operation modes recorded using a steam/hydrogen ratio of 1:1 at temperatures between 850 °C and 950 °C.

Figure 4. AC impedance experiments performed applying 50 mA of current load in order to analyse the SOEC regime at 850 °C, 900 °C and 950 °C.

Figure 5. SEM micrographs (fractured transverse-cross sections) showing (a) the clean interface between the Ni/YSZ electrode and the $\text{LaNb}_{0.84}\text{W}_{0.16}\text{O}_{4.08}$ electrolyte; and (b) slight delamination of the LSM/YSZ electrode.

Table 1.

Summary of the j -V parameters

Temperature (°C)	OCV (mV)	ASR _{cell} (SOFC) (Ω cm ²)	ASR _{cell} (SOEC) (Ω cm ²)	Current density at 0.5V (mA cm ⁻²)	Current density at 1.3V (mA cm ⁻²)
850	958	13.8	10.14	-34	39
900	937	3.55	2.05	-124	178
950	910	1.65	1.41	-199	256

Table 2.

Summary of the AC impedance parameters

Temperature (°C)	R _{ohm} (Ω cm ²)	R _{pol} (Ω cm ²)	ASR _{cell} (Ω cm ²)
850	11.40	2.97	14.37
900	3.37	2.46	5.83
950	1.47	2.36	3.83

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