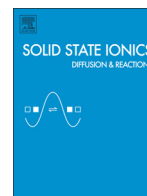




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# La<sub>2</sub>NiO<sub>4</sub> + δ as electrode material for solid oxide fuel cells and electrolyzer cells

Andreas Egger<sup>a,\*</sup>, Nina Schrödl<sup>a</sup>, Christian Gspan<sup>b</sup>, Werner Sitte<sup>a</sup>

<sup>a</sup> Chair of Physical Chemistry, Montanuniversität Leoben, Franz-Josef-Strasse 18, 8700 Leoben, Austria

<sup>b</sup> Institute for Electron Microscopy and Nanoanalysis (FELMI), University of Technology & Graz Centre for Electron Microscopy (ZFE), Steyrergasse 17, 8010 Graz, Austria

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## ABSTRACT

In this work, the mixed ionic–electronic conducting ceramic La<sub>2</sub>NiO<sub>4</sub> + δ is investigated with respect to its applicability as SOFC cathode as well as SOEC anode material on the basis of electrolyte-supported button cells. Results are obtained by electrochemical impedance spectroscopy and current–voltage analyses on symmetrical cells with screen printed La<sub>2</sub>NiO<sub>4</sub> + δ electrodes under both anodic and cathodic polarization, where special emphasis is put on the chromium tolerance of the material. The long-term behavior of electrodes in pure oxygen/argon as well as in humidified chromium-containing atmospheres is studied at 800 °C both under open circuit conditions and with applied current load. Once a chromium source is introduced in humid conditions, a strong decline in the cell performance occurs which can be mainly ascribed to a deactivation of the SOFC cathode layer. Post-test analytical investigations of cell cross sections by SEM and TEM suggest differences in the extent of Cr-contamination to be the main factor for the pronounced discrepancy between degradation rates of both electrodes.

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## 1. Introduction

Poisoning of ceramic electrodes by chromium emitted from components made of Cr-based alloys or stainless steel is a well-known degradation mechanism in solid oxide fuel cells (SOFCs) which can cause severe performance loss at the SOFC cathode side [1]. Solid oxide electrolyzer cells (SOECs), proposed for high temperature steam electrolysis, are based on similar materials and principles of construction and operation but show different degradation behavior due to reversed current flow, altered gas compositions and endothermic reaction enthalpies, which leads to differences in component partial pressures (e.g. pO<sub>2</sub>, pH<sub>2</sub>, pH<sub>2</sub>O) and distribution patterns of temperature, overpotentials and current density [2–5]. It is therefore interesting to compare the chromium-based degradation of air electrodes in SOFC and SOEC modes of operation.

Chromium poisoning of SOFC cathodes has been extensively investigated for various materials (see e.g. [1,6–8]) but much less is known about Cr-induced degradation on SOEC anodes under current load [5, 9]. There are different methodologies for investigating the effect of Cr-poisoning at the component or cell level. One method uses a Cr-source in direct physical contact with the sample, either by pressing a Cr-containing alloy onto the electrode [10], by deposition of a thin Cr-layer on the sample surface [11] or by infiltration of the porous electrode layer with Cr-containing solutions [12–14]. Another method avoids

direct physical contact between the chromium source and the sample, thus providing a defined transfer mechanism by means of gas phase transport of volatile Cr-species [15–18]. The latter method has been employed in this work to investigate the mixed ionic–electronic conducting ceramic La<sub>2</sub>NiO<sub>4</sub> + δ (LNO) with respect to Cr-induced degradation when used as SOFC cathode and SOEC anode material.

LNO has been proposed as a promising material for various applications such as electrodes for solid oxide fuel cells (SOFCs) and electrolyzer cells (SOECs) as well as for ceramic membranes. The material features fast oxygen diffusion, high catalytic activity for the oxygen surface exchange reaction and adequate electronic conductivity [19]. Since oxygen transport through the material is based on an interstitial (more precisely interstitialcy [20]) diffusion mechanism, acceptor doping with alkaline earth metals is not required to enhance the oxygen ionic conductivity. This should improve long-term stability with respect to various well-known degradation mechanisms such as surface or grain boundary segregation of alkaline earth elements or reaction of alkaline earths with impurities in the gas phase.

In this work long-term degradation studies are performed on a symmetrical cell at 800 °C over a period of >2000 h. By applying a constant current load to the cell both electrode sides are oppositely polarized, corresponding to SOEC anode and SOFC cathode operating conditions. This approach allows for the simultaneous assessment of a potential electrode material for applications as SOFC cathode and SOEC anode during a single cell test [21] and provides a direct comparison of the effect of polarization on degradation phenomena under identical ambient conditions. This is especially relevant for the oxidant side in solid oxide

\* Corresponding author.

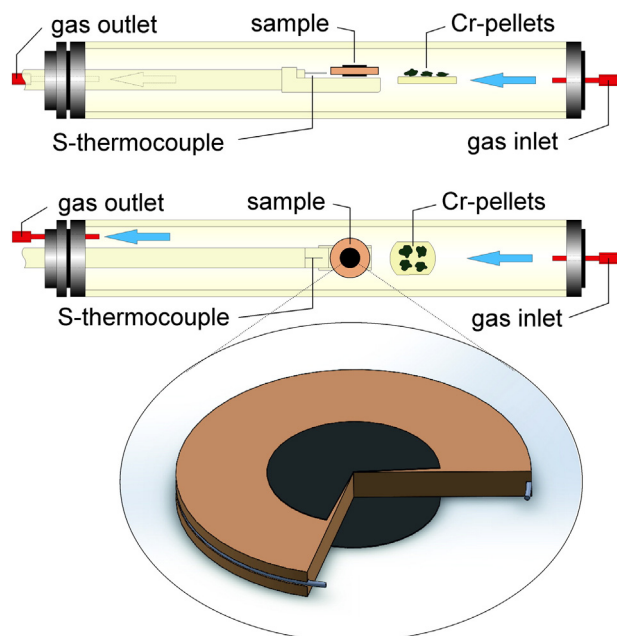
E-mail address: [andreas.egger@unileoben.ac.at](mailto:andreas.egger@unileoben.ac.at) (A. Egger).

cells, where both the SOFC cathode and SOEC anode are expected to be operated with ambient air in real devices. Electrolyte-supported symmetrical button cells are examined at 800 °C inside a single gas chamber constantly flushed with a mixture of 20% oxygen in argon.  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO) is used as electrolyte material since it is well known that LNO reacts with yttria-stabilized zirconia (YSZ) during the sintering process – forming the electrically insulating pyrochlore phase  $\text{La}_2\text{Zr}_2\text{O}_7$  [22,23] – but appears to be less reactive with CGO [23, 24] although some side reactions have been observed [25]. Nevertheless, results presented in this work are also representative for YSZ-based cells, where a thin layer of CGO is usually employed as diffusion barrier between the electrolyte and the air electrode.

## 2. Experimental

### 2.1. Sample preparation

The preparation of symmetric button cells was based on 20 mm-diameter disk-shaped electrolyte substrates made of  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO). CGO powder (Treibacher Industrie AG) was isostatically pressed at 200 MPa, sintered for 10 h at 1450 °C to a relative density of 98% and polished to 1.75 mm thickness. Rather thick electrolyte substrates are used in order to simplify the attachment of the reference electrode, which consists of a Pt-wire fixed with Pt-paste in a groove cut along the perimeter of the electrolyte (Fig. 1). Furthermore, imperfect alignment of electrodes on thin electrolytes can cause errors and artifacts in impedance spectra of three-electrode measurements [26–28] but is of less concern for thick electrolytes.  $\text{La}_2\text{NiO}_{4+\delta}$  powder (Treibacher Industrie AG) was processed into a screen printing paste and two LNO disk electrodes of 1 cm diameter were screen printed symmetrically on both sides of the electrolyte and sintered at 1250 °C for 2 h. Gold grids were employed as current collectors and were sintered to the electrodes using gold paste.



**Fig. 1.** Schematics of the reactor (side view and top view, not to scale) and of the cell design. Arrows denote the direction of gas flow. The cutaway view of the cell shows the CGO electrolyte substrate (orange) with symmetrically screen-printed LNO electrodes (black) and a Pt-wire reference electrode (gray) along the circumference of the electrolyte. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

### 2.2. Electrochemical characterization

The cell was mounted inside a tubular alumina reactor (Fig. 1) and heated to 800 °C in a horizontal tube furnace. During the long-term degradation study the reactor was constantly flushed with a gas mixture of 20%  $\text{O}_2$  in Ar at a flow rate of 2 L/h. Gas humidification was implemented by bubbling the gas stream through a water flask filled with deionized water and thermostatted to a temperature corresponding to the targeted equilibrium partial pressure of water (9.35 mbar  $p_{\text{H}_2\text{O}}$  in this study). Chromium pellets (99.996% purity) were placed approximately 1 cm upstream of the cell without any physical contact to the sample, thus acting as Cr-source via gas phase transport of volatile chromium species. Electrochemical characterization was carried out by a Novocontrol Alpha-A frequency response analyzer interfaced to a Novocontrol 15 V/10 A potentiostat/galvanostat in 4-wire two- and three-electrode configuration. Electrochemical impedance spectroscopy (EIS) was performed between 10 mHz and 1 MHz with 20 mV (rms) excitation voltage under open circuit voltage (OCV) conditions. Current-voltage ( $I$ - $V$ ) curves were measured up to current densities of  $\pm 110 \text{ mA cm}^{-2}$  with sweep rates of  $1 \text{ mA s}^{-1}$ . WinFit (v3.4) was used for complex non-linear least squares (CNLS) fitting of impedance data.

### 2.3. Post-test analyses

Scanning electron microscope (SEM) images of electrode microstructures were recorded using a Zeiss EVO 50 operated at 15 kV and equipped with an SE and a 4QBSD detector. A Zeiss Ultra 55 scanning electron microscope equipped with an EDAX Phoenix EDXS detector and an EDAX TEX WDXS detector was used for EDX elemental mapping and WDX point analyses of polished cell cross sections. EDX elemental distribution maps were obtained by spectra imaging and peak deconvolution with EDAX Genesis software (v6.5). Investigations by scanning transmission electron microscopy (STEM) were performed on a FEI Tecnai F20, operated at 200 kV and a FEI Titan<sup>3</sup> G2 60-300, operated at 300 kV and equipped with a  $\text{C}_s$  probe corrector. Lamella preparation was realized using a Focused Ion Beam (FIB) NOVA 200 Nanolab dual beam microscope.

## 3. Results and discussion

### 3.1. Electrode microstructure

Fig. 2 shows micrographs of a cell cross section with porous LNO electrode layers deposited on a dense CGO electrolyte substrate. The electrode layers are of 10–15  $\mu\text{m}$  thickness and exhibit a rather coarse microstructure.

### 3.2. Cr-poisoning study

The long-term degradation study was carried out at 800 °C over a period of 2200 h and consists of 3 consecutive stages. In the first stage (*stage 1*) no current load was applied to the cell and EIS-measurements were performed in dry chromium-free  $\text{O}_2/\text{Ar}$  atmospheres to check the intrinsic stability of the cell and to obtain a baseline for later comparison. In the next stage (*stage 2*) an electric current was continuously drawn through the cell, loading both electrodes with a current density of  $110 \text{ mA cm}^{-2}$  while maintaining dry and Cr-free conditions. By applying a current to the symmetrical cell, molecular oxygen is reduced and incorporated into the electrolyte in the form of oxide ions which are oxidized and released as oxygen at the opposite electrode side. Thus, one electrode layer is effectively acting as an SOFC cathode while the other electrode is working as SOEC anode. In the final stage (*stage 3*) of the degradation experiment a chromium source was placed upstream of the cell and the moisture of the gas stream was adjusted to a water content equivalent

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