



Steam as sweep gas in SOE oxygen electrode

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ABSTRACT

The interest in producing hydrogen as energy storage medium for renewable electricity brought to the development to high efficient electrolyzers such as Solid Oxide Electrolyzer (SOE). Recent studies on SOEs focus mainly on the effect of the Hydrogen Electrode composition into performances varying the concentration of steam and hydrogen. This study investigates the Oxygen Electrode side where normally air is used as a sweep gas to flow pure oxygen, produced by SOE operation, out of the system. Water, in the form of steam, is proposed as an innovative sweep gas in oxygen electrode. The use of a different gas, such as steam, has the effect both of reducing oxygen concentration and changing thermodynamic local conditions of the SOE. Both phenomena influence electrochemical reaction and, consequently, cell voltage. At system level, this operation strategy allows to easily produce an oxygen flow as SOE by-product because no nitrogen is present in the oxygen electrode off gas and steam can be easily separated by condensation. Experimental study performed on a SOE single cell demonstrated that steam can be used in the oxygen electrode with the production of 100% oxygen on dry base. Negligible reduction of performance was measured and can be hardly distinguish from normal aging due to the test campaign. Open circuit voltage of 0.804 V and Area Specific Resistance of $0.582 \Omega \text{ cm}^{-2}$ were obtained at 800 °C. The new concept was for the first time assessed on experimental base and opens new paths for system design and integration of SOE electrolyzer units.

1. Introduction

The new energy requirements related to the development of renewable energy sources brought researchers to increase the study on the use of hydrogen as energy storage medium. Economic viability of electrolysis for hydrogen production as energy storage is strongly limited by the cost of the technology [1–3]. Main efforts are focused on achieving higher efficiency and lower cost and other advantages (e.g. no caustic, power density) moving from standard alkaline technology to PEM and, as a third generation, SOE. High temperature electrolyzers, such as SOE, allow high efficiency and, in future, low cost [4–6].

Research on SOE moved from the recent development on the same technology applied for power production: Solid Oxide Fuel Cell (SOFC). While knowledge derived from SOFC was recovered for what concerns stack design, interconnect materials and production process, research activities is extremely active on development of innovative materials for the electrodes.

In particular main issues are related to the oxygen electrode (OE) that has higher contribution to ohmic losses during operation [7] and degradation due to delamination of the electrode/electrolyte interface [8–11]. Literature studies dedicated to hydrogen electrode (HE) are

mainly focused on the performance evaluation varying temperature and steam to hydrogen ratio [12–14]. A relatively new field of research evaluates hydrogen electrode strategies introducing carbon dioxide as reactant for the production of CO and/or syngas [15–17].

The present paper proposes an additional pathway to reduce hydrogen production cost. Specifically, technology productivity is increased by the valorization of by-products, such as oxygen, through an innovative management of the oxygen electrode. An interesting potential development of the technology involves the study of the oxygen electrode gas. In general air is used as a sweep gas to flow oxygen out of the system and reduce O_2 concentration in the electrode surface. High oxygen concentrations drive against electrolysis reaction and increase polarization losses. Authors already investigated on the reduction of air flow to improve system efficiency and increase O_2 concentration in the OE off gasses [18]. Results indicate that an increase in efficiency can be achieved and oxygen concentration can reach up to 50% at the oxygen electrode output. The latter aspect is extremely interesting considering the SOE not only as a hydrogen production device but, at the same time, as an oxygen generator. Even if oxygen is not a fuel and no energy can be recovered from the molecule, pure O_2 has an important market value that accelerates the economic feasibility of the concept. An additional

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study, based on experimental study, demonstrated that air reduction down to 9.2% of nominal value has negligible effect on performances [19].

Literature reports also the so called fuel enhanced electrolysis. Hydrogen or, in general, a fuel, is added to the oxygen electrode. Oxygen is reduced chemically or electrochemically in the electrode reducing partial pressure of produced hydrogen. The electrolyzer acts as a concentration cell, with the overall result of moving hydrogen from the oxygen electrode to the hydrogen electrode [20–22].

The use of steam in the OE, as air substitute, can bring to further improvements in hydrogen production efficiency and, at the same time, produces a mixture of oxygen and steam that can be easily separated providing an additional chemical product of a SOE system. In this study we propose the use of steam as a carrier gas for produced oxygen. Compared with other gases such solution has two main advantages: (i) steam is already available in the system for the production of hydrogen in the HE and (ii) separation of oxygen from steam can be easily realized just condensing water. As a drawback additional heat is necessary for the production of steam but energy recovery can be implemented in the system and optimized. In this study a single SOE cell was tested using air and steam as a sweep gas to compare differences in performances. Literature reports only one study that deals with the use of steam as sweep gas [23]. In details the study, focused only on assessments at system level, provides the theoretical analysis of a tri-generation system. Three different strategies for hydrogen electrode sweep gas are evaluated (air, syngas and steam) and steam was selected as the most profitable one.

An open issue on the use of steam is related to electrode stability and material corrosion. To this regards, literature reports a large experience in using humidified air as reaction gas in SOFC operation [24]. Even if preliminary results show electrode degradation for both most diffused electrode materials LSM and LSCF [25], literature does not give a clear indication due to experience where LSCF did not show any degradation [26]. In general, such aspects are poorly studied and very little is clarified in terms of degradation mechanism and no experience is presented in electrolysis operation. Regarding corrosion issue, both the presence of steam and oxygen can cause material degradation [24] due to the production of volatile chromium both in form of $\text{CrO}_3(\text{g})$ and $\text{CrO}_2(\text{OH})_2(\text{g})$ that can contaminate cell material [27]. Strategies to prevent chromium production are the doping of cathode composition or the use of special stainless steel that can prevent the formation of contaminants [28].

For what is in the knowledge of the authors this is the first study that reports an experimental activity of a SOE operating with steam as sweep gas in the oxygen electrode demonstrating the feasibility of the concept and the production of pure oxygen.

2. Materials and methods

Experimental test was performed on a single square commercial planar cell, active area 16 cm^2 , anode supported with Ni/8YSZ as HE, 8YSZ electrolyte and GDC + LSCF as OE. Thicknesses of each layer are reported in Table 1.

Nickel mesh was used as HE current collector and gold mesh for OE. Steel manifolds were used to distribute gasses to the electrodes. Water was evaporated inside the furnace in a pre-reactor for the HE gas flow and in the pipes for the OE flow. Two voltage and two temperature

Table 1
Details of cell layers.

Layer	Composition	Thickness
Anode	Ni/8YSZ	$240 \pm 20 \mu\text{m}$
Electrolyte	8YSZ	$8 \pm 2 \mu\text{m}$
Bilayer Cathode	GDC + LSCF	$50 \pm 10 \mu\text{m}$

sensors were placed in the meshes and in the manifolds respectively. Gas and water flows were regulated through flow meters controllers. A scheme of the set-up in the furnace is depicted in Fig. 1. The set-up, developed for this study, allows to obtain stable voltage values even with high steam content in the gas mixture feeding the OE.

Performance analysis was realized; polarization curves were measured at constant furnace temperature of $800 \text{ }^\circ\text{C}$. OE gas was pre heated up to $200 \text{ }^\circ\text{C}$. For each polarization curve, steps of 1 A were kept for one minute up to maximum current of 1000 mA cm^{-2} . Results are reported in the following paragraph 2 in terms of average profiles; each number is calculated as the average of the values acquired in the time interval, one minute, at 1 Hz. Data standard deviations is always below 0.5%, even if not indicated in the graphs to guarantee their readability in consideration of the multiple depicted trends. HE gas flow was kept constant during all tests. Gas quality and quantity were defined via two indirect parameters: hydrogen inlet molar concentration (x_{H_2}) and reactant utilization at 1000 mA cm^{-2} (RU@1000). The latter is defined as follows (1):

$$RU@1000 = \frac{1000 \cdot A}{2 \cdot F \cdot H_2O} \quad (1)$$

Where A is the cell surface in cm^2 , F is Faraday constant and H_2O is molar flow of steam. Thus while x_{H_2} indicates the amount of hydrogen in the HE necessary to keep a reducing atmosphere, RU@1000 indicated the maximum conversion rate that can be achieved in the cell and, once defined, can be used to calculate steam flow. Based on literature 10% of H_2 was used in all tests. Hydrogen flow is not necessary for the reaction and, vice versa, due to the fact that it is a reaction product, its presence inhibits the electrochemical reaction and increases operative voltage. Thus, minimum amount was used to keep higher performance results. RU@1000 was fixed at 0.5 so to achieve nearly operative conditions and, at the same time, to reduce the contribution of HE to polarization losses and focus on OE contribution. Three groups of five polarizations each were performed changing OE composition: standard air flow (AIR), mixture of steam and air 50:50 (H2O) and, finally, steam and air mixture with composition variation (MIX) up to the case of 100% H_2O fed to the OE. To design OE flows, the parameter $m_{\text{O}_2@1000}$ was used. This parameter was introduced as an indirect criteria to define inlet gas flows of air and steam; it is defined as the molar flow of oxygen produced at 1000 mA cm^{-2} with respect to the inlet flow (2):

$$m_{\text{O}_2@1000} = \frac{O_2@1000 + 0.21 \cdot Air_{in}}{n_{\text{OEin}}} \quad (2)$$

Where $O_2@1000$ is the molar flow of oxygen produced at 1000 mA cm^{-2} , Air_{in} is the molar flow of air entering (when fed to the electrode) the OE electrode and n_{OEin} is the total molar flow of inlet gas. $O_2@1000$ is calculated as follows (3):

$$O_2@1000 = \frac{1000 \cdot A}{4 \cdot F} \quad (3)$$

In AIR and H2O tests, $m_{\text{O}_2@1000}$ was varied from 30 to 70% at steps of 10. In MIX tests, $m_{\text{O}_2@1000}$ was kept constant at 50% and steam concentration was varied to values of 0, 25, 50 and 100%. Test campaign is reported in Table 2. In the table also $x_{\text{H}_2\text{O}}$ and x_{air} are reported, calculated as molar concentrations of steam and air respectively at the oxygen electrode inlet.

Based on design condition reported in Table 2 gas flows were calculated as reported in Table 3. The table reports also parameters such as $O_2@1000$, already defined, and the equivalent $H_2@1000$, calculated as the hydrogen production of the system when operating at 1000 mA cm^{-2} . Finally the table reports the HE/OE parameter, calculated as the ratio between the hydrogen electrode and oxygen electrode total flows. Table 3 reports also oxygen concentration on wet (x_{O_2}) and dry (x_{O_2d}) basis of OE off gasses at 1000 mA cm^{-2} .

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