Modelling of anode delamination in solid oxide electrolysis cell and analysis of its effects on electrochemical performance

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ABSTRACT

Degradation of a solid oxide electrolysis cell (SOEC) during long-term operation remains to be the key obstacle to their massive production and commercialization. One of degradation processes within SOEC is anode delamination. The anode of SOEC splits at the interface with solid electrolyte due to elevated pressure of oxygen that is produced by electrochemical reactions. The main assumption that anode delamination starts at the fuel inlet is based on post-mortem analysis of SOEC. This paper addresses numerical modelling of a single, electrolyte supported, SOEC. The anode delamination is modelled by implementing the modifications of SOEC's geometry. A brief overview of the model is also given. Verification of the implemented model relies on the measurement data from literature. The simulation results show that increasing the area of delaminated anode ($A_{delaminated}$) increases the operating voltage of the SOEC if a constant electrolysis current is applied. This strongly influences the conversion efficiency (η) of the SOEC. Indeed, if linear growth of $A_{delaminated}$ over time is assumed, the η of SOEC degrades very fast at the beginning of SOEC's operation. The presented model also helps analyze the hot spots of current density, where high pressure of oxygen appears.

Introduction

The global energy consumption has been increasing very fast in the last few decades. Consequently, the pollution caused by burning fossil fuels increases [1]. Hence the utilization of renewable energy sources has emerged as a viable option to reduce pollution rates. The renewable energy sources (e.g. solar or wind energy) are site-specific and intermittent by their nature, so it seems reasonable to use excessive renewable energy for producing a fuel that can be stored and, when the energy is unavailable, efficiently re-used [2]. The electrolysis of water (H_2O), which is an abundant element on our planet, is a promising way to produce hydrogen (H_2). The H_2 is a clean, storable and transportable energy carrier [3–5]. It can be directly converted into electricity by fuel cells without producing greenhouse gases (e.g. carbon dioxide).

The solid oxide electrolysis cell (SOEC) technology is becoming increasingly interesting now, since it provides carbon-free production of H_2 [6]. SOEC can be used also in co-electrolysis process for production of syngas, which consist of H_2 and carbon monoxide (CO), where H_2O and carbon dioxide (CO_2) are consumed [7]. The consumption of CO_2 may be important to reduce the fraction of greenhouse gases in the atmosphere and mitigate the global warming.

Besides the benefit for environment, SOECs have some other advantages. SOECs can achieve higher conversion efficiency (η) of electrical to chemical energy compared to

common electrolysis devices, since they operate at high temperature ($T > 650\ °C$), in contrast to common devices that operate at low T [8]. High T allows that a part of the electrical energy, which is needed for electrolysis, is replaced by thermal energy. An example is waste heat in nuclear reactors that operate at high T. Therefore, high-temperature operation could be advantageous in a sense that SOEC efficiently utilizes waste heat for production of hydrogen [9].

The η of the SOEC should be calculated with care and thermodynamic limitations must be considered properly. For more details, the interested reader is referred to a sound study about η of the electrolysis and fuel cells [10]. An advantage of operation at high T is lower electrolyte's ohmic resistance and higher electrode's reaction kinetics [11]. The latter allows that a noble metal, such as platinum (Pt), which is commonly used for electrodes at low-temperature electrolysis, is replaced by less precious oxide ceramic material, such as nickel (Ni) doped yttria-stabilized zirconia (YSZ) or lanthanum strontium manganite (LSM), so the production costs are greatly reduced [8].

Despite many efforts to improve life-time of the SOECs, and make them economically viable, it seems that relatively fast degradation processes within these devices are still the major obstacles to massive production and commercialization. The degradation occurs due to different reasons so that three main types of degradation are distinguished: chemical/electrochemical degradation, structural degradation and mechanical failure caused by thermal stress, as explained in Ref. [12]. One of the most critical structural degradation processes that occurs during long-term operation is delamination of the oxygen (O_2) electrode at the interface with electrolyte. This process has been extensively investigated by a number of researchers [13—18]. This phenomenon has been studied from various perspectives. To gain more profound understanding of delamination a detailed first principles electrochemical model for degradation of SOECs is proposed in Ref. [13]. The model relies on local equilibrium in oxygen ion conductors that are in global thermodynamic non-equilibrium.

On the other hand, experimental studies have been undertaken to get evidences on degradation of O_2 electrodes in SOEC. In Ref. [14] different techniques (i.e. X-ray fluorescence, four-point resistivity, scanning electron microscopy - SEM, energy dispersive spectroscopy - EDS, X-ray diffraction and Raman micro-spectroscopy) for analysis of microstructural properties after a long-term operation have been applied.

It was found that high production rate of O_2 at the interface between anode and electrolyte causes a greater ability of zirconia to release O_2 and a lesser ability of the anode material to transfer O_2 ions through the anode layer. As a result, more O_2 would be produced than released into the air flow channel, so the pressure would increase and cause a crack that could initiate anode delamination.

Anode supported, YSZ-based, micro-tubular, solid oxide fuel cells (SOFCs) were tested at high voltages (up to 2.8 V, under electrolysis mode) in Ref. [15]. It was found that high partial pressure of O_2 at the interface between the O_2 electrode and electrolyte caused degradation of adjacent regions. This effect causes delamination of the O_2 electrode and such degradation also increases the impedance of the tested SOFCs.

The first-principles, density-functional-theory (DFT) calculations and thermodynamic modelling were employed to reveal the main processes that cause delamination in typical SOEC device made of YSZ electrolyte and Sr-doped LaMnO$_3$ (LSM) O_2 electrode [16]. Another study showed a durability test of anode-supported SOFC that was operated for 9000 h as SOEC with a current density (J) of 1 A cm^{-2} [17]. The long-term tests show a voltage increase of about 40 mV kh^{-1}, which results in overall voltage degradation rate of 3.8% kh^{-1}. Similar voltage degradation rates were observed in Ref. [18]. The tested device operated at $T = 800\ °C$ and alternating $J = \pm 300$ mA cm^{-2} (repeated SOFC or SOEC operation cycle). At constant galvanostatic conditions (constant J) the cell had higher voltage degradation (5.9%) under electrolysis mode than under fuel cell mode (2.7%). There are a lot of studies that show area specific resistance (ASR) [19], current-voltage (J-V) characteristic [20] or impedance (Z) [21] of SOECs after a long-term operation under specific test conditions. Although these studies are valuable, good understanding of complex processes is needed. For that purpose, it is reasonable to build a model that is capable to predict the performance of degraded SOEC.

There are some papers that focus on SOEC or SOFC modelling [22—26], but no paper presenting a model of SOEC with delaminated anode has been found. Thus, to the best of the authors' knowledge, there is a gap in modelling of anode delamination on the device level.

This paper focuses on modelling of anode delamination and studies the effects of partly delaminated anode on electrochemical performances of modelled SOEC by means of numerical simulations. The aim is to understand how locally increased electrolyte J can elevate the pressure of O_2 as the O_2 is produced by the electrochemical reactions. The main novelty of this paper is modelling of degraded SOEC on device level and analysis of anode delamination effects on electrochemical performances of the SOEC.

Modelling

Two-dimensional (2-D), axisymmetric structure of SOEC was modelled in COMSOL Multiphysics® 4.3, as shown in Fig. 1. The data about the structure geometry, dimensions, materials, and most of input parameters were adopted from the literature [27]. Some of input parameters for this SOEC model were estimated from other experimental data or fitted accordingly, as explained in Section Model fitting.

Table 1 shows dimensions of each layer in the modelled SOEC. It is considered that modelled SOEC structure operates within a sealed chamber where constant $T = 800\ °C$ is maintained. The flow rate of hydrogen (H_2) fuel gas, containing 40%, 60%, or 80% of water (H_2O) steam, is 150 cm^3 min^{-1}, whereas an open air is used at air electrode, as explained in Ref. [27]. The electrochemical performances of the real electrolysis cell were initially tested at $J = -0.8$ A cm^{-2}. The next step was measuring the J-V curves when the cell operated as SOEC (negative J) or as SOFC (positive J). In order to simulate the J-V curves of the modelled SOEC, a set of governing equations has to be implemented for each subdomain of this SOEC model, and solved with appropriate numerical method (e.g.