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Localized carbon deposition in solid oxide electrolysis cells studied by multiphysics modeling

Maria Navasa[a,b,*], Henrik Lund Frandsen[a], Theis Løye Skafte[a,c], Bengt Sundén[b], Christopher Graves[a]

[a] Department of Energy Conversion and Storage, Technical University of Denmark, Denmark
[b] Department of Energy Sciences, Lund University, Sweden
[c] Haldor Topsoe A/S, Denmark

HIGHLIGHTS

- Gas diffusion and temperature are important driving forces for C deposition.
- C formation occurs primarily by the Boudouard reaction for the cell considered.
- C deposition can be avoided by thinner and more porous electrodes.

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ABSTRACT

Solid oxide electrochemical cells (SOCs) can store electrical energy in the form of chemical fuels with high efficiency by electrolysis of CO_2 and H_2O. However, achieving commercially relevant lifetime is hindered by degradation mechanisms such as carbon deposition, which can even destroy the cell especially during electrolysis where carbon formation is electrochemically driven at the electrode-electrolyte interface. Here we used a three-dimensional multiphysics model to simulate a SOC performing CO_2 electrolysis and determine the operating conditions and locations in the porous nickel-based electrodes where carbon deposition is expected based on local conditions (gas composition, temperature and overpotential) crossing local thermodynamic thresholds. It is found that CO/CO_2 gas diffusion gradients and cooling from the endothermic electrolysis reaction are important driving forces for carbon deposition to occur locally when it is not expected based on the outlet CO concentration. Furthermore, correlation with a set of experimentally determined threshold operating points indicates that carbon deposition occurs primarily by the Boudouard reaction rather than by direct electrochemical reduction of CO or CO_2 to carbon for the studied cell type. Variation of fuel electrode porosity and thickness shows that these methods of reducing gas diffusion limitations widen the operating window that avoids carbon deposition.

1. Introduction

Today, the energy demand is mainly met by fossil fuels and nuclear power as they can supply electricity on demand. A major drawback to the success of renewable energies is that they are nature dependent supplying electricity only when the wind blows, the sun shines, depending on the sea tides or the availability of biomass to just give a few examples. For renewable energy sources to be successful and meet a significant fraction of energy demand there is a need for large-scale economical energy storage devices to meet the supply-demand imbalance. Different energy storage alternatives are under development as current energy storage technologies are extremely expensive to scale up as a result of their dependency on limited resources or locations [1].

One of the promising devices that are under development is the solid oxide electrochemical cell (SOC). The interest in the development for this technology has increased considerably in the last ten years but most of the development has been focused on employing SOCs as fuel cells, known as solid oxide fuel cells (SOFCs), for power generation. However, SOCs can be operated reversibly so that electrical energy is supplied into the cell to drive electrochemical reactions obtaining chemical energy stored as fuels. This is the electrolytic operation mode and SOCs are then known as solid oxide electrolysis cells (SOECs). In

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* Corresponding author. Department of Energy Conversion and Storage, Technical University of Denmark, Denmark.
E-mail address: marnav@dtu.dk (M. Navasa).

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SOECs, hydrogen (H_2), carbon monoxide (CO) or syngas (H_2 and CO) can be obtained via high temperature electrolysis of steam (H_2O), carbon dioxide (CO_2) or co-electrolysis of H_2O and CO_2, respectively. An advantage of SOCs as energy storage devices is the easiness of scaling up systems by assembling individual cells into stacks to meet the desired output power. Although conventional batteries are more popular as energy storage devices, they store the electrical energy in expensive metals (Li, Pb, etc.) whereas SOECs store the electricity in the form of relatively economic fuels [1]. Withal, for SOECs to become commercially interesting, a long-term stability for a period of 5–10 years must be guaranteed which is currently not possible due to degradation of cell performance during operation.

When performing co-electrolysis of CO_2 and H_2O at high current densities, which provides the highest syngas production rate, degradation at the interface between the nickel-yttria-stabilized zirconia (Ni-YSZ) electrode and the YSZ electrolyte has been reported due to the formation of small amounts of carbon. Duboviks et al. [2,3] used Raman spectroscopy to show that carbon formation in CO/CO_2 electrolysis takes place at the mentioned interface, where CO is generated, in comparison to carbon formation in fuel cell mode, which first occurs at the outside of the electrode. Carbon formation in fuel cell mode is more commonly known and it can happen via methane cracking, CO disproportion (Boudouard deposition) or other thermochemical reactions depending on the hydrocarbon gas composition. In electrolysis mode, the formation of carbon at the active sites of the Ni-YSZ electrode may reduce the amount of active sites and, in the worst case, cause a delamination of the electrode/electrolyte interface. The Boudouard reaction, Eq. (2), is the most well-known way carbon can be formed in CO/CO_2 mixtures. Carbon deposition could also occur by electrolysis of carbon dioxide to solid carbon, Eq. (3), which is thermodynamically equivalent to the two-step reaction of electrolysis of CO_2 to CO, Eq. (1), followed by the Boudouard reaction. Another equivalent possibility to the two-step process described is the electrolysis of CO_2 to CO followed by the electrolysis of CO to C, Eq. (4) [4]. Although carbon deposition is thermodynamically favored only at higher reactant conversion than typically used in the operation of an SOEC, it has been observed at "safe" conversion conditions based on outlet CO concentration and average cell temperature. Thus, understanding why the thermodynamic threshold is surpassed and where this happens locally in the cell would be of great interest when choosing operating conditions and to avoid possible degradation of the cell [5].

$$2CO_{2(g)} + 4e^- \rightarrow 2CO_{(g)} + 2O^{2-} \tag{1}$$

$$2CO_{(g)} \rightarrow C_{(s)} + CO_{2(g)} \tag{2}$$

$$CO_{2(g)} + 4e^- \rightarrow C_{(s)} + 2O^{2-} \tag{3}$$

$$CO_{(g)} + 2e^- \rightarrow C_{(s)} + O^{2-} \tag{4}$$

Computational simulations are valuable tools for studying the performance of SOCs and optimizing their operation conditions. Despite the fact that numerical modeling can decrease the time cost and resources for cell testing, a small number of studies have been reported in comparison to experimental studies. SOFCs have attracted the major number of simulation investigations as the development of SOECs slowed down around the 1990s due to the low fossil fuel prices, but have increased in the last years due to the growing interest in green energy technologies [6]. In addition, steam electrolysis has been the main application for SOECs and consequently, it is reflected in the amount of research compared to CO_2 electrolysis or co-electrolysis of CO_2 and H_2O. Regarding modeling, very little work has been reported in literature about electrolysis of CO_2. Ni [7] developed a one dimensional (1D) electrochemical model where the overpotentials were considered and a two dimensional (2D) model where the electrochemical reactions were coupled with heat and mass transfer. Shi et al. [8] studied the current density and the species concentration distributions within the fuel electrode using an elementary reaction based 1D model for a button cell. Narasimhaiah et al. [9] presented a modified Butler-Volmer equation by considering multi-step single-electron transfer reactions to model CO_2 electrolysis in a button cell. The 1D model was evaluated when considering that the electrochemical reaction takes place at the electrode/electrolyte interface and through the porous electrode. Other authors [10–12] have also developed 1D or 2D models for co-electrolysis, studying the effects of some geometry or operating parameters.

The aim of this study is to show where and under which operating conditions carbon deposition is locally induced by performing multiphysics simulations on a three dimensional (3D) model of an SOEC that considers the main physical phenomena that characterize these devices, i.e. electrochemical reactions, transport of charged species, momentum transfer, mass transfer and heat transfer. The model is validated with experimental data. Moreover, possible solutions to the problem will be studied by varying the thickness and porosity of the fuel electrode. Both parameters will influence the effective transport properties of the diffusion layer and carbon deposition may be avoided or minimized.

2. Experimental

A number of cell test experiments have been performed under different operating conditions to validate the multiphysics model and to study the carbon deposition phenomenon in SOECs.

Single-cell measurements have been performed on planar supported SOCs produced by Haldor Topsoe A/S. A cell sketch with the components considered in the multiphysics model is shown in Fig. 1a). The cell is comprised of a Ni-YSZ support (porous support in Fig. 1a)), a Ni-YSZ active layer (fuel electrode in Fig. 1a)), a YSZ electrolyte, and a lanthanum strontium cobalt ferrite (LSCF)-based oxygen electrode plus a contact layer. A gadolinia doped ceria (CGO) layer is present between the electrolyte and the LSCF-based electrode.

All cells were tested at DTU Energy (Technical University of Denmark, DTU Risø campus). A cell of 5.3 cm × 5.3 cm with an active area of 16 cm^2 is mounted into a cell test rig. The contacting of the cell is realized with corrugated Ni and Au meshes for the fuel and oxygen electrodes, respectively, which provide a uniform contacting and gas distribution. The flow configuration in the cell test rig is shown in Fig. 1b).

A number of current density-voltage (*i*-V) measurements were carried out with a 50% CO/50% CO_2 feedstock with air as oxidant gas at three different gas inlet temperatures ranging from 750 to 850 °C for validation of the model. This model has also been validated for H_2/H_2O as feedstock in Ref. [13]. The inlet temperature, flows and gas compositions (CO partial pressure, p_{CO}) used in the tests are specified in Table 1.

Furthermore, other *i*-V measurements were performed on the same type of cells for the detection of carbon formation. The inlet conditions for these measurements, where the inlet temperature of the gases was set to 750 °C for all the tests, are specified in Table 2. The current of the cell, when in electrolysis mode, was gradually increased in steps until the voltage became unstable and started increasing due to coking in the cell. For more details about the measurements performed, refer to [5]. Further information regarding carbon detection can be found in the Supplementary Information.

3. Model description

A 3D multiphysics model of an SOEC has been developed using the finite element method (FEM) based commercial software Comsol Multiphysics 5.3 to study the degradation phenomenon of carbon deposition in SOECs.

The model developed for simulation of CO_2 electrolysis considers the following physical phenomena: electrochemical reactions, transport of charged species, momentum transfer, mass transfer and heat transfer. The main equations are summarized in Table 3. Besides, overall