Review of modeling approach of different porous materials for potential utilization in SOFCs

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ABSTRACT
Fuel cells are promising due to environmental advantages with higher efficiency and lower emissions of SO\textsubscript{X}, NO\textsubscript{X} and CO\textsubscript{2} than conventional power generation. Solid oxide fuel cell (SOFC) is a high temperature fuel cell, which operates at 600-1000 °C. A single unit cell of a SOFC consists of air and fuel channels, two porous electrodes which are separated by an electrolyte. The fuel electrode is the anode and the oxidant electrode is the cathode. The electrolyte should not be permeable for gases, but the porous electrodes should be permeable for gases and liquid. The anode is usually nickel/zirconia cermet which provides high electrochemical performance and good chemical stability and the cathode is usually a perovskite material. SOFC are generally more tolerant to contaminants than other fuel cells which make them more applicable. Due to the increasing global awareness of how energy use affects the environment, the interest of use of renewable energy has increased and fuel cells have the potential to be a part of a sustainable solution. Attractive materials, which are considered in this study, are Au, Ag, Cu, Pt, Pd, Ni, Co, Ru and W. It is concluded that it is feasible for SOFC to handle the studied materials but with varying success. Further studies needs to be conducted to investigate better as well as cheaper catalyst material to efficiently handle reforming and be easily commercially produced. More advanced methods to investigate surface reactions are prospected to contribute, in combination with better catalysts compositions, to understand the materials functions. A constantly issue is to more often validate the modeling results by experimental work.

NOMENCLATURE

Abbreviations
FC fuel cell
LHV lower heating value
IT intermediate temperature
SOFC solid oxide fuel cell
TPB three-phase boundary
YSZ yttria-stabilized zirconia

Chemical
CH\textsubscript{4} methane
CO carbon monoxide
CO\textsubscript{2} carbon dioxide
H\textsubscript{2} hydrogen
H\textsubscript{2}O water
O\textsubscript{2} oxygen
Ni nickel

INTRODUCTION
Fuel cells are energy conversion devices, which produce electricity and heat directly from a hydrogen-based fuel through the electrochemical reactions when the device is fed with an oxidant. Fuel cells do this in one step and differ from conventional heat engines where this process unfolds in several steps. The heat engine’s major loss of efficiency is the conversion of thermal energy to shaft work. The heat engine is limited by the efficiency of the Carnot cycle \[1\]. Since the step from thermal energy to shaft work is not included when a fuel cell converts energy to electrical power, this reduction gives a significant difference in efficiency between a heat engine and a fuel cell. Besides this, there are several interesting features of fuel cell systems. They are flexible in sizing and quite in operation. Fuel cells are also good candidates for a clean energy generation for a sustainable environment, due to lower emissions and higher efficiency than conventional power generation. The general interest in the research society has increased remarkable in recent years. The possibilities to feed renewable fuels to some types of fuel cells only make them even more attractive in this time of climate change anxiety. The number of scientific articles published has increased tremendously since 2000 \[1\]. In spite of the increase, research on fuel cells is still in its infancy of development. This is due to a lack of functional design for a mass production for commercial systems and the low market demand. Today’s fuel cell research challenge is to understand micro and nano scale transport phenomena in the electrochemical active materials.
Solid oxide fuel cells (SOFCs) are particularly interesting because they can handle the reforming of hydrocarbon fuels directly within the cell. This is possible due to their high operating temperature [1]. A single unit cell of a SOFC consists of air and fuel channels, two porous electrodes which are separated by an electrolyte. The fuel electrode is the anode and the oxidant electrode is the cathode. The electrolyte works as a passage for the ions and blockage for the electrons. The oxygen ions react with hydrogen and carbon monoxide in the fuel mixture at the anode/electrolyte interface, and produce water and carbon dioxide while releasing electrons that flow via external circuits to the cathode/electrolyte. The electrolyte should not be permeable for gases, but the porous electrodes should be permeable for gases and liquid. The electrolyte is a non-porous ceramic; normally Y$_2$O$_3$ stabilized ZrO$_2$ (YSZ). At SOFC’s operating temperature between 600 – 1000 ºC, the ceramic electrolyte becomes non-conducting for electrons but conductive for the oxygen ions. The anode is usually nickel/yttria stabilized zirconia (Ni/YSZ) cermet which provides high electrochemical performance and good chemical stability. The cathode is usually a perovskite material, made from electronically conducting ceramics or mixed with ion conducting ceramics. Figure 1 shows a schematic drawing of a planar SOFC and where the various reactions take place. A experimentally obtained figure of the components and its structure of SOFC is illustrated in Fig. 2 [3]. The overall global reactions are stated below for methane as a fuel. The reactions are in reality multi step and the reaction chain consists of several intermediate steps. More detailed surface reactions can be found in the literature [1].

\[
O_2 + 4e^- \leftrightarrow 2O^{2-} \quad (1)
\]
\[
H_2 + O^{2-} \leftrightarrow H_2O + 2e^- \quad (2)
\]
\[
CO + O^{2-} \leftrightarrow CO_2 + 2e^- \quad (3)
\]
\[
CH_4 + H_2O \leftrightarrow 3H_2 + CO \quad (4)
\]
\[
CO + H_2O \leftrightarrow H_2 + CO_2 \quad (5)
\]

The reduction of oxygen in the cathode is described in eq. (1). Equations (2) and (3) are the electrochemical reactions at the anodic three-phase boundary (TPB). TPB is the region where the electrolyte and electrode meet. The steam reforming of methane, which needs to be carried out before the electrochemical reactions, and which is usually called catalytic steam reforming reaction is shown in eq. (4). Carbon monoxide can be oxidized as in eq. (3) or react with water as in eq. (5). Equation (5) is often called water-gas shift reaction.

The configuration of SOFC can be arranged differently but is usually planar or tubular. Planar is built up with alternating flat layers and interconnect. They are normally more compact than tubular ones and are often considered as a simpler configuration. The tubular configuration has the flow of air and fuel inside and outside the tube as. Tubular fuel cells can be stacked electrically in series or in parallel [4]. Beside the configuration mentioned above, SOFCs are electrolyte-, anode- or cathode supported. If the case is electrode-supported (anode...
or cathode), it means that the thickest part is the electrode (either anode or cathode depending on the configuration) and that part works as the supporting structure. Similarly, the electrolyte is the thickest and supporting part for the electrolyte-supported configuration. The anode-supported structure makes it possible to reduce the temperature to a moderate level (600–800 °C [1]) and these fuel cells are classified as intermediate temperature solid oxide fuel cells (IT-SOFCs).

The reforming in SOFC systems can be done both externally and internally. In the internal reforming approach, the reforming process occurs together with the electrochemical reactions at the anode. The high temperature of SOFCs and the YSZ material provides a sufficiently good environment to internally reform the hydrocarbon-based fuel within the cell. For this reason it is possible to work with a broader variety of fuels, e.g. methane, methanol and ammonia [1]. This gives the SOFCs a major advantage because pure hydrogen is problematic to handle and costly to store [4]. It should also be mentioned that pure hydrogen is difficult to obtain since it has to be extracted from another source, most commonly natural gas.

The currently fast growing need of more energy production has created an interest for these fuel cells but they are still too costly to use. A general overview of materials and structure of SOFCs, and a brief description of SOFCs models is outlined in this review.

SOFC MODELS

A CFD-approach can be applied to solve the equations for momentum-, heat- and mass transport simultaneously. It is high-lighted below what parts of the modeling needs to be especially cared for when considering the porous media.

Mass transport

To represent the mass transport for the gases within the cell, the Maxwell-Stefan equation for mass diffusion and convection is used. The Maxwell-Stefan equation is a simplified description of the Dusty Gas Model. For flows with a low velocity in the porous medium, it is often assumed that the transport process is dominated by diffusion [4]. The Knudsen term is used when the pores are small compared to the free mean path of the gas [1]. The Maxwell-Stefan equation is defined for the domain including the electrodes, the fuel and air channels, as below [1]:

\[ \nabla \cdot \rho_i w_i \sum D_{ij} \nabla x_j + (x_j - w_j) \frac{\nabla p}{p} \cdot u - D_i^T \cdot \frac{\nabla T}{T} = S_i \] (8)

where \( w \) is the mass fraction, \( D_{ij} \) the Maxwell-Stefan binary diffusion coefficient, \( x \) the mole fraction, \( D_i^T \) the thermal diffusion coefficient and \( S_i \) the source term. The source term can be defined as an interface condition due to the active layer is considered to be very thin compared to the thick electrode [5]. The diffusion coefficient in the porous electrodes is \( D_{ij,\text{par}} \), calculated as [1]:

\[ D_{ij,\text{par}} = D_{ij} \cdot \frac{\varepsilon_p}{t} \] (9)

where \( \varepsilon_p \) is the porosity and \( t \) the tortuosity.

Electrochemical reactions

The amount of fuel gases transported to the active surface for the electrochemical reactions are governed by different parameters, such as porous micro structure, gas consumption, pressure gradient between the fuel duct and the porous anode, and inlet conditions [5]. The electrochemical reactions occur at the TPB, where the gas molecules diffuse. Ions migrate in the ionic phase and conduction of the electrons occurs in the electronic phase. This leads to the importance of understanding the electrochemical phenomena. The electrolyte functions on one hand to transport the oxygen ions to the anode and on the other hand to block the electrons to cross from the anode to the cathode. The flow of electronic charges through the external circuit balances the flow of ionic charges through the electrolyte. This transport is described by considering the ion transport from the conservation of charge [1]:

\[ \nabla \cdot i = 0 = \nabla \cdot \phi_{io} + \nabla \cdot \phi_{el} \] (10)

\[ -\phi_{io} = \nabla \cdot \phi_{el} \] (11)

\[ \phi_{io} = -\sigma_{io}^{\text{eff}} \cdot \nabla \phi_{io} \] (12)

where \( \phi_{io} \) and \( \phi_{el} \) are charge fluxes for ions and electrons, respectively, and \( \phi_{io} \) is the ionic potential in the electrolyte. The Nernst potential is calculated as the sum of the potential differences across the anode and the cathode as [1]:

\[ E = \Delta \phi_{io} + \Delta \phi_{c} \] (13)

where \( E \) is the reversible electrochemical cell voltage and \( \phi \) the charge potential. At the interface between the electrode and the electrolyte the Butler-Volmer equation is used to calculate the volumetric current density [1]:

\[ i = i_0 \exp \left( \beta \cdot \frac{n_e \cdot F \cdot \eta_{\text{act,e}}}{R \cdot T} \right) \] (14)

\[ -\exp \left( -\beta \cdot \frac{n_e \cdot F \cdot \eta_{\text{act,e}}}{R \cdot T} \right) \]

where \( i_0 \) is the exchange current density, \( F \) the Faraday constant, \( \beta \) the transfer coefficient, \( n_e \) the number of electrons transferred per reaction, \( \eta_{\text{act,e}} \) the electrode activation polarizations over-potential, and finally \( R \) the ideal gas constant.

\[ \eta_{\text{act,e}} = \frac{2 \cdot R \cdot T}{n_e \cdot F} \cdot \text{sinh}^{-1} \left( \frac{i_e}{2 \cdot i_0} \right) \] (15)
\[ i_0 = \frac{R \cdot T}{n_e \cdot F} \cdot k'' \cdot \exp \left( -\frac{E_a}{R \cdot T} \right) \]  

(16)

where \( k'' \) is the pre-exponential factor and \( E \) the activation energy. The gas species distributions are implemented by source terms due to the electrochemical reaction as [1, 11]:

\[ r_{H_2} = -\frac{i}{2 \cdot F} \]  

(17)

\[ r_{H_2O} = \frac{i}{2 \cdot F} \]  

(18)

\[ r_{O_2} = \frac{-i}{4 \cdot F} \]  

(19)

where \( i \) is the current density and \( F \) the Faraday constant.

**Modeling**

A basic two-dimensional model of the components is illustrated in Fig. 3 [1].

![Fig. 3: A schematic illustration of a model of SOFC [1].](image)

A model of an SOFC can be described by different length scales: macro scale, meso scale and micro scale, as well as the latest interest for nano scale. Not only proper length scales are needed to describe various parts of an SOFC, also different time scales need to be considered. A general relation between time- and length scales with proper modeling methods is illustrated in Fig. 4.

![Fig. 1: Characteristic time and length scales for various methods [1].](image)

The micro scale corresponds to an atom or molecular level, where thermo- and fluid dynamics and detailed chemical reactions are studied. The meso scale corresponds to a larger size than a particle but a smaller than the global flow field, which corresponds to a macro scale. Empirical data obtained from results from micro- and meso scale can further be used to derive empirical parameters. Ni has been commonly used as reforming catalysts for catalysis so a great deal of information is available for. For SOFC anodes the ceramic oxygen-ion conductor YSZ itself also has catalytic activity for partial oxidation.

Most reaction rates are represented in an Arrhenius equation-type or as a sticking coefficient. A constructed kinetic model can be obtained by combining chemical values for each species with computed activation energies and transition-state properties. The original kinetic data is often taken from a variety of different catalysis studies which makes the mechanism thermodynamically inconsistent. Due to this issue, some of the original kinetic parameters are often modified to ensure the overall consistency concerning the enthalpy and entropy. This approach permits the computation of the reverse reaction rate coefficients, which in turn is dependent on the forward reaction rate coefficients [6]. This mechanism is based on elementary steps and further it is represented in all the global processes in the anode.

For surface reactions and desorption reactions, often the Arrhenius form is applied for the reaction rate constants, at least for small or moderate variations of the temperature for the reaction [7]. The reaction rate constant of a generalized modification of an Arrhenius equation-type including the species coverage can be expressed as [4]:

\[ \text{[4]} \]
\[ k_i = A_i \cdot T^{n_i} \cdot \exp \left( \frac{-E_i}{R \cdot T} \right) \cdot \prod_{k=1}^{K} \theta_k^{\mu_k} \cdot \exp \left( \frac{-\varepsilon_k}{R \cdot T} \right) \]  

(20)

where \( A_i \) is the pre-exponential factor, \( T_i \) is the reaction temperature, \( n_i \) is the temperature exponent fraction and \( E_i \) is the activation energy for the reaction \( i \). To describe the coverage dependency, \( \mu_k \) and \( \varepsilon_k \) are introduced for the parameters for species \( k \) and reaction \( i \).

The species molar production rates depend on the surface species concentration which is sometimes expressed as the coverage \( \theta_k \). The coverage is the fraction surface sites covered by the adsorbed species \( k \) by to the active sites on the catalyst surface. The relation between surface coverage or surface concentration is expressed as [8]:

\[ \theta_k = \frac{\chi_k \cdot \sigma_k}{\Gamma} \]  

(211)

where \( \theta_k \) is the surface coverage, \( \sigma_k \) the co-ordination number (number of sites required for a species of adsorption), \( \chi_k \) is the concentration and \( \Gamma \) is the surface site density.

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The electrical power output of a SOFC depends on many factors, including the material choice and fuel composition [5]. As an alternative to the conventional SOFCs (SOFC-O) with an electrolyte of YSZ, the concept of proton ceramic electrolyte (such as BaCeO₃ based on ceramics) has been developed. It has been shown that complete fuel utilization is possible, since the water is produced in the cathode (instead of the anode) and no dilution of the fuel occurs. Thermodynamic analysis has shown that a higher theoretical efficiency can be reached, compared to conventional SOFC-O [9].

Internal reforming reactions inside the porous anodes enable the conversion of hydrocarbon fuels and water to hydrogen, which makes them extremely important to understand in detail. The heat, needed by the steam reforming reaction, is generated in the electrochemical reactions at the active surface (TPB) between the porous anode and electrolyte as well as the porous cathode and electrolyte. The probability for carbon deposition depends on the steam-to-carbon ratio. It has been well established that the key reactions occur over a surface layer of nickel atoms. If a layer of carbon is allowed to occur to build up and attach to a nickel crystallite, rapid catalyst breakdown can occur due to the graphite formation. An important area of research within SOFC development is to design an anode material with the aim of decreased steam reforming activity but still fulfill the requirement of electronic conductivity. The risk of carbon deposition can be decreased if pre-reforming is carried out before the cell, or changes can be made to the anode structure [10]:

- Complete or partial replacement of doped zirconia with doped ceria or ceria-zirconia possessing a higher

lattice oxygen reactivity/mobility. This can be combined with complete or partial replacement of Ni by Cu.

- Replacement of doped zirconia by complex perovskites with their doping by metals active in the steam reforming reaction.

- Complete or partial replacement of Ni by precious metals in cermet with complex perovskites or doped zirconia as oxide phases.

Jones et al. perform a thermodynamic analysis to observe overall trends in reforming reactivity of the pure metals. Suitable catalytic metals for the methane steam reforming are investigated. Au, Ag, Cu, Pt, Pd, Ni, Co, Ru and W are included in the concerned analysis. All of these metals are counted as transition elements in the periodic table. Potential metals are excluded stepwise:

- An overall energy diagram tells that the noble metals (Au, Ag and Cu) are unsuitable for steam reforming reaction, since the first steps of the reactions are significantly uphill energetically.

- It is also concluded that W binds C* and O* very strongly, and the further reaction is unlikely to appear.

- In terms of the free energy profiles of the reaction, Pt and Pd are found to be unfavorable for the adsorption and desorption of molecular water.

This simple investigation revealed that Ni and Ru might be suitable for the catalytic methane steam reforming reaction [11]. SOFCs contain in general a porous Ni/YSZ structure in the anodes, which enables the electrochemical reactions at the TPB at the anode/electrolyte interface [1]. It can be concluded that Ni is a good choice as catalytic material in the anodes, due to its low cost and possibility for both the electrochemical reactions and also the reforming reactions.

**Interaction issues**

The mass-, heat-, momentum- and charge transport as well as the chemical reactions physics are dependent on each other. The fluid properties and the momentum transport depend on the temperature and the species concentration. The electrochemical reactions rates depend on temperature, species concentrations and available active surface area for the catalytic reactions. The chemical reactions affect the temperature distribution by generation and consumption of heat. The leads to the conclusion that all the governing equations need to be solved coupled for the modeling.

**Porous media considerations**

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Functional electrode structures are known to work in favor of both electrochemical reaction and mass transport. It was found by Kim et al. that when the thickness of the electrolyte was decreased by 4 μm, the maximum power density increased by slightly more than 50%. Kim et al. clearly mentions that further research needs to be done in reducing the thickness and improving the homogeneity of the anode microstructure. Equally important aspects, such as the chemical stability, the thermomechanical properties and the microstructure of the electrode material need to be carefully considered. Further development and research is needed of understanding the catalytic processes, ionic-electronic phenomena. Also the phenomena at the interface at the active surface are a top priority area of interest. The electrolyte can be a fluorite, perovskite, brownmillerite or apatite-type structure. When designing as well as modeling the properties of the electrode and electrolyte materials, it should be based on the theory of nonstoichiometric defects and the analysis of their electronic structure to achieve high catalytic activity.

Jones et al. was able to probe different catalytic materials for a wide range of temperature and pressure. It was found for low temperature and for the noble metals the CO formation step is kinetically the most important step. As the temperature increases and the reactivity of the metal increases (i.e. the metal becomes less noble) the most important step for the kinetics is the dissociative methane adsorption. Jones et al. explains the fact that different studies, conducted under different conditions, find different rate determining steps.

CONCLUSIONS

In this study, the applications of different catalytic phenomena in porous media in SOFCs have been reviewed. SOFCs provide a good enough environment for reforming hydrocarbons due to their high operating temperature. This demands that the catalytic materials are conducting and reactive to reform the fuel as subsequently electricity is produced. Development of new catalyst material could considerably help in promoting alternative fuels in SOFCs, so they can better tolerate impurities and effectively reform the fuel. The high cost for both SOFCs and there is still a concern for market implementation. SOFCs are promising and have shown good tendency as an energy provider but it is concluded that further research is needed to fully understand the transport and reactive phenomena at the active sites.

REFERENCES
