THIN FILM FUEL CELLS

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ABSTRACT

In recent years there has been an enormous increase in the application of thin film technologies in the fabrication of solid state electrochemical devices. Devices in which thin film components are utilized are, e.g. solid oxide fuel cells (SOFCs), thin film rechargeable batteries, and chemical gas sensors. Chemical vapour deposition (CVD) is one of the synthesis techniques for the fabrication of thin film components for solid state electrochemical devices. This paper will focus on the application of novel CVD techniques for the fabrication of the thin film components of one of these devices, i.e. the solid oxide fuel cell. A new SOFC design concept which uses only one gas phase synthesis method will be presented.

INTRODUCTION

A solid oxide fuel cell is a device for the generation of direct-current electric power. An advantage fuel cells have over most conventional forms of power generation is that they are not Carnot limited. While many other modes of power generation involve the thermodynamic inefficient conversion of heat to mechanical energy, fuel cells convert the free energy of a chemical reaction directly into electrical energy. Therefore, high fuel efficiency and potentially very large power density (W/kg) are possible\(^1\). A SOFC consists of a gastight oxygen ion conducting solid electrolyte, a porous oxygen electrode (cathode), and a porous fuel electrode (anode). The solid electrolyte has to be gastight in order to prevent direct combustion of the fuel. The electrodes have to be porous in order to allow easy gas transport to the electrode-electrolyte interface. Charge transfer reactions take place at the ternary interface gas-electrode-electrolyte. SOFCs operate at high temperatures (>800°C), which has a favourable effect on the reaction kinetics at the ternary interface and mass transfer through the electrolyte. The fast kinetics eliminate the necessity of using expensive noble metal catalysts. To form a power generator, several elementary cells have to be connected parallel or in series, using an appropriate interconnection material. The interconnection material connects the anode of one cell with the cathode of the next. Therefore, it has to be gastight in order to prevent direct combustion of the fuel.

Because of the high operation temperature of SOFCs, and because SOFCs are ceramic devices, the materials used for the various components have to fulfill stringent requirements depending on their primary function. Furthermore, the materials need to be chemically compatible, and need to have a comparable thermal expansion coefficient (TEC) with neighbouring components. The requirements for the individual components are summarized in Table I.

A variety of configurations is now being considered for the SOFC. These include tubular, monolithic, and planar concepts\(^2\). There is a continuous search for component materials...
which can fulfill all the requirements presented in Table I at process temperatures as low as possible. The research and development of SOFCs has led to the "state-of-the-art" materials, and fabrication techniques listed in Table II.

Table I. General cell component requirements at operating temperature.

<table>
<thead>
<tr>
<th>Requirement</th>
<th>Anode</th>
<th>Cathode</th>
<th>Electrolyte</th>
<th>Interconnect</th>
</tr>
</thead>
<tbody>
<tr>
<td>High ionic conductivity</td>
<td>preferable</td>
<td>preferable</td>
<td>essential</td>
<td>detrimental</td>
</tr>
<tr>
<td>High electronic conductivity</td>
<td>essential</td>
<td>essential</td>
<td>detrimental</td>
<td>essential</td>
</tr>
<tr>
<td>Chemical and TEC compatibility</td>
<td>electrolyte/interconnect</td>
<td>electrolyte/interconnect</td>
<td>anode/cathode</td>
<td>anode/cathode</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>reducing environment</td>
<td>oxidizing environment</td>
<td>reducing/oxidizing environment</td>
<td>reducing/oxidizing environment</td>
</tr>
<tr>
<td>Catalytic activity</td>
<td>essential</td>
<td>essential</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Microstructure</td>
<td>porous</td>
<td>porous</td>
<td>impervious</td>
<td>impervious</td>
</tr>
</tbody>
</table>

The performance of a SOFC can be improved by using materials with superior electrical properties or by minimizing the thickness of the cell components. Both methods will lead to a reduction of the ohmic polarization losses. In recent years there has been an increased interest in the use of thin film components in SOFCs. Because all components are solid state materials, advanced thin film technology can be applied for the synthesis of fuel cell components, or complete fuel cells. For the planar and monolithic SOFC designs all components can be produced by tape casting and subsequent sintering. However, the advantages of synthesizing the cell components by a CVD process are that, in general, lower process temperatures are required than with sintering, and that thinner films can be produced. In principle, all thin film components of the SOFC can be fabricated using the conventional CVD technique.

Table II. "State-of-the-art" materials, and fabrication techniques for SOFC components.

<table>
<thead>
<tr>
<th>component</th>
<th>material</th>
<th>fabrication technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrolyte</td>
<td>YSZ (8 - 10 mol%)</td>
<td>Electrochemical Vapour Deposition, tape casting</td>
</tr>
<tr>
<td>interconnect</td>
<td>LaCr$_2_4$Mg$_2$O$_3$</td>
<td>Electrochemical Vapour Deposition, tape casting</td>
</tr>
<tr>
<td>cathode</td>
<td>La$<em>{1_4}$Sr$</em>{1_4}$MnO$_3$</td>
<td>slurry coating, tape casting</td>
</tr>
<tr>
<td>anode</td>
<td>Ni-YSZ cermet</td>
<td>slurry coating, tape casting</td>
</tr>
</tbody>
</table>
However, the gas impervious components, i.e. the electrolyte and interconnect, have to be deposited onto the porous electrodes. With conventional CVD it is difficult to deposit pinhole-free layers on porous substrates. Therefore, this technique as such is not well suited for the production of these components. For the production of the solid electrolyte and the interconnect Westinghouse Electric Corporation has developed a special form of CVD called electrochemical vapour deposition (EVD), which has become the key technology for the production of these components for the tubular concept SOFC\textsuperscript{67}. Advantages of this technique are that thin dense films, typically a few microns, of uniform thickness can be deposited on porous substrates, and that the technique is not restricted to flat substrates. The EVD process is similar to the chemical vapour infiltration (CVI) process using a counter reactant flow. Depending on the design of the SOFC, the CVI process itself might also be an applicable synthesis method. Other CVD techniques are expected to be suitable as well for the production of SOFC components. In principle, particle-precipitation-aided CVD (PP-CVD) can be a suitable method for the synthesis of the components of a SOFC, as it has been proven that PP-CVD is a suitable method for the synthesis of thin layers of ceramics with controlled porosity\textsuperscript{69}, and for the synthesis of gas impervious films on porous substrates.

First, the principles of the EVD, CVI, and PP-CVD processes will be discussed briefly, and some of the aspects which are illustrative for these CVD processes will be highlighted. Finally, a new SOFC design concept will be presented, using only one gas phase synthesis method.

**CHEMICAL VAPOUR DEPOSITION TECHNIQUES**

CVD is a process for the synthesis of solid products by chemical reactions between gaseous reactants. With CVD, ceramics and refractory metals are formed at moderate reaction temperatures. The reaction temperature lies well below the melting point of the product. The materials can be synthesized in the form of coatings, powders, or formed solid products\textsuperscript{10-13}.

EVD\textsuperscript{67,14-19} and PP-CVD\textsuperscript{89,10,21} are modifications of the conventional CVD process of which the names refer to the type of chemical process involved. CVI is the CVD process for the densification of a porous preform to make a matrix composite material. In the field of fabrication of thin films of SOFC components EVD is a key technology, whereas CVI and PP-CVD are, in principle, suitable techniques. The principles of these processes will be briefly discussed below.

**Electrochemical Vapour Deposition**

EVD is a modified form of CVD, developed by Westinghouse, which utilizes a chemical potential gradient to grow thin, gas impervious layers of either electronically, or ionically conducting metal oxides on porous substrates\textsuperscript{67,14-19}. The primary application of EVD to date has been in the fabrication of the solid electrolyte YSZ, and the Interconnection material magnesium-doped lanthanum chromium oxide as used in SOFCs.

The steps involved in the EVD process are shown in Figure 1. A porous substrate separates the reactant metal chloride vapours from a mixture of oxygen (O\textsubscript{2}) and steam (H\textsubscript{2}O). The first step in film formation involves pore closure by a normal CVD-type
reaction between the reactant metal chloride and steam (or oxygen). Once pore closure is complete, the reactants are no longer in direct contact. Film growth then proceeds by oxygen ion diffusion through the film owing to the presence of a large oxygen chemical potential gradient across the deposited film. In this step oxygen ion vacancies and electrons formed at the metal chloride side diffuse through the thin metal oxide layer to the oxygen-rich side. This results in a net flux of oxygen to the metal chloride side, where the oxygen reacts with the metal chloride vapour to form the metal oxide product.

The pore closure step is very important in determining the ultimate properties of the deposited film. Ideally, the pore plugging layer (CVD layer) should form on the substrate surface at the metal chloride side, and barely penetrate the substrate pores, be thin, and as close to the composition of the EVD layer as possible.

During the EVD process on a porous substrate the overall film growth can be limited by a) gas diffusion in the substrate pores, b) surface kinetics on either side of the film, or c) solid state diffusion in the growing film. When the rate of film growth is controlled by solid state diffusion, the kinetics are similar to the Wagner oxidation of metals, and the film growth rate is inversely proportional to the oxide thickness\(^{22,23}\),

\[
\frac{dL}{dt} = \frac{K_0}{L}
\]

where \(L\) is the film thickness and \(K_0\) the parabolic growth rate constant.

The diffusion processes which can take place during EVD growth are shown in Figure 1. The large oxygen partial pressure gradient across the growing film results in a flux of oxygen ions. Oxygen ion diffusion is only possible if at the same time a counter diffusion of a species with the same charge or a parallel diffusion of a species with opposite charge occurs to preserve electroneutrality.

**Chemical Vapour Infiltration**

In CVI a porous preform is densified with a solid deposit to produce a ceramic composite with high toughness and strength. CVI is mainly used for the production of special products for the automotive and aerospace industry\(^{24}\). The main difference between CVI and EVD is that in CVI deposition of a solid should occur in the pores of a preform, whereas in EVD
deposition should occur on the porous preform. Furthermore, in the CVI process the reactants are fed to the same side of the preform, instead of to the opposite sides, as in the EVD process.

If the CVI process is performed in a hot wall reactor, the process is referred to as the Isothermal CVI (ICVI) process. The CVI process can be divided into two classes depending on process conditions and its application, i.e. CVI processes using long process times of up to 500 hours for the synthesis of dense composites, and CVI processes using relatively short process times of less than 10 hours for the surface modification of porous systems.

A well known CVI process using long process times is the densification of porous fibre preforms to produce ceramic composites with high toughness and strength. In general, these long process times are necessary for full densification of the porous preform. The search for improved densification using short process times has resulted in the development of different reactor geometries. For example, a forced flow through the substrate will result in shorter process times because of the higher deposition rates, and a temperature gradient opposite to the reactant flux in the porous preform will result in a higher final density. A combination of these two processes has resulted in the development of the ORNL (Oak Ridge National Laboratory) CVI process. It has been reported that these modifications of the CVI process shorten the process time considerably.

The CVI process using relatively short process times can be used to modify the internal surface of a porous preform with only a thin deposit. For example, a bundle of fibres can be coated with a thin layer for the protection of the individual fibres. In this case, each fibre has to be coated with a thin chemically inert layer, without interconnecting the fibres in the bundle. This process can also be used for the modification of ceramic membranes, or for the improvement of the mechanical strength of sintered porous metals and ceramics. Furthermore, the CVI process using relatively short process times is promising as a novel synthesis method for catalyst materials.

Mathematical modelling of the process can give a better understanding of the influence of the individual process parameters on the deposition characteristics such as final porosity and deposition profiles in the pores. The model should describe the change in pore geometry due to the deposition of a solid in the pores, and as a result, the change in diffusion rate of the reactants in the pores during the process. The conditions for optimal experimental circumstances for the CVI process can only be deduced from a CVI model if it describes the mass transfer in a realistic pore network, and if a correct kinetic expression is implemented. In recent years, starting with the work of Van den Brekel et al., quite a number of reports have been published on the modelling of the CVI process.

Particle-Precipitation-Aided Chemical Vapour Deposition

In general, powder formation in the gas phase in a CVD process should be avoided, because this will considerably deplete the reactants necessary for the heterogeneous (CVD) reaction, leading to a non-uniform film thickness. In addition, powder formed in the gas phase can diffuse towards the substrate and deposit onto the surface. Often this will lead to an undesirable microstructure of the film. However, under certain experimental conditions powder formation can be used to our advantage. The hot-wall CVD process can be modified to control the microstructure of the layer by a controlled deposition of the particles on the substrate. In Particle Precipitation aided CVD (PP-CVD) an aerosol is formed at elevated temperatures, and the particles are precipitated on the substrate by introducing an external force for particle deposition, such as thermophoresis,
electrophoresis, or forced flow. Particle precipitation on the substrate will result in a loose powder deposit with a poor mechanical stability. In order to obtain a coherent layer, the powder should be sintered, or a heterogeneous reaction should occur simultaneously to interconnect the individual particles. Thus, the PP-CVD process consists of three steps, i.e. particle formation, particle precipitation, and interconnection or sintering of the particles, as illustrated in Figure 2.

The PP-CVD process was introduced by the group of Komiyama\textsuperscript{26,45-48}. Using this technique, they synthesized titania (TiO\textsubscript{2})\textsuperscript{46,66}, zirconia (ZrO\textsubscript{2})\textsuperscript{56}, and aluminium nitride (AlN)\textsuperscript{47,48}. The driving force for particle deposition was thermophoresis. Dense to highly porous layers were obtained depending on the experimental conditions. The microstructure of the layers seemed to be determined by a combination of particle deposition, sintering, and heterogeneous reaction.

Dekker et al. have investigated the synthesis of titanium nitride (TiN) by the PP-CVD process\textsuperscript{21}. Because TiN has a poor sinterability, a heterogeneous reaction is necessary to interconnect the precipitated particles. Hence, the reactant mixture used in the PP-CVD process has to serve as a source for powder formation as well as for the heterogeneous reaction. In principle, two separate reaction mechanisms, i.e. one for the homogeneous, powder formation, reaction and one for the heterogeneous reaction, which can occur at the same reaction temperature and reactor pressure should be used. In principle, a variety of compounds, such as nitrides, oxides, carbides, and metals can be deposited using this technique.

Figure 2. The principle of the PP-CVD process
In principle, PP-CVD might be a suitable technique for the synthesis of all components of a SOFC, as it has been demonstrated that it is possible to obtain layers with controlled porosity and good mechanical strength, and that also dense layers can be formed on porous supports, as is shown in Figure 3.

Figure 3. SEM micrographs of cross sections of TiN layers deposited using the PP-CVD technique. a) Porous layer typical for layers grown at intermediate temperature gradients in the gas phase, and low reaction temperatures; b) porous layer typical for layers grown at intermediate temperature gradients in the gas phase, and high reaction temperatures; c) dense layer typical for layers grown without cooling the substrate.
SOFC FABRICATION USING NOVEL CVD TECHNIQUES

PP-CVD

In theory the PP-CVD technique can be used to produce all components of a single SOFC, as discussed above. Hence, it should be possible to form all SOFC components in one process step, using one CVD technique, by only altering the reactant supply and reaction conditions. This production method has the following advantages over the conventional way of producing a complete SOFC:

- less temperature cycles during production; hence, less risk of mechanical failure of the components;
- if produced at operating temperature, the SOFC will be stress-free during operation;
- thin film components are produced, so ohmic polarization losses will be minimal;
- no contamination of the interfaces between the components.

As mentioned before, to obtain uniform coherent layers two separate reaction mechanisms are required under the same experimental conditions. There should be a homogeneous reaction in the gas phase as well as a heterogeneous reaction. Thus, for the successful deposition of a SOFC component by the PP-CVD process knowledge of the heterogeneous CVD reaction and of the aerosol synthesis of the material is essential. Unfortunately, this information is scarce or proprietary. However, some general conditions concerning the chemistry of the PP-CVD process can be presented.

For the formation of metal oxides by CVD metal chlorides and oxidant vapours, e.g. H₂O, O₂, or carbon dioxide/hydrogen (CO₂/H₂) can be used as reactants. In general, a reaction at a high temperature between metal chloride vapour and H₂O results in powder formation. A CO₂/H₂ mixture is usually used as oxidant source for the formation of a metal oxide film[7,8]. It is believed that this mixture generates a low concentration of H₂O. Usually, this formation takes place at the CVD surface, which will favour the formation of metal oxide at the surface by a heterogeneous reaction. Because oxygen is less reactive than steam, it might be possible that oxidation of the metal chlorides with oxygen can only take place by a heterogeneous reaction. Thus, a reactant input mixture of MeCl₄, H₂O, and CO₂/H₂ or O₂, where CO₂/H₂ or O₂ are in excess of the MeCl₄, and the MeCl₄ is in excess of the H₂O will result in powder formation as well as a heterogeneous reaction.

Until now, all materials deposited by means of PP-CVD are binary compounds. However, the SOFC cathode material and interconnection material are perovskite oxides, which are ternary compounds. Because there are few reports on powder synthesis of perovskite oxides in the gas phase, we have started to investigate the possibility to synthesize a perovskite oxide aerosol by gas-to-particle conversion, i.e. the first step in the PP-CVD process. We have investigated the formation of the perovskite oxide yttrium chromium oxide (YCrO₃) from the gas phase using yttrium trichloride (YCl₃), chromium trichloride (CrCl₃), and H₂O and/or O₂ as precursors under conditions expected to be typical for the formation of the material by heterogeneous reaction, which is essential in the PP-CVD process. The reaction temperature was kept constant at about 1283 K, while the ratio of the reactants was varied. The experimental details are reported elsewhere[9]. YCrO₃ is chosen instead of LaCrO₃, which is commonly used as interconnection material in a SOFC (Table II), for practical reasons. It is easier to obtain the necessary high gas phase concentrations of YCl₃ than of LaCl₃, because LaCl₃ is much less volatile than YCl₃. YCrO₃ is isostructural with LaCrO₃ and has almost the same electrical and thermal properties as LaCrO₃[10].

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In experiments where only oxygen, and no steam, was present no powder was formed, but only deposition on the reactor wall by a heterogeneous reaction could be observed. This indicates that the reactivity of the gas mixture without steam is not high enough to induce nucleation in the gas phase, and that oxygen may be a suitable reactant for heterogeneous CVD of YCrO₃. In experiments where steam was present powder was formed. Hence, for powder formation the presence of steam is necessary.

XRD analysis of the powders revealed that it is possible to synthesize the perovskite oxide YCrO₃ from the gas phase, using metal chlorides, and steam and oxygen as precursors. At the reaction conditions chosen, Cr₂O₃, or mixtures of Cr₂O₃ and YCrO₃ are formed. Formation of single phase YCrO₃ is inhibited by either thermodynamic or kinetic limitations. Thermodynamic equilibrium equations could elucidate this problem. In case of thermodynamic limitations, experimental conditions have to be chosen such that YCrO₃ is the only stable solid species. In case of kinetic limitations, it is possible that, although according to thermodynamic equilibrium calculations only one solid phase is stable, e.g. YCrO₃, other solid phases, e.g. Cr₂O₃, are formed. Then, it is more difficult to obtain the optimal reaction conditions.

In combination with these calculations, further experiments need to be performed in order to determine the range of reaction conditions, in which single phase YCrO₃ powder is formed. If these conditions are known, it is useful to determine the conditions for the heterogeneous formation of YCrO₃ in separate experiments, using experimental conditions within the range necessary for the homogeneous reaction to take place. Then, it might be possible to choose reaction conditions such that the homogeneous and heterogeneous reactions occur simultaneously, which is a necessity in the PP-CVD process, for the formation of films of perovskite oxides with controlled morphology.

New SOFC Design Using CVI Techniques

The configurations considered for a SOFC include tubular, planar, and monolithic concepts. Virtually all configurations are based on a multi-layer laminate of the anode components (cathode-electrolyte-anode). Depending on the cell concept a separate porous support (cathode or interconnect) gives the cell the necessary mechanical stability. A different design concept by Dekker® using only one gas phase synthesis method will be described here. This new concept has not the characteristic laminate structure, and the electrolyte material gives the cell its mechanical stability. A schematic representation of the individual process steps in the production of this fuel cell is given in Figure 4. A porous body of an arbitrary shape of the electrolyte material is used as preform (0 in Figure 4). This preform is partially densified with the electrolyte material by CVI. During densification it is intended that there is only pore plugging in the middle of the porous body (1 in Figure 4). As a result an electrolyte is formed consisting of two porous compartments separated by an impermeable deposit of the electrolyte material. Consequently, the electrodes have to be deposited into the two separate porous compartments by CVI (2 and 3 in Figure 4). In this case, pore plugging should be avoided. The result will be the formation of one fuel cell. The proposed production method can be applied for the tubular concept as well as for the planar concept. If a planar concept is used the interconnect can be similar as the electrolyte (A and B in Figure 4). A schematic representation of a complete cell using planar porous supports is given in Figure 5.
Figure 4. A schematic representation of the synthesis route for the production of a fuel cell by CVI. 0) Porous preform of electrolyte material; 1) pore closure in the middle of the preform; 2) deposition of a thin cathode layer, 3) deposition of a thin anode layer; A) porous preform of the interconnect, B) pore closure in the middle of the preform.

Figure 5. Schematic representation of a planar SOFC fabricated using only CVD techniques.
This production method offers several advantages over conventional production techniques. The temperature required for CVI is lower than for sintering of the component materials. This reduces thermal stresses, and the chance of undesirable interface reactions between the individual cell components. The number of thermal cycles during synthesis can be reduced to one, because, in principle, the three CVI production steps can be performed in one reactor. In addition, the accessible electrode/electrolyte surface area is higher than for the conventional planar or tubular concepts with a laminated structure. It is expected that the mechanical stability of such a cell is good, because the mechanical strength is determined by the tough YSZ electrolyte. The realisation of this proposed fuel cell relies entirely on knowledge of the kinetic laws of the reactant mixtures for the synthesis of the individual cell components, because the dependence of the growth rate with respect to the reactant concentrations, in combination with the mass transport into the pore network will determine the mass distribution of the deposit. The implications of the desired mass distribution for the individual cell components will be discussed next.

For the production of the electrolyte the densification should occur from the inside to the outside of the porous preform until there is pore plugging in the middle of the preform. A preferential pore closure in the middle of a porous preform is only possible if the CVD reaction rate of the electrolyte has a negative order dependence with respect to at least one reactant concentration. In addition, this reactant may not be present in excess with respect to the other reactants. For example, YCl₃, ZrCl₄, and CO₂/H₂ can be used for CVD of YSZ. The reaction mechanism responsible for the growth of YSZ using these reactants is not known. However, some ZrO₂-CVD experiments implicitly indicate that the growth rate has a negative order dependence on one of the reactant concentrations⁴⁹. Such an order dependence favours pore filling from the inside to the outside⁴⁴.

CVD of the perovskite oxide La₁₋ₓSrₓMnO₃₋₅ has not been reported in literature. However, the formation of a doped perovskite oxide should be possible at high reaction temperatures using gaseous oxygen containing species and metal halides. The thickness of the deposit in the porous preform should be as thin as possible in order to reduce the oxygen ion transfer resistance through the cathode layer. On the other hand, the deposit should be as thick as possible to reduce polarization in the electrode material.

CVI of nickel oxide (NiO) can be used for the production of the anode material. After deposition of NiO the CVI layer can easily be reduced leaving a porous nickel electrode layer on the internal surface of the support. Such an electrode has a large accessible ternary (electrode-electrolyte-gas) interface area. Optionally, the electrode surface can be immobilized by an additional EVD process for the deposition of YSZ to prevent sintering of the Ni during cell operation¹³. NiO can be formed using nickel tetracarbonyl (Ni(CO)₄) and O₂.⁵⁵

CONCLUSIONS

An outlook has been given with respect to the potential application of novel CVD techniques for the fabrication of solid oxide fuel cells. It has been shown that relative new CVD techniques, e.g. CVI, EVD, and PP-CVD, offer new possibilities in the field of SOFC production, and that these techniques are a valuable contribution to the already available more conventional synthesis routes.
REFERENCES

47. T. Osawa and H. Komiyama, in New Materials Processing, World Congress III of Chemical Engineering (Tokyo, Japan, 1986), p. 250.