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# Direct carbon, integrated gasification, and deposited carbon solid oxide fuel cells: a patent-based review of technological status

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## Abstract

This review presents three directions in solid oxide fuel cell (SOFC) technology development involving solid-state carbon in some stage of the fuel-to-electricity conversion process: direct carbon (DC-SOFC), integrated gasification (IG-SOFC) and deposited carbon (rechargeable SOFC). Recent achievements of science and technology were studied in order to identify the most widely developed concepts. In addition, the review contains a statistical approach to published patents and articles, naming the people and institutions active in the field. Simultaneous development of all three technologies could bring synergies and contributed to a major breakthrough in the efficiency of coal-fired power plants.

*Keywords:* Direct Carbon Fuel Cell; DC-SOFC; DCFC; IG-SOFC; Clean Coal Technologies

## 1. Introduction

Global electricity generation currently exceeds 22,000 TWh/a, with the highest share (41.3%) taken by coal and brown coal power plants [1]. Conventional technologies of coal-to-electricity thermal conversion efficiencies are limited by Carnot cycle efficiency, increasing alongside rising parameters (temperature, pressure) of the working fluid. Therefore, the efficiency of thermal power plants is restricted by the properties of the materials used. Modern coal-fired steam power plants present electrical net efficiencies of over 47% with the application of advanced combustion technologies and ultra-supercritical steam cycles; coal conversion efficiency of 50% is theoretically achievable with the advanced ultra-supercritical cycle (A-USC) [2] and much research is ongoing into the latter worldwide. The electrical efficiency of newly-installed capacity has shown a linear increase over the last few decades, but during the last few years there has been an observable stabilization.

Alternative approaches to electricity generation from coal include integrated gasification combined cycle or electrochemical coal conversion. Development of the latter may lead to a significant reduction in $CO_2$ emissions due to the high efficiency and the ease of $CO_2$ sequestration.

Electrochemical carbon conversion has the potential to shepherd in a whole new chapter in coal-powered power plant development. The technology of the solid oxide fuel cell (SOFC) is one of the possible avenues available for direct carbon conversion. Its working principle is based on the phenomenon of oxygen ions transport through the ceramic electrolyte material. In the SOFC, the oxidant (usually air) is passed through the cathodic side of the cell, while on the anodic side, a fuel (e.g. $H_2$, CO, reformate, producer gas or solid carbon) flow is maintained. At elevated temperatures, when the ionic conductivity of the electrolyte is sufficiently high, the cell is able to electrochemically oxidize the fuel with the oxygen anions conducted through the electrolyte. As a result of this reaction an electric current can be generated by the electrons moving to the cathodic side through the external circuit. The efficiency of these systems in their present early stage of development is already comparable (exceeding 61%) to state-of-the-art steam power plants [3, 4]. The modelling and optimization of SOFC-based power systems plays a key role in maximizing the performance, by adjusting the operating parameters of fuel cells and identifying the optimum working conditions [5–8]. Moreover, new configurations of systems are sought to increase their efficiency and operational flexibility [9]. Increasing the efficiency beyond 70% is eyed through the application of steam turbine or gas turbine bottoming cycles [10]. Introducing solid carbon as fuel for the fuel cells is still a challenge. This task can be accomplished with alkaline, molten carbonate and solid oxide electrolytes and some hybrid solutions. In the last

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decade, numerous groups investigated these technologies, as has been thoroughly analyzed in review papers published by some of the most important researchers in the field [11–15]. From the three electrolyte types, the solid oxide one was chosen by the authors both for development as well as for investigation within this review. Despite enjoying the highest operating temperature, the SOFC-based carbon-fueled systems are seen as having the greatest simplicity because they are dry-type systems and need no recirculation of $CO_2$ to the cathode stream. These systems have recently undergone the most rapid development, resulting in the highest currently demonstrated power density: 0.5 W/cm$^2$ [16–18] and the highest number of published papers and granted patents. The presented paper concentrates on carbon fueled SOFCs, with a special emphasis on membrane electrode assembly (MEA) materials as well as on the engineering solutions published in the scientific literature, publicly available reports and patents.

The worldwide activities frequently take advantage of the latest achievements in gas-fed SOFC technology, adapting them to carbon-fueled setups to improve the performance and durability of the carbon-fueled cells. The development of these highly efficient carbon conversion technologies has the potential to achieve a major breakthrough in the stationary and distributed power generation sectors in the years ahead.

On the other hand, mobile and transport applications are also an emerging group for the implementation of SOFC technologies fueled by solid carbon. This is due to the ease of carbon storage and the very high volumetric and gravimetric energy density of this solid fuel in comparison to existing gaseous fuel storage technologies (pressurized, liquid, hydrides, and others), as presented in Table 1.

Many methods of carbon-to-electricity conversion with the application of SOFCs can be proposed. This paper concentrates on technologies in which carbon exists in a solid state at some stage of the power generation process. The authors of the present paper propose to categorise carbon-fueled SOFC technologies as follows: direct carbon (DC-SOFCs), deposited carbon (rechargeable SOFCs), and integrated gasification (IG-SOFCs). In general, these technologies are uniquely characterized by a carbon compound supplied to the anode: solid carbon, hydrocarbon, or carbon monoxide. However, anodic electrochemical reactions and their mechanisms apply to all of the described technologies.

In the authors' understanding, the term DC-SOFC applies to a high-temperature single- phase solid oxide electrolyte fuel cell fed with a dry solid carbonaceous fuel that remains in direct contact with a solid anodic surface (possibly porous) during operation. This excludes liquid metal anode systems, molten carbonate fuel/anode additives, and hybrid electrolytes (i.e. ceramics + molten carbonate) that are not considered as classic, commercially available SOFC solutions.

The other systems which fall within the scope of the current review are deposited carbon SOFCs, in which carbon is introduced into the anodic chamber in the form of dry gas containing carbon-rich compounds (e.g. hydrocarbons). The fuel gas undergoes thermal cracking reactions directly on the surface of the anode catalyst. Solid carbon formed in this process is a substrate for anodic cell reactions. As opposed to DC-SOFCs, this concept enables high and effective utilization of the porous anode surface area for carbon electrooxidation. These cells are 'charged' with hydrocarbons and are referred to as rechargeable SOFCs.

The final proposed type comprises integrated gasification SOFCs (IG-SOFCs). This review narrows the gasification of carbonaceous fuels down to a $CO_2$-driven process in a reverse Boudouard reaction (1).

$$C + CO_2 \rightarrow 2CO \tag{1}$$

In this way, hydrogen, water, and hydrocarbons are eliminated from the group of reactants for all investigated systems. The small group of remaining reactants includes C, $O_2$, $CO_2$, and CO. Gasification can be accomplished in a separate reactor (external gasification) or in the anode chamber (internal gasification). The latter process can be performed in a detached configuration, whereby carbon is separated from the anode surface (e.g. to minimize anode poisoning), or in a direct contact configuration, which has been assigned to the DC-SOFC category.

The categories characterized above are presented in Table 2, including the number of patents and articles regarding each one. Although most of these publications and patents fall directly within the described categories, there are some whose content is general to all types of carbon-fueled SOFCs, including system design, integration of carbon-fueled SOFC power systems with gas turbines, and control equipment.

## 2. Technological overview

### 2.1. Fundamentals of carbon-fueled SOFCs

Carbon in elemental form is characterized by high specific enthalpy equal to -394.801 kJ/mol at 1100 K, 1 bar (calculated on the basis of data from [19]). In systems based on DC-SOFC and IG-SOFC technology, solid carbon plays the role of a primary fuel, in contrast to the rechargeable SOFC technology, where solid carbon is only an intermediate step in gaseous fuel conversion. The electrooxidized species differ between IG-SOFCs (CO only) and the other two, DC-SOFCs and rechargeable SOFCs, where the oxidized species are CO and solid carbon.

Each type of carbon-fueled SOFC is characterized by a system of parallel reactions. The equations and selected thermodynamic parameters of the investigated reactions for 1100 K are presented in Table 3. The relevant half-cell anodic reactions (also specified in Table 2) for each technology are:

$$C + 2O^{2-} \rightarrow CO_2 + 4e^- \tag{2}$$

$$C + O^{2-} \rightarrow CO + 2e^- \tag{3}$$

Table 1: Energy density for different fuels

| Fuel | Storage state | Tank type | Specific energy of fuel, MJ/kg | Volumetric energy density of the storage system, MJ/l | Gravimetric energy density of the storage system, MJ/kg |
|---|---|---|---|---|---|
| Compressed hydrogen | Gas, 70 MPa | High-pressure cylinder | 141.86 | 5.6 | 7 |
| Compressed natural gas | Gas, 25 MPa | High-pressure cylinder | 47.4 | 9 | 13.8 |
| Coal | Solid | Any | 32.5 | 22.7 | 32.5 |

Table 2: Energy density for different fuels

| Carbon-fueled SOFC technology | Fuel source type | Carbon compound supplied to the anode | Anodic half-reactions | Number of patents | Number of peer-reviewed articles |
|---|---|---|---|---|---|
| DC-SOFC | Carbonaceous, solid | C | (2), (3), (4) | 22 | 43 |
| Rechargeable SOFC | Hydrocarbons | $C_mH_n$ | (2), (3), (4) | 7 | 5 |
| IG-SOFC | Carbonaceous, solid | CO | (4) | 10 | 52 |

Table 3: Fuel reactions in carbon fueled SOFCs for 1100 K, where $\Delta H$—enthalpy of rection, $\Delta G$—Gibbs free energy of reaction, $\Delta s$—entropy of reaction, $\eta_{thermo.}$—thermodynamic efficiency, $OCP$—open circuit potential, calculations based on [12]

| Reaction | $\Delta H^{1100K}$, kJ/mol | $\Delta G^{1100K}$, kJ/mol | $\Delta s^{1100K}$, J/(mol K) | $\eta_{thermo.}$, % | $OCP^{1100K}$, V |
|---|---|---|---|---|---|
| 6 | -394.80 | -395.98 | 1.08 | 100.30 | 1.026 |
| 7 | -112.57 | -209.08 | 87.74 | 185.73 | 1.084 |
| 8 | -282.23 | -186.90 | -86.66 | 66.22 | 0.969 |
| 1 | 169.66 | -22.18 | 174.40 | - | - |

$$CO + O^{2-} \rightarrow CO_2 + 2e^- \tag{4}$$

The cathodic half-cell reaction assumed for all oxygen-ion-conducting membranes is described by the following equation:

$$O_2 + 4e^- \rightarrow 2O^{2-} \tag{5}$$

Carbon monoxide gas can be supplied to the SOFC anode from several sources. It can be produced in situ in an electrochemical reaction (7) or be introduced from outside the cell, e.g., from a coupled carbon gasification reactor. Moreover, at temperatures above 700°C, CO is internally generated in the synproportionation (Boudouard) reaction (1) between $CO_2$ and C in the anodic chamber.

The partial pressure of gaseous reactants is not uniform in the anodic compartment due to the specific nature of particular reactions that take place in different zones. Moreover, these reactions strongly influence one another because of common reactants or products, and local heat transfer.

The thermodynamic parameters and potentials of DC-SOFC reactions are summarized in Table 3 for a common SOFC operating temperature of 1100 K. As can be seen, the thermodynamic efficiency of a DC-SOFC varies depending on the reaction path.

$$C + O_2 \rightarrow CO_2 \tag{6}$$

$$C + \frac{1}{2}O_2 \rightarrow CO \tag{7}$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2 \tag{8}$$

It is very important to note that fuel cells make direct use of the Gibbs free energy of a reaction converting it to electrical power. Irreversible losses are dissipated as heat, as opposed to heat engines that convert the enthalpy of a reaction to kinetic energy, which is later converted in an electric generator to electric power. Thus, the theoretical efficiency of a fuel cell, calculated as the ratio of Gibbs free energy to the enthalpy of reaction, might exceed 100%, which is the case for reactions (6) and (7). Since the analyzed system of reactions does not contain water, both HHV- and LHV-based efficiencies of reaction (6) equal 100.3% (at 1100 K and 1 bar).

During actual fuel cell operation, thermodynamic efficiency is reduced due to operational losses. Losses in a fuel cell are usually categorized as follows: activation loss, ohmic loss, concentration loss [20]. The voltage drop caused by these unwanted phenomena influences the technically important voltage efficiency. Additionally, at the system level, fuel utilization and Faradaic efficiency describing losses caused by chemical depletion of fuel (e.g. due to the Boudouard reaction) must be taken into account.

In an ideal DC-SOFC, where carbon particles are in direct contact with the TPB (three-phase boundary), only reaction (6) occurs (half-reactions (2) and (5)), generating a potential of 1.026 V at 1100 K (1.022 V at 298.15 K). In the existing laboratory systems, all of the reactions (1–8) are usually reported [21, 22]. Desclaux et al. [23] proved that in their experimental setup only about 3% of the fuel cell power was generated in reaction (8); most of the generated power came from reactions (6) and (7). In contrast, Bai et al. [16] reported a solid oxide fuel cell optimized to operate on the basis of reactions (1) and (8). Catalyzed activated carbon powder was applied as fuel in a DC-SOFC of their design. As products, relatively high values of current density and almost pure CO were generated.

In general, the efficiency of a carbon-fueled SOFC is the product of individual efficiencies according to the formula:

$$\eta_{DC-SOFC} = \eta_{TH} \times \eta_V \times \eta_F \times F_U \tag{9}$$

where: $\eta_{DC-SOFC}$—overall DC-SOFC efficiency; $\eta_{TH} = \frac{\Delta G}{\Delta H}$—thermodynamic efficiency; $\eta_V = \frac{V^{op}}{E^{t,p}}$—voltage efficiency (relationship of operating voltage to the theoretical thermodynamic potential of the reaction); $\eta_F = \frac{I}{n \times F \times \dot{m}}$—Faradaic efficiency (relationship of electrochemical fuel conversion to overall fuel-consuming reactions, e.g. leakage, Boudouard reaction); $F_U$—Fuel utilization (percentage of fuel stream utilized in a fuel cell in a single pass).

Different approaches to minimize losses and to improve fuel cell performance and lifetime are continually being undertaken. The efficiency of various carbon-fueled SOFC systems is estimated to fall within the range 75 .. 80% [24, 25].

### 2.2. Overview of patents and literature

DC-SOFC technology is being developed using the achievements of many related disciplines. Crucial technical issues are associated with SOFC technology as well as with carbon gasification technology.

Scientific literature and patent databases were searched in order to outline the present technological status. The main tools used in the search were the European Patent Office database Espacenet (http://ep.espacenet.com) and the Science Direct scientific database (http://www.sciencedirect.com/). Other databases of scientific publications and patents (i.e. Korean and Chinese) have been used as well to review the most recent achievements of science and industry.

The patent database was filtered using a category search combined with a keyword search to obtain documents unique to the carbon fueled SOFC topic. The basic query included the H01M8 (manufacture of fuel cells) and H01M4 (electrodes) international patent categories. The queries included specific keywords (solid, oxide, SOFC, battery, cell, direct, carbon, coal, Boudouard) in abstracts. Subsequently, patents were viewed in order to exclude patents not within the scope of current review. As a result of the agreed criteria, 39 granted patents were retrieved. An additional 16 patent applications were filed worldwide and the patent procedure is on-going.

For peer-reviewed scientific papers, a similar approach was used. Databases of articles and books were searched for groups of keywords similar to those used in searching for patents. Additionally, the connections and experience of the authors were helpful in finding scientific documents related to the topic, especially official reports and articles not indexed in popular databases (most often written in languages other than English). 72 original research articles dealing with experimental carbon-fueled fuel cell or fuel-cell stack tests were found and reviewed by the authors of this paper. All of the analyzed papers were published in the years 1995–2016, 58 from the years 2010–16.

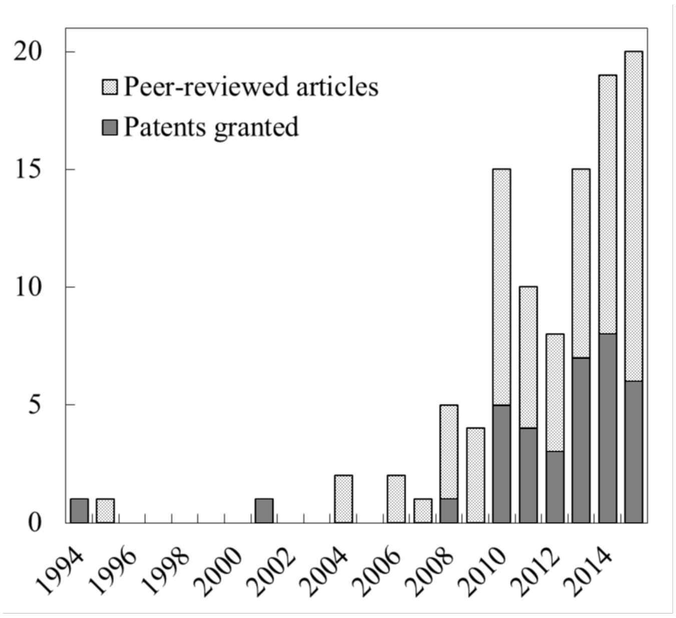

Figure 1: Number of patent applications and patents granted and scientific papers on carbon-fueled SOFCs in the years 1994–2015

In the past decade an upward trend has been observed in the number of patents as well as of peer-reviewed scientific papers published on DCFC technology (Fig. 1). Patent literature is considered a fair indicator of technological growth. Although continuous progress is expected over the coming years, institutions which hold at least one patent in this area are still not numerous. Table 4 presents a list of institutions with respect to the number of patents granted, patent applications, and scientific papers. Fig. 2 presents the country-distribution of the patents granted in the field.

## 3. SOFCs fueled with solid carbon directly to the anode chamber (DC-SOFCs)

Direct oxidation of solid carbon in SOFCs is attractive due to the theoretical efficiency of energy conversion in the cell. However, there are still many problems of a technical nature hindering the construction of these DC-SOFCs, of which the most important are their relatively low power density and the issue of continuous fuel supply.

The main restriction leading to limited power density is the limitation of surface between solid carbon particles and electrochemically active sites in comparison with gaseous fuels. This difference is estimated to be several orders of magnitude [49]. There are three possible ways to increase power density: chemical and structural tailoring of MEA (membrane electrode assembly) materials, adjustment of fuel properties by means of chemical and physical treatment, and fuel additives. A cell setup designs promoting improved delivery of solid carbon to the anodic surface are also under investigation.

Table 4: Patents and scientific papers by institution

| Country | Patentee/Institution | On-going pat. applications | Patents granted | Scientific papers | References |
|---|---|---|---|---|---|
| JP | Tokyo Institute of Technology | | 6 | | [26–31] |
| JP | Mitsubishi Chemical Corporation | | 5 | | [26, 27, 29–31] |
| KR | Pusan National University | | 4 | 2 | [32–37] |
| CN | Huaneng Group Clean Energy Technology Research Institute Co., Ltd. | | 4 | 1 | [38–42] |
| US | Turgut M. Gür / Direct Carbon Technologies, Clean Coal Energy, Stanford University | | 3 | 7 | [18, 43–50] |
| PL | Institute of Power Engineering | | 2 | 13 | [42, 51–61] |
| CN | Tsinghua University | 1 | 2 | 5 | [42, 62–68] |
| KR | Korea Energy Research Institute (KIER) | | 2 | 3 | [37, 69–72] |
| KR | Gwangju Institute of Science and Technology (GIST) | | 2 | 2 | [72–75] |
| US | The University of Akron / S. Chuang | | 2 | 1 | [21, 76, 77] |
| US | Pratt and Whitney Rocketdyne | | 2 | | [69, 78] |
| CN | South China University of Technology | | 1 | 7 | [16, 79–85] |
| CN | Shanxi University | | 1 | 3 | [86–89] |
| CN | Shanghai Institute of Ceramics | | 1 | 2 | [90–92] |
| JP | National Institute of Advanced Science And Technology (AIST) | | 1 | 1 | [11, 93] |
| KR | Korea Institute of Industrial Technology (KITECH) | 1 | 1 | | [94, 95] |
| CN | China University of Mining And Technology | | 1 | | [90] |
| JP | Honda Motor Co. Ltd | | 1 | | [28] |
| JP | Japan Science and Technology Agency | | 1 | | [96] |
| KR | Research Institute of Industrial Science and Technology (RIST) | | 1 | | [97] |
| US | EGT Enterprises / B. Ennis | | 1 | | [98] |
| US | Gas Technology Institute | | 1 | | [99] |
| US | Thermochem International / R. Chandran | | 1 | | [100] |
| PL | AGH Univeristy of Science and Technology | 1 | | 8 | [53–55, 60, 61, 101–104] |
| AUS | Monash University / CSIRO Energy Flagship | | | 8 | [105–112] |
| CN | Nanjing Tech University | | | 4 | [87–89, 113, 114] |
| DE | Bayerisches Zentrum für Angewandte Energieforschung | | | 4 | [23, 115–117] |
| PL | Jerzy Haber Institute of Catalysis and Surface Chemistry | | | 4 | [53–55, 103] |
| UK | University of Cambridge | | | 3 | [42, 53, 54] |
| US | Georgia Institute of Technology | | | 3 | [83, 84, 118] |
| CN | Qingdao University of Science and Technology | | | 2 | [83, 84] |
| CN | Shanxi Institute of Coal Chemistry, Chinese Acad. of Sci. | | | 2 | [87, 88] |
| GRE | Aristotle Univ. of Thessaloniki | | | 2 | [119, 120] |
| GRE | Chemical Process & Energy Resources Institute (CERTH) | | | 2 | [119, 120] |
| GRE | Technical University of Crete | | | 2 | [119, 120] |
| GRE | University of Western Macedonia | | | 2 | [119, 120] |
| IR | University of Limerick | | | 2 | [42, 54] |
| US | Lawrence Livermore National Laboratory (LLNL) | | | 2 | [24, 25] |
| US | University of Utah | | | 2 | [11, 18] |
| CN | Guangdong Institute of Education | | | 1 | [82] |
| CN | Harbin Institute of Technology | | | 1 | [121] |
| CN | Huazhong University of Science and Technology | | | 1 | [122] |
| CN | Shanxi Lanyan Coalbed Methane Group Co., Ltd. | | | 1 | [89] |
| CN | Tianjin University | | | 1 | [123] |
| FR | CNRS Universite de Nantes | | | 1 | [124] |
| FR | GEPEA, UMR CNRS Ecole des Mines de Nantes | | | 1 | [124] |
| FR | S3D-Solutions Dechets et Developpement Durable | | | 1 | [124] |
| IT | University of Perugia | | | 1 | [125] |
| JP | Kobe Steel Ltd. | | | 1 | [103] |
| JP | National Institute of Material and Chemical Research | | | 1 | [126] |
| JP | Tohoku University Katahira | | | 1 | [127] |
| KR | Korea Inst. of Ceramic Engineering Techn. (KICET) | | | 1 | [36] |
| NED | Energy Research Centre of The Netherlands (ECN) | | | 1 | [128] |
| NED | TU Delft | | | 1 | [125] |
| NOR | GasPlas GaAS Oslo | | | 1 | [53] |
| NOR | University of Oslo | | | 1 | [120] |
| PHI | University of the Philippines Diliman | | | 1 | [75] |
| POR | Instituto Politecnico de Setubal | | | 1 | [58] |
| SAU | Water and Energy Research Institute, King Abdulaziz City for Science and Technology (KACST) | | | 1 | [119] |
| UK | Imperial College, London | | | 1 | [129] |
| US | Massachusetts Institute of Technology, Cambridge | | | 1 | [42] |
| US | University of South Carolina | | | 1 | [130] |
| JP | Toyota Motor Corporation | 1 | | | [131] |

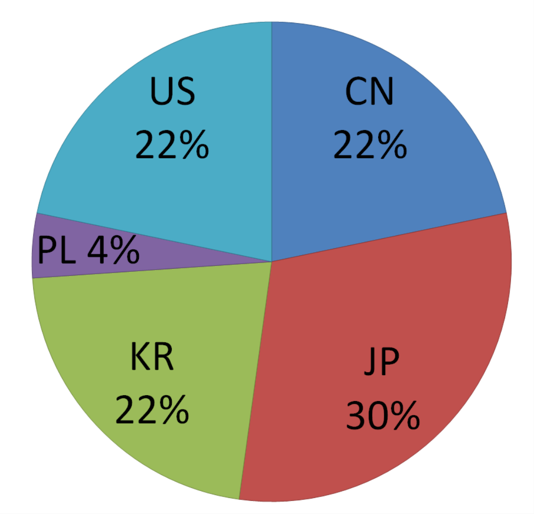

Figure 2: Carbon-fueled SOFC granted patents by country

Fundamental research on novel MEA materials and fuels must be validated under SOFC operating conditions. For the purpose of fundamental research, a wide spectrum of experimental single cell arrangements is being designed. Although the main purpose of single-cell setup designs is to research fundamental processes, these designs contain technical solutions which are ready for implementation in power generation devices.

Another very important DC-SOFC research area is related to stack design. This includes particular engineering solutions as well as technical issues connected to solid fuel supply to the anodic compartment and the removal of unreacted residues therefrom.

The obvious issue of insufficient durability, related mostly to contamination of fuel by sulfur, is considered a secondary issue due to existing methods of fuel clean-up [72, 103, 104].

### *3.1. Fundamental research on DC-SOFC MEAs and fuels*

The main fields of fundamental DC-SOFC research include the materials and microstructure of DC-SOFC membrane electrode assemblies (MEAs) as well as fuels that could be efficiently electrooxidized in such a fuel cell. A MEA is composed of three layers: a ceramic electrolyte conducting oxygen ions and two electrode layers, the anode and the cathode. Despite the existence of established methods of MEA preparation, many labs focus on the development of new electrode or electrolyte materials and manufacturing methods in order to improve carbon electrooxidation properties. The research is aimed at improving the properties of all MEA elements, with the greatest emphasis on the anode electrode. Another field of research concentrates on the characterization and modification of carbonaceous fuels used in SOFC. Carbonaceous fuels from various sources (i.e. coal, biomass, petroleum-derived), both pure as well as pre-treated, have been widely reported in the scientific literature.

#### *3.1.1. Research on MEA cathode layer materials and microstructure*

Because the oxidant chamber of a DC-SOFC is in principle identical to that of a gas-fed SOFC, the materials and microstructure of state-of-the-art cathodes can be successfully applied in this technology. Researchers and manufacturers worldwide apply perovskite manganese-based oxide structures as cathode materials in high-temperature SOFCs [129].

In almost all recent publications in the DC-SOFC field, lanthanum-strontium-manganite (LSM) was applied as cathode material [16, 21–23, 37, 42, 46, 48, 53–61, 66–68, 75, 81, 84, 87–89, 91, 92, 103, 104, 113–117, 121, 127, 130, 132]. In some cases LSM was additionally mixed with electrolyte material to enhance the ionic conductivity of the cathode [21, 22, 37, 42, 54, 57–59, 66–68, 81, 84, 91, 92, 103, 104, 113, 116, 117, 130, 132]. Another suitable material for a SOFC cathode is Lanthanum-Strontium-Cobalt-Ferrite (LSCF); however, only the Australian CSIRO [105–112], Chinese Huazhong University [122] and Korean KIER [71] have published results with such a cathode in a DC-SOFC. Another material—BSCF (barium strontium iron cobaltite) was used by only one group [123] as a DC-SOFC cathode.

Platinum-based porous cathodes, despite their poor performance, are being used for comparative research purposes (e.g. optimization of fuel additives). Some researchers utilize pure platinum [36, 47, 101] for cathodes; others use Pt/electrolyte composite materials [47].

#### *3.1.2. Research on MEA anode layer materials and microstructure*

The anode layer in a DC-SOFC MEA is of crucial significance for DC-SOFC performance. Carbon and carbon monoxide oxidation reactions take place on its catalytic surface. The reaction sites are located on the TPBs, where the electronic conductor is simultaneously in contact with the oxygen ion conductor and the fuel particles. To date, researchers have reported the use of a number of materials as anodes. In recent years, an emerging trend in research leading to optimization of the anode materials for DC-SOFC application has been observed in the scientific literature. Individual research programs for DC-SOFCs cover issues specific to solid carbon fuel, including catalysis of carbon reactions: electrooxidation (6–8) and Boudouard (1), structural designs for improving the contact area and increasing the chemical stability against sulfur poisoning and nickel carbide formation.

The anodic materials of the greatest technological importance for SOFC technology are composites of ceramic and metals (cermets). Metal particles, finely dispersed in ceramics, show catalytic activity in electrooxidation reactions and electronical conduction, while the ceramic phase presents the oxygen-anion-conductivity. The content of the metal phase in the range of 40–60% is considered to maintain sufficient activity and electronic conductivity. It is generally considered that cermets used for carbon and carbon monoxide oxidation can be adapted from hydrogen and syngas SOFC technology.

It is widely assumed that in the case of carbon oxidation the charge transfer may occur on the carbon particle in contact with oxygen ions delivered from the oxygen ion conductor. In this case, metal particles in the cermet function as the electrical current conductor. Li researched the mechanism of solid carbon oxidation using a carbon-oxygen species formation on a Ni/YSZ cermet using Raman spectroscopy and electron imaging techniques [68]. He concluded that the mechanism of oxidation involves an $O^{2-}$ adsorption step on a carbon particle followed by a carbonyl group formation step. The release of two electrons from a carbonyl group results in carbon monoxide production. Oxidation of a carbonyl group with another $O^{2-}$ ion results in the formation of $CO_2$.

The mechanism of carbon monoxide oxidation on cermets is different from that for solid carbon. The reaction takes place on the metallic catalyst particle, where the oxidizing species flow is maintained. Existing studies assume that the first step of the mechanism is adsorption of CO on the metallic catalyst surface [58, 133]. According to [58, 134], the substrate for a reaction with adsorbed CO is $O^{2-}$, accessible at the phase boundary. The value of the charge transfer coefficient equal 0.5 indicates that the geometry of the active complex is intermediate between the adsorbed CO and $CO_2$ products. On the other hand, results obtained using the impedance spectroscopy technique [133, 135] indicate that the reaction involves a charge transfer from $O^{2-}$ with the formation of an O radical. $CO_2$ is formed subsequently between the adsorbed CO and O radical formed from $O^{2-}$ in the charge transfer reaction step. It has also been suggested that CO can be oxidized directly from the gaseous phase without being adsorbed on the catalyst surface [135].

Among many others, Ni/YSZ, Ni/ScSZ, Ni/GDC and Ni/$CeO_2$ materials are widely used in DC-SOFC research [16–18, 21, 22, 37, 42, 46, 48–50, 53–60, 66–68, 71, 72, 75, 81, 87–89, 91, 92, 103, 104, 112, 114, 115, 122, 124, 127, 128, 130, 136] but cermets of ionic conductors with other metals, such as copper, silver or cobalt also start to emerge [54, 80, 82–85, 119, 120].

Authors of the present review, in collaboration with others [55], published electrochemical measurements for a DC-SOFC with various anode compositions. The cells were tested under the same conditions with the same carbon fuel (biomass-derived charcoal, Merck). At 800°C, performances of three different cermet anodes (Ni-YSZ, Ni-GDC, and ($Ni_{0.9}$-$Fe_{0.1}$)-GDC) and one MIEC anode ($La_{0.8}Sr_{0.1}Ca_{0.1}CrO_3$, LCCr) were done. Open-circuit voltages close to 1 V were measured for Ni-YSZ, Ni-Fe-GDC, and LCCr anodes; for a Ni-GDC anode, OCV was about 50 mV lower. Maximum power densities equaled 47, 62, 78, and 109 mW/cm$^2$ for LCCr, Ni-YSZ, Ni-GDC, and Ni-Fe-GDC anodes, respectively. The performance of the MIEC anode at 800°C was comparable to Ni-YSZ. A Ni-Fe-GDC anode presented the highest maximum power density (MPD), most probably due to the improved catalytic activity in the Boudouard reaction (1). The ferrite-based oxides are known as good catalysts of this reaction. The impregnation of Ni-based cermet SOFC anode with $Fe_2O_3$ (as catalyst) was proposed by Skrzypkiewicz et al. [59]. The results show a stable 22 h of DC-SOFC operation on a single batch of non-catalyzed activated carbon fuel. This approach allowed lower CO-concentration in the anode exhaust in comparison to the direct impregnation of the carbon powder and 17-fold less catalyst usage.

Costa-Nunes (2005) compared Ni-YSZ cermet with materials demonstrating high activity in carbon monoxide oxidation, namely Cu–$CeO_2$–YSZ and Cu–Co–$CeO_2$–YSZ. With the latter, a power of over 310 mW/cm$^2$ has been measured with a relatively thick, 60 $\mu$m YSZ electrolyte [137].

Cu-$CeO_2$ has been introduced to the anode of solid carbon fueled SOFCs by Xie et al. [82] and Konsolakis et al. [119]. The material shows good activity towards CO oxidation, but long-term operation on carbonaceous fuel has not yet been achieved.

Nickel-copper-YSZ cermet as a direct carbon SOFC anode, produced by inkjet printing method has been demonstrated by Dudek et al. [54]. Such DC-SOFC configuration allowed a ca. 50% increase in the maximum power density of the cell when fueled by the product of methane RF plasma splitting in comparison to a standard Ni-YSZ cermet anode. The Cu-based cermets were also investigated by Xie et al. [82] and Konsolakis et al. [119] with solid carbon fuels. A promising power density of 140 mW/cm$^2$ was achieved by the former. These results indicate the prospective application of copper cermets in DC-SOFCs.

Ag-GDC cermets were investigated by Tang and Liu [80] as well as others from the same group [83–85]. Power densities as high as 383 mW/cm$^2$ were measured [83] and the concept has been developed to a level of a 2-cell stack of an overall active area equal 8.0 cm$^2$ reaching 320 mW/cm$^2$ on a Fe-loaded activated carbon fuel [84].

Very important for the operation of a SOFC are the processes of carbon deposition inside the anode material. In general, it is known that metallic nickel catalyzes the hydrocarbon cracking reaction at high temperatures. As a result, carbon is deposited on the catalyst surface. In the case of a syngas/hydrocarbon-fueled SOFC, this phenomena leads to a reduction in cell performance, because the deposited carbon blocks the active sites for gas oxidation. The phenomenon of carbon deposition is the basis for the operation of carbon-deposition SOFC, which will be discussed later.

It has been shown that doping or impregnation of the anode material with noble metals or their alloys is a way to improve the anode's tolerance to carbon deposition [128]. The idea is also interesting because nanoparticles of gold improve the electronic conductivity of the anode. Gür proposed the modification of a standard cermet anode with catalytic particles of noble metals and their alloys [138]. His main claim identifies decoration as the method of preparation of a catalytically active surface. The difference between decoration and other surface modification techniques is that the former aims at obtaining separated particles of the catalyst, which thus do not form a dense layer. Besides the economic aspect of minimizing noble-metal loading, Gür points out the benefit of a highly-enhanced catalytic surface obtained by noble metal decoration in terms of anode performance. In this case, the particles are present not only on the anode surface, but also are likely to penetrate into the 3D gradient structure of the cermet, additionally enhancing the active surface in the carbon oxidation reaction.

The application of perovskite-based MIEC (mixed ionic-electronic conducting) materials as anodes for a DC-SOFC enables shifting the electrochemical reaction from the electrolyte surface to the electrode-carbon interface and therefore is a promising direction for development [14, 55, 105]. MIEC materials usually show lower overall oxygen conductivity than standard oxygen-anion-deficient oxide ceramics, as well as lower electroactivity in the carbon oxidation reaction compared to cermets. However, the kinetic barriers are compromised by the high surface area active in an electrochemical reaction. This type of material can be used for both cathode and anode active layers. The Australian group CSIRO showed numerous results measured on symmetrical planar DC-SOFCs with dense LSCF anode and cathode layers and YSZ [105–109] and GDC [108] electrolytes. Power densities of 62 mW/cm$^2$ and 89 mW/cm$^2$ were obtained for YSZ and GDC electrolytes, respectively, with this novel approach to planar geometry. A symmetrical cell has some benefits compared to standard designs, of which the most important are a lower level of inner mechanical stress (symmetry minimizes the stress caused by the differing TEC of electrodes) and tolerance to oxygen leakage into the anode compartment (the accidental presence of oxygen will cause only chemical oxidation of the fuel and will not oxidize the anode itself).

Raw fossil carbon (coal/lignite) usually contains significant amounts of sulfur. It is known that nickel-based anodes are poisoned by sulfur because of the formation of Ni-S compounds [118]. In terms of long-term durability, sulfur tolerance is a significant issue for nickel-based cermet anodes. Besides the ferrite-based perovskites, the titanate-based ones outstrip the sulfur tolerance of known anodic cermet materials, as was shown back in 2004 by Mukundan et al. [139]. This group of materials was adapted to a DC-SOFC by Kulkarni et al. through the addition of 2 wt% of ruthenium catalyst [110] to achieve a moderate performance of ca. 25 mW/cm$^2$. The authors show a 16 h stable cell performance in a CO atmosphere.

Optimization of the anode microstructure and catalytic additives could further improve the electrode performance. Another promising direction for MIEC materials is their implementation to a silver based cermet, which enabled a stable 48 h operation of a tubular DC-SOFC with a 10.9 cm$^2$ active area [111].

A patent application by Turgut M. Gür claims an MIEC catalyst for the oxidation of carbon anode for use in DC-SOFC cells. The catalyst, ruthenate doped with transition metals, is characterized by a perovskite structure. The physicochemical properties of this type of compound, which include electronic conductivity, the ionic conductivity of oxygen anions, and stability in reducing and CO$_2$ environments at the temperatures of fuel cell operation, predispose it to the proposed application. An example from the literature of this type of compound is $La_{1-x}Sr_xRuO_3$, where lanthanum and strontium cations occupy space (A), or $La_{1-x}Sr_xFe_{1-y}Ru_yO_3$, where ruthenate is doped with ferrite or manganese dioxide to produce a defect in the coordination of oxygen [140].

The formation of nickel carbides was suggested by Horita et al. [126], but no systematic studies on their formation under DC-SOFC operating conditions are known to the authors.

Pure metallic materials are of limited interest because of their poor performance in DC-SOFCs, caused by a lack of the direct access of solid fuel to the TPB. Of this group, only porous platinum [36, 47] has been reported within the past ten years as DC-SOFC anodes.

Other materials such as vanadium carbide (VC) can be potentially implemented in DC-SOFC anodes. A patent, US6183896 B1, held by AIST, presents VC as the material for a production of a catalytic anode for direct carbon oxidation in SOFCs. The anode is made by mixing vanadium carbide with carbon powder (>40% VC) and pressing the resulting mixture against the solid electrolyte. On the basis of thermodynamic analysis, the authors of the patent propose a two-stage reaction sequence. In the first stage, vanadium carbide particles in direct contact with solid electrolyte react with oxygen anions to form vanadium oxide, which subsequently reacts with carbon. The products of this reaction are carbon monoxide and vanadium carbide. Solid oxide fuel cells employing this type of anodic catalyst reached a level of 30 mW/cm$^2$ [93].

The simple concept of a consumable carbon anode with no dedicated anode layer in MEAs has been successfully demonstrated [23, 115]. No technical applications for this system have been proposed, and its applicability remains questionable.

An efficient process of simultaneous solid carbon and gaseous carbon monoxide electrooxidation in one anode would require advanced materials and an optimized microstructure. The catalytic properties of the anode materials are essential in order to sustain sufficient reaction rates and to promote efficient reaction paths. To enhance the electrooxidation rate of CO by-products, TPB length can be extended by introducing (preferably optimized) porosity to the anode material. An actual system incorporates a combination of both solid and gaseous substrates; therefore the anode properties should match the particular fuel properties, working conditions and designed reaction path. Moreover, a further improvement in performance is also a competitive advantage.

### *3.1.3. Research on electrolyte materials*

Electrolytes in SOFC applications should provide sufficient ionic conductivity, mechanical strength, thermal expansion coefficients, gas tightness, and long-term chemical stability. Typical electrolyte materials are zirconia-based, fluorite-type solid oxides such as 3 mol% yttria-stabilized zirconia (3YSZ, TZ3Y), 8 mol% yttria-stabilized zirconia, and 10 mol% scandia-stabilized zirconia. Because of its great mechanical strength, 3YSZ is used for the fabrication of electrolyte foils, whereas 10ScSZ shows a very high level of ionic conductivity, with values over 0.2 S/cm. Another group comprises ceria-based electrolytes such as 10 mol% gadolinia-doped ceria. Ceria compounds show good ionic conductivity at lower temperatures, but their chemical stability in an SOFC anode environment is questionable. Another type of electrolyte that has been applied in DC-SOFC is a perovskite LSGM (strontium- and magnesium- doped lanthanum gallate). The electrolytes mentioned above are present on the market in the form of powders, flat or tubular substrates, and foils, or in commercial MEAs.

Most researchers, however, use yttrium-stabilized zirconia (YSZ) [16–18, 21–23, 36, 37, 46–50, 53–60, 65, 71, 72, 75, 80–82, 84, 85, 87–89, 101, 103–107, 109–113, 115–122, 124, 127, 130, 132, 133, 136, 137]. The highest performance in terms of power density (500 mW/cm$^2$) was demonstrated by Gür et al. [18]. In their IG-SOFC setup, a tubular fuel cell with Ni-YSZ anode, YSZ electrolyte and perovskite cathode was operated at 850°C. The cell was installed directly on the outlet of a separately heated (to 930°C) Boudouard gasifier filled with coal char. On the other hand, the highest power density, in the case of direct contact of the carbon fuel with the anodic surface (DC-SOFC, YSZ electrolyte), was shown by Bai et al. [16] in 2011. The single cone-shaped anode supported cell achieved a power density of 424 mW/cm$^2$.

As mentioned previously, Wu et al. [114] demonstrated a direct carbon fuel cell with a scandium-stabilized zirconia electrolyte. A maximum power density close to 300 mW/cm$^2$ was recorded at 850°C. ScSZ is thus a promising high-ionic-conductivity electrolyte material.

GDC has been applied as the main DC-SOFC electrolyte layer by [108] and LSGM by [83, 123].

### *3.1.4. Physicochemical properties of carbonaceous fuels*

Many classifications of carbonaceous fuels and biomass exist worldwide (e.g. based on volatile matter content, carbon content, calorific value, other fuel properties, and many other criteria). From the point of view of DC-SOFC technology, the differences between particular carbon powders are:

- carbon content
- ash content
- sulfur content
- particle size distribution
- specific area
- crystallographic order

In reality, all of these parameters are related to the fuel source. Three main sources of fuels are currently under investigation: fossil carbon (lignite, coal, graphite, etc.), biomass-derived carbon (wood and other biomass, biomass-derived chars, activated carbons) and carbon black (obtained from acetylene $C_2H_2$, methane $CH_4$, and the decomposition of other hydrocarbons).

The source of carbon exerts a dramatic influence on the composition and structure of the carbon powder subsequently supplied to a direct carbon fuel cell and therefore on fuel cells performance. Moreover, the total $CO_2$ emissions of an analyzed system based on direct carbon fuel cells, taking into account the whole energy generation cycle, depend very strongly on the origin of the fuel. The estimated $CO_2$ emissions from a theoretical 60% electric efficiency DCFC power plant would be ca. 687 kg/MWh for a fossil carbon (assuming for simplicity a dry anthracite of nearly 100% C and 33 MJ/kg), 38 kg/MWh for carbon sourced from the decomposition of natural gas and nearly zero for a biomass sourced carbon, since generally each carbon atom contained in biomass comes from a single $CO_2$ particle reduced during photosynthesis.

Regarding the characteristics of particular fuels, fossil carbons are characterized by lower levels of crystallographic disorder and therefore lower reactivity compared to biomass derived fuels. Fossil fuels are also characterized by higher sulfur content. Biomass carbonaceous fuels are most suitable for DC-SOFCs due to their low sulfur content and the high crystallographic disorder of their carbon atoms. Additionally, well established technologies for increasing the specific surface area of chars are used for activated carbon production. Activated carbon reaches a specific surface area from 500 to over 3000 m$^2$/g depending on the feedstock and production technology. Most often these substances are produced commercially from biomass. Carbon blacks are substances derived from acetylene or hydrocarbons decomposition. They are characterized by very small particle sizes, but their porosity is poor, affecting their overall specific area. Some ordered graphite-like structures were found by [53]. The sulfur content of carbon blacks is also very low, provided low-sulfur substrates are used in their production. The overall reactivity of carbon blacks as DC-SOFC fuel is moderate.

Experimental comparative studies using different carbon fuels in identical fuel cells have been done by some groups. It is generally assumed that the reactivity of carbonaceous fuels increases with the crystallographic disorder of carbon atoms.

In 2008, Lee et al. [46] compared two different fuels for DC-SOFCs: synthetic carbon (Osaka Gas Co., spheres 20–25 $\mu$m, 80.9% C, 0.31% S, 2.45% ash) and biomass from almond shells (100 $\mu$m, 27.2% C, 0.04% S, 36.21% ash). A tubular SOFC MEA with the structure (from inside) Ni-Ceria|YSZ|LSM was applied, and the fuel was supplied in a $CO_2$-fluidized bed mode inside the tube. The process was maintained at 900°C. Maximum power densities of 140 and 40 mW/cm$^2$ were measured for synthetic carbon and almond shell fuels, respectively. The authors also investigated another fuel cell with the inverted structure (from the inside) LSM|YSZ|Ni-Ceria. This second cell was fed with bituminous coal (LK, 50-$\mu$m particles, 65.7% C, 1.6% S, 17.03% ash) in a fluidized bed outside the cell. The second cell was characterized by lower power densities, approximately 43 mW/cm$^2$. The authors observed rapid performance loss for the second cell, which they attributed to sulfur poisoning of the anode material due to the high sulfur content of the fuel (1.6%).

Carbon blacks are widely applied in DC-SOFC development due to the availability and controlled quality of these commercially available products. Experiments of feeding the DC-SOFC with these fuels were performed by many [23, 42, 46, 53, 54, 61, 66, 67, 72, 75, 101, 105, 106, 108–111, 115–117, 119, 132] and the most widely applied fuel was the Vulcan® XC72 by Cabot. Moderate power densities achieved with various carbon blacks in DC-SOFC mode do not exceed 100 mW/cm$^2$ at temperatures below 900°C. Dudek et al. [53] investigated two different carbon blacks: N-220 (Konimpex) and a product of RF plasma methane splitting. Tests were performed in four different cell structures, of which two could be classified as DC-SOFCs; the other two utilized molten carbonate additives to the fuel and were thus excluded from the DC-SOFC category as we understand it. The DC-SOFC tests were performed at temperatures of 660–800°C. The standard parameters, specific area, and ohmic resistance were favorable for commercial carbon black N-220. However, in all fuel cell tests, the carbon produced during RF plasma methane splitting performed slightly better (MPD equal 60 mW/cm$^2$) than commercial carbon black (MPD equal 52 mW/cm$^2$). This is associated with the lower graphite content and greater number of surface defects in the former fuel. Desclaux et al. [117] compared six fuels to determine the influence of general fuel morphology on DC-SOFC performance. The group of fuels consisted of: Printex® XE2-B, Vulcan® XC72, graphite nanopowder, carbon nanotubes (CNT) and two graphitic powders: ECOPHIT® GFG 50M and TIMREX® KS10. The samples were characterized with TEM, EDX, XRD and BET methods. Both carbon blacks (Printex® XE2-B and Vulcan® XC72) outperformed other fuels in DC-SOFC. These two fuels presented also the highest crystallinity rank, smallest particle size, and highest specific surface area. These presented parameters can be to some extent correlated to fuel cell performance.

Biomass-sourced fuels are also widely investigated [16, 18, 21, 22, 46–49, 55, 56, 59, 61, 71, 75, 80, 82–85, 87, 106, 113, 114, 121, 122, 130] because of their low mineral contaminants and high reactivity. Relatively simple processes, such as conversion to char in high temperature and low oxygen partial pressure, steam activation, or acid/dye leaching lead to significant improvements in fuel reactivity towards gasification and electrooxidation. Various biomass fuels have been applied to DC-SOFC by Dudek et al. [55] in cooperation with our group. The results were compared to a graphite powder. All four fuels were tested in a button cell setup with an active area of 2 cm$^2$ and a selected charcoal (Merck) was applied as fuel for a planar single DC-SOFC cell, with dimensions of 5×5 cm and active area of 13 cm$^2$. Electrochemical measurements demonstrated the favorable level of activity of biomass fuels in DC-SOFCs. Measurements of the button cell's MPD at various temperatures (660–800°C) revealed an almost linear correlation with operating temperature. Assuming further linear increase of performance, MPD at 850°C would be about 75 mW/cm$^2$. The MPD of the 13 cm$^2$ planar cell was 54 mW/cm$^2$ at 850°C. This was 28% lower than the predicted value for the button cell, which was attributed to current collection and sealing issues that are easier to solve in button cells. A 12-h stability test was also performed for the larger cell. A linear decrease in cell voltage was observed during batch-mode operation. This was attributed to constant depletion of the fuel in the carbon bed during the test. Biomass-derived fuels and biomass itself (wood chips) were demonstrated as sources of clean fuel for a DC-SOFC. Significant power density of 320 mW/cm$^2$ was obtained by Zhu et al. [121] with willow leaves as fuel. Their very small (0.28 cm$^2$) cell was built around YSZ electrolyte, and YSZ-LSCM was used as the anode. Regarding extended-time operation, no long-term operation has been shown, but some groups operated the cell successfully for 10..20 hours [59, 121, 122].

Although there have been many investigations of expensive activated carbons or conductive carbon blacks as fuels for DC-SOFCs, the future of this technology lies in the utilization of cheap fuels. Various groups investigated coals as fuels for DC-SOFC [37, 60, 72, 88, 103, 104, 122] of which noteworthy are especially the methods for coal preparation allowing obtaining 330 mW/cm$^2$ power density [88] and 150 h long durability tests on a purified "Hypercoal" performed by Dudek et al. [103]. Concerning non-catalyzed bituminous coals and lignite, the highest power density of 199 mW/cm$^2$ was shown by Xu et al. [122] with an anode supported SOFC operated at 850°C. In the same work, the operation of a DC-SOFC on lignite fuel is compared to bituminous coal (162 mW/cm$^2$) and anthracite (161 mW/cm$^2$). The higher performance of the lignite-fueled cell was assigned to the electrochemical oxidation of the more calorific pyrolysis gases. Our group [57, 58] published the results of measurements performed on an increased active area planar cell (16 cm$^2$). The power density of 140 mW/cm$^2$ made it possible to achieve a total output of 2.25 W/cell. Operation of DC-SOFC on lignite was also investigated by [46, 57, 58, 87, 108, 112, 120, 122]. Another group of fuels presenting potential for economic feasibility are wastes, of which waste coffee grounds (WCG) in particular were investigated by Jang et al. [75]. In comparison to carbon black, WCG fuel achieves two-times higher power with the same fuel cell setup.

If carbonaceous fuel supplied to a fuel cell must present a high level of crystallographic disorder of carbon atoms, as well as low sulfur content and a high specific surface area, raw fossil coal or biomass will have to be physically and/or chemically treated prior to its introduction into the anode chamber. Any evaluation of fuels of various origins needs to take into account not only the price of the raw fuel, but also the cost of its treatment. Removing sulfur from coal or lignite to a ppm level can be more costly than producing char from biomass, even allowing for the difference in raw fuel costs.

### 3.1.5. Chemical carbonaceous fuel modification and fuel additives

The speed and path of fuel cell reactions can be controlled not only by engineering of anode material and preprocessing of carbonaceous fuel, but also by means of chemical fuel modifications with catalysts and other fuel additives.

The most widely investigated modification is catalysis of the Boudouard reaction (1). Metal oxides such as iron oxides are known to be good catalysts for this reaction. In this case carbonaceous fuel is usually impregnated with metal-oxide catalysts prior to fuel cell tests. As a result, higher CO concentration is obtained on the anode surface. This causes a shift in the anodic reactions rates in favor of reaction (8).

In 2009, Wu et al. [114] investigated $Fe_mO_n$–$M_xO$ (M = Li, K, Ca) as a catalyst. Graphite (specific area 4.2 $m^2/g$) and two activated carbons of specific areas 227.4 and 1214.2 $m^2/g$ were impregnated with an aqueous solution of a mixture of metal nitrates and calcined at 700°C in nitrogen. The CO formation rate was measured in a dedicated reactor. According to the published results, the introduction of catalysts drastically improved the rate of CO formation, reaching a formation rate up to ca. 350 times higher for the first activated carbon at 750 and 800°C. The introduction of catalysts has the greatest influence at lower temperatures for the tested activated carbons, whereas for graphite no clear temperature dependence was shown. The same group together with others [87] considered application of similar catalysts on raw coal (Shanxi, China), industrially produced cokes and activated carbon. The experiments performed with the temperature programmed oxidation technique (TPO), conducted on the mentioned carbons in a $CO_2$ atmosphere, proved that the approach is also applicable for fossil coal and coke, but the catalyst introduction effect was much smaller (2-4 times higher maximum power density) than for the activated carbon (14-times MPD increase).

Iron oxide catalysts were investigated by [59, 71, 80, 82, 84, 85, 130], resulting in high values of power density recorded during cell operation. The group of Bai [16] recorded the highest published value of power density for a single DC-SOFC, equal to 424 $mW/cm^2$. Cai et al. [85] proposed a more economically justified way of preparation of a Fe-loaded fuel without high temperature treatment. The method utilizes a polyvinylbutyral (PVB) binder to decorate the fuel particles with solid catalyst powder. The approach achieves similar electrochemical performance of the cell compared to fuel wet-impregnation, and much higher performance compared to mechanical mixing of fuel with $Fe_2O_3$.

In 2011, Dudek and Tomczyk [101] proposed the introduction of other metals, namely nickel and silver, as catalysts to the carbonaceous fuel. The application of silver enabled a 3.6-fold improvement of MPD in a fuel cell with no anode. Nickel was found to cause a slightly lower improvement in performance, which was explained in terms of possible nickel carbide $Ni_3C$ formation. However, silver is an expensive metal and would require recycling of the fuel residues following the reaction. The influence of these additives was investigated on a half cell with a platinum cathode and no anode layer. Platinum mesh was applied as a current collector. The authors also introduced the concept of composite fuels, consisting of carbon powder mixed with ion-conducting ceramic powder (8YSZ or 20GDC). This enables the extension of the carbon oxidation reaction volume into the carbon bed, resulting in a significant increase in power density. In optimized cases (10 wt% of ceramic powder addition), the recorded MPD increased 4.6-fold and 2.9-fold for 20GDC and 8YSZ powders, respectively. A similar approach to the latter was applied to Cu-$CeO_2$ catalyst by Konsolakis et al. [119]. Ca. 60% higher power was achieved in the case of mixing the catalyst with the carbon fuel (Vulcan VXC72R, Cabot) in comparison to the no-catalyst case (both with $CO_2$ feed).

Another class of additives was proposed by Gür [44], who proposed in his patent, the addition of minerals such as lime or magnesia. These compounds introduced inside the carbon bed reacted with $CO_2$ and $SO_2$ gases, producing solid carbonates and sulfates. This modification has been proposed as an alternative method of chemical sequestration of these gases.

## 3.2. DC-SOFC single-cell and stack design

Direct utilization of solid carbon fuel in SOFCs imposes special requirements on cell construction. Although DC-SOFCs can employ the same MEA designs as standard gas-fed SOFCs, the anodic chamber has to be redesigned considering the fuel type and the method of fuel distribution in the fuel bed. Moreover, it has to provide a maximum degree of contact between the carbon fuel and the anode surface. These requirements make the scaling-up of a DC-SOFC a complicated technical problem.

In DC-SOFCs, fuel is present in the anode chamber in the form of powder, chunks, or pellets. Depending on the form of the fuel, its contact with the anodic surface can be implemented by various means. Existing solutions assume that the fuel can be transported gravitationally, mechanically, or, in the case of pulverized fuel, suspended in gas.

An important technical issue related to DC-SOFC stack design is carbon fuel distribution inside the system. This includes the introduction into and circulation of fuel within the anode compartment/compartments, as well as the removal of impurities and residues.

The simplest approach assumes that carbon fuel is supplied to the anodic chamber in batches. The batch mode is most widely applied in research into the fundamentals of DC-SOFC technology. In a batch-mode operated cell, solid residues remain in the anodic chamber until cell operation is stopped. This kind of system includes no sophisticated solutions for fuel supply or removal of solid residues. Most often, the whole setup, after it has cooled down, is disassembled and the next test is performed with a new membrane electrode assembly and fresh fuel. Even though this type of fuel cell is considered mostly for fundamental research, there are

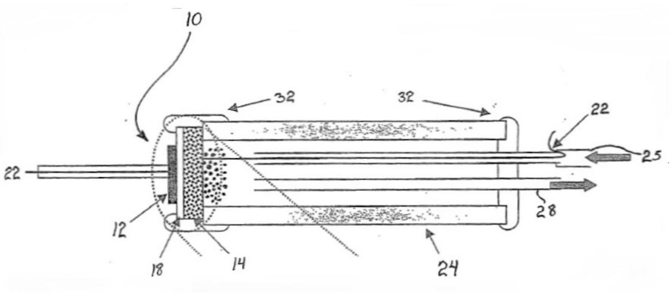

Figure 3: A DC-SOFC planar cell with carbon placed on the anode surface [76]: 10—cell, 12—cathode, 14—anode, 18—electrolyte, 22—electrical contact, 24—ceramic housing, 25—anodic gas inlet, 28—cathodic gas inlet, 32—ceramic seal

some existing batch-operated power generation devices in use.

DC-SOFC technology is still in the early stages of development. Data in the scientific literature on working DC-SOFC stacks or even continuously-operated single cells is very limited. The problem of stacking the cells is technically challenging and remains at the conceptual level. Most technical solutions contributing to the field of DC-SOFCs are presented in patent literature.

### *3.2.1. Carbon placed in the anode chamber*

The most popular approach, due to its technical simplicity, is an experimental setup where carbon fuel is placed directly on the anode of a planar SOFC. This type of design promotes prolonged contact between the fuel and the anode surface. Its application for the direct oxidation of carbon was popularized by Chuang, whose patent [76, 77] presents a cell setup in which a planar electrolyte-supported cell is mounted with its anode side on one end of a ceramic tube, as presented in Fig. 3. The anode of the cell faces the interior of the tube, forming the anodic compartment. The anodic current collector is mounted on the anode surface with platinum paste. Gas pipes, used for delivering gases to the anodic compartment, are installed in the seal on the other end of the ceramic tube (outside of the reactor) as shown in Fig. 3.

While the author claims that solid fuel can be refilled during cell operation, no methods of accomplishing this task are described in the application. The most valuable part of his patent application seems to be the experimental examples of cell assembly. Chuang uses this direct carbon fuel cell design in his investigations, described elsewhere [132]. Many authors use similar designs for their investigations [53–55, 57, 59, 60, 67, 83, 85, 88, 101, 103, 104]. A system of this kind can be refueled during operation, as has been successfully demonstrated by some groups [109, 121]. Among others, one group [121] demonstrated a solution that allows a constant supply of carbonaceous solid powder to the reaction zone in the form of a powder-gas suspension. The fuel is supplied through a perforated u-tube placed in the anodic compartment of the cell. The authors demonstrated ca. 17 hours of cell operation with constant load of 150 mA/cm$^2$ and no evident degradation. Rapid voltage decrease was not observed until the end of the continuous supply of solid-state fuel.

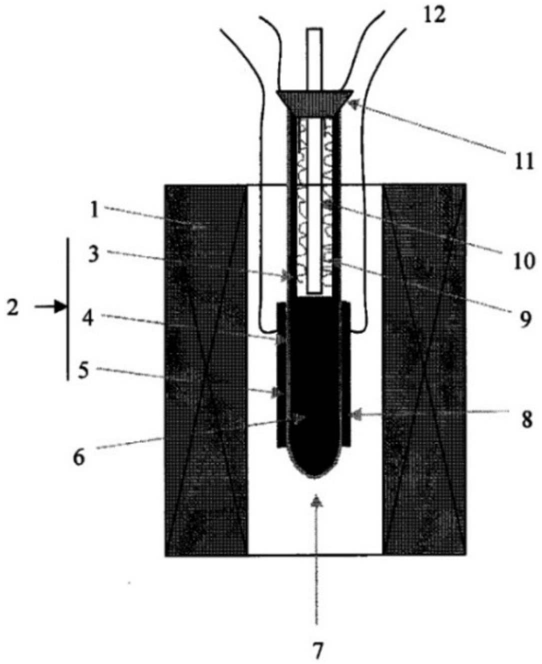

Figure 4: DC-SOFC closed-end tubular cell with anodic chamber inside the tube [141]: 1—furnace, 2—tubular SOFC, 3—anode, 4—cathode, 5—electrolyte, 6—carbon, 7—oxygen flow, 8—cathodic current collector, 9—anodic current collector, 10—anodic reagents conduit, 11—sealing, 12—anodic current leads

A different approach is presented in a Chinese patent from Tsinghua University [63]. In this design, a carbon bed is placed on a ceramic support. The cell is designed with its anode side facing downward. The electrical contact between the anode surface, current collector, and carbon bed is obtained by compression.

Standard open-end tubular SOFCs used in gas-fed systems are rarely applied in laboratory DC-SOFC cell designs in which carbon is placed in the anode chamber. An arrangement of the anodic chamber providing efficient utilization of the anodic surface is difficult to implement in batch operation mode. Some publications and patents describe the design of DC-SOFC stacks based on open-end tubular cells containing gravitational or fluidized beds [62, 64, 132]; these will be discussed later.

Very simple and reliable single-cell laboratory test stands can be assembled using a tubular fuel cell with one end of the tube closed and the anodic side in the interior of the tube. This type of anodic chamber design enables easier sealing of the MEA and offers the potential for higher utilization of CO generated in situ.

Scientists from the Shanghai Institute of Ceramics published a paper [91] on and applied for a patent [141] for an anode-supported SOFC cell for oxidizing pulverized carbon. Their cell is presented in Fig. 4.

To build the cell, the authors used a dip-coating technique; however, they claim that other fabrication techniques

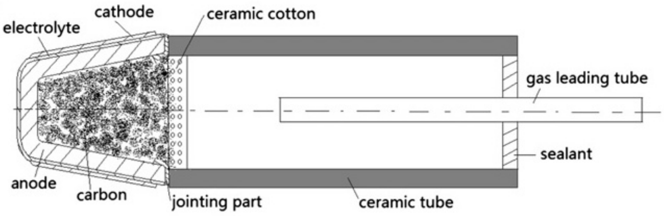

Figure 5: A conical closed-end DC-SOFC [16]

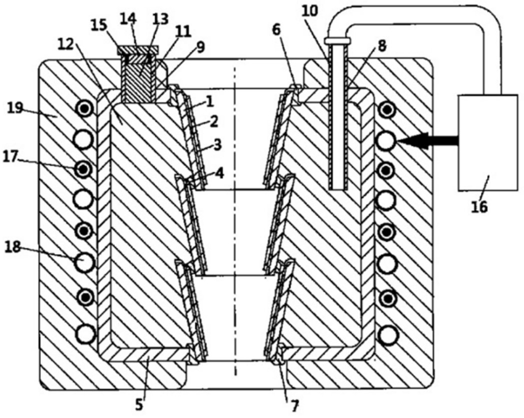

Figure 6: A DC-SOFC stack based on conical DC-SOFCs connected in series [79]: 1—anode, 2—electrolyte, 3—cathode, 4—interconnector, 5—fuel container, 6—opening, 7—opening, 8—gas line opening, 9—fuel line opening, 10—gas line, 11—fuel line, 12—carbon fuel, 13—insulation cap, 14—fuel inlet, 15—washer, 16—combustion chamber, 17—heating element, 18—exhaust heat from the fuel line, 19—heat-retaining layer

such as spraying and extrusion are also possible. They published results from a closed-end tubular fuel cell utilizing a scandium-stabilized zirconia (ScSZ) electrolyte. The cell consisted of a support tube made of NiO-YSZ cermet, a NiO-ScSZ cermet anode functional layer, a ScSZ dense ceramic electrolyte, and an LSM–ScSZ cathode. The active area was approximately 10 cm$^2$. Power densities of 47, 75, and 104 mW/cm$^2$ were achieved at temperatures of 750, 800, and 850°C, respectively.

Bai et al. [16, 79, 81, 142] proposed a modification of a tubular SOFC for which they constructed conical solid oxide cells, with both open and closed ends (Fig. 5). The authors developed their idea based on an electrolyte-supported design; however, the best results were obtained using a Ni-YSZ anode-supported design. This interesting modification of a tubular SOFC is claimed to be easily stackable in series using ring-shaped steel interconnects.

The authors tested single cells and three-cell stacks fueled with iron oxide catalyst-loaded activated carbon. The MPD obtained from the 3-cell stack was 465 mW/cm$^2$ [16]. This is the best result published in the literature for SOFCs fueled with solid carbon directly to the anode chamber. Although the authors suggest that their technology can be applied as a high-temperature battery, their technology is suitable for use in a fuel-cell (solid carbon fueled) mode [79]. The authors also proposed a fuel cell with a series of conical cathode-supported cells (Fig. 6). The same concept was later adapted in cooperation between the same group and others as a gas-electricity cogeneration device [84]. A very similar approach, but equipped with a $CO_2$ separation membrane closing the outlet from the anode chamber, was introduced by Yang et al. [113].

Korean patent no. KR101010535 (B1) describes an adjustable-angle coal fuel cell unit [32]. The unit, basically a planar SOFC stack operating directly on solid pulverized coal, incorporates a novel type of fuel distribution system. Pulverized coal fuel is transported from the fuel tank to the anode compartment pneumatically, in the inert gas stream, and supplied through an inlet nozzle located on one side of the planar anode. The fuel flow over the anode surface in the direction of the outlet nozzle is regulated by adjusting the angle of tilt of the fuel cell stack. This is accomplished through the angle-adjusting unit, which is an integral part of the fuel distribution system. The authors of this patent manufactured a laboratory single-cell test stand of their own invention [37]. They combined an electrolyte-supported closed-end tubular SOFC with a system for the continuous pneumatic feeding of carbon fuel. A YSZ tube support 1.5 mm thick was covered with a 20-$\mu$m Ni-YSZ cermet anode which formed the outer surface, with a LSM-YSZ composite cathode on the inner surface. The cell was positioned vertically, with its closed end upwards, which enabled carbon fuel to be supplied to the top of the anode (Fig. 7). Pure de-ashed carbon fuel was transported pneumatically in the stream of $CO_2$ from the fuel container directly to the anode plane. The authors obtained power densities at the level of 3 mW/cm$^2$ at 750°C. This low value resulted from a non-optimized system.

### *3.2.2. Fluidized-bed design*

Fluidized-bed design is a prospective approach with two very important advantages. First, the fluidization process enables the carbon particles to recirculate and uniformly contact the anodic cermet, thus enhancing the TPB area and improving the utilization of solid fuel. Second, when $CO_2$ or $H_2O$ flue gas is used, the anodic chamber functions as a carbon gasification reactor. The combination of the SOFC anode with this reactor influences the heat and mass balance of the gasification reaction. Anodic reactions are exothermic and produce the heat consumed in the endothermic gasification reaction. $CO_2$, the product of anodic reaction, is the substrate for the gasification reaction in the carbon bed. These conditions shift the chemical equilibrium of the anodic reaction and the gasification reaction to the product side. This is the 'source-sink' effect.

The fluidized-bed concept has been developed by only a few research groups. One of the most important and original solutions contributing to the construction of fluidized-bed DC-SOFC systems was patented by Turgut M. Gür of Stanford University [43], who described the concept of an SOFC reactor containing fluidized carbon fuel, with closed-end SOFC tubes protruding into the anodic chamber. The cell comprised two heating zones. The first contained a carbon fuel bed; the second comprised MEAs with the anode

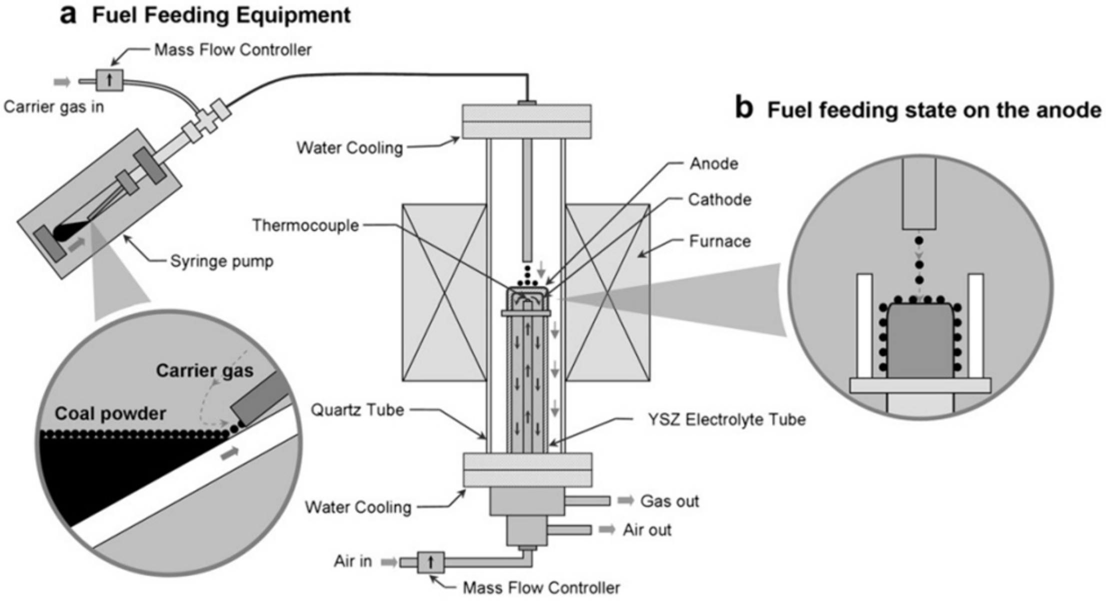

Figure 7: A sample of pneumatic feeding of a DC-SOFC system [37]

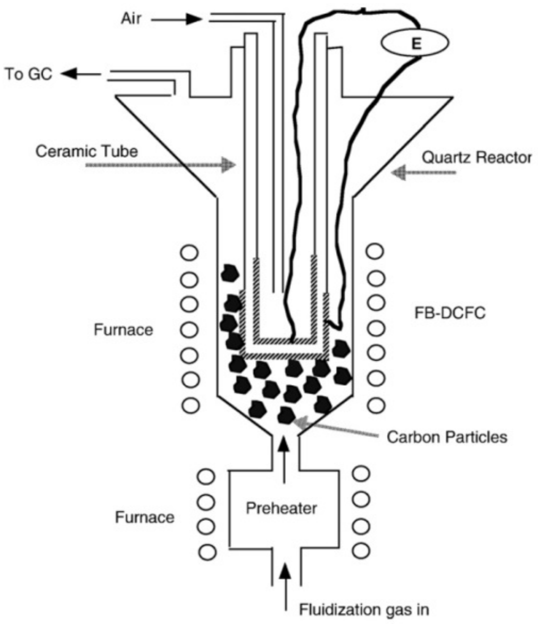

Figure 8: A fluidized-bed DC-SOFC [47]

side facing the carbon bed. The purpose of employing two temperature zones was to independently control the kinetics of the Boudouard reaction (1) taking place in the carbon bed and the kinetics of cell reactions (6–8). The ideas contained in his early patent (1994) were reviewed and expanded in a patent granted in 2010 [44].

The most spectacular power density, 220 mW/cm$^2$, was achieved by Lee et al. at 905°C with an anode supported tubular cell with the structure C|Ni-YSZ|YSZ|LSM|Air, fueled by activated carbon (Fisher Scientific) [48]. The active area of the tubular cell was approximately 5 cm$^2$. The same group achieved a maximum power density of 140 mW/cm$^2$ at 900°C with a planar fuel cell with the structure C|Ni-Ceria|YSZ|LSM|Air. Synthetic carbon (20–25-$\mu$m spheres) was used as fuel; the button cell active area was 2 cm$^2$. In contrast to most published results, the cell was operated in a fluidized bed mode, with carbon dioxide used as a fluidizing gas. The authors proposed a mechanism of fuel oxidation based on a reverse Boudouard reaction (1) and CO electrooxidation [46].

The authors from Stanford University constructed fluidized-bed cells with a carbon bed [46, 47], using a specially shaped quartz reactor body. A tubular MEA was positioned coaxially in the dish so as to form electrode chambers (Fig. 8).

The best results were obtained using an MEA constructed by sealing the planar SOFC to the ceramic support tube so that its anode faced the interior of the quartz reactor, thus forming the anode chamber. This design required the carbon bed to be placed at the bottom of the reactor.

A preheated helium stream was introduced through the gas inlet at the bottom of the reactor. The anodic product gas was collected in the gas outlet located on the top of the cell assembly. However, the authors did not consider optimization of the carbon bed mechanics. They recorded an MPD as high as 140 mW/cm$^2$ using $CO_2$ as a fluidization gas and 60 mW/cm$^2$ using helium.

Integration of the anode side of the cell into the fluidized-bed carbon gasification reactor constitutes the main approach to DC-SOFC stack design as addressed through the patent literature.

Interesting DC-SOFC fluidized-bed stack designs involving both planar and tubular SOFCs have been developed in recent years. One of the first patents concerns a tubular SOFC stack buried in a fluidized carbon bed [62]. A stack comprises tubular SOFCs, a gas distribution plate placed at

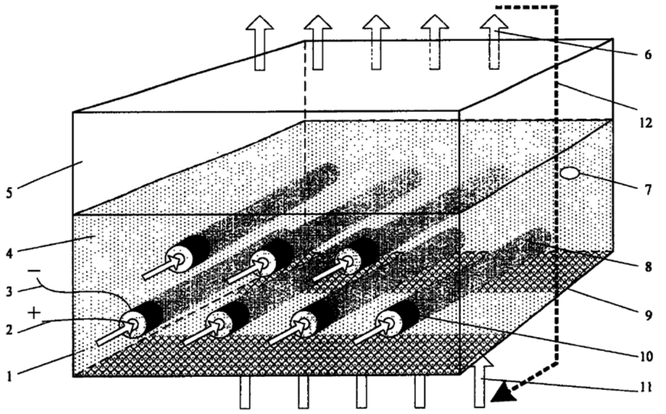

Figure 9: Buried bubbling bed carbon fuel cell [62]: 1—anodic chamber, 2—cathode, 3—anode, 4—carbon bed, 5—anodic gas propagation area, 6—anodic exhaust gas flow, 7—blower, 8—tubular SOFC, 9—gas distribution plate, 10—seal, 11—fluidizing gas flow

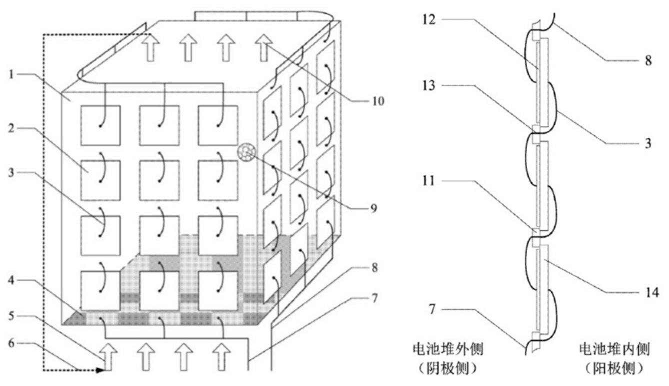

Figure 10: DC-SOFC fuel cell stack with a bubbling bed [40]: 1—reaction chamber, 2—SOFC, 3—series interconnect, 4—distribution plate, 5—stream of fluidizing gases, 6—anode gas recycle stream, 7—negative terminal, 8—positive terminal, 9—carbon bed, 10—anodic exhaust gases, 11—ceramic spacer, 12—cathode, 13—interconnect passage, 14—anode

the bottom of the carbon bed chamber, and a blower for recirculating gaseous reactants. SOFC tubes of either the closed or open type are placed parallel to the carbon bed. The basic design of the invention is presented in Fig. 9. Other forms of the invention feature modified arrangements of the SOFC tubes.

The same group applied an upgraded version of this invention [64]. The design includes two groups of cells, one introduced into and the other placed over the carbon bed. The idea behind grouping SOFCs in this way is to increase the surface available for the carbon monoxide oxidation reaction (8) to occur. Being in direct contact with carbon in the bed, the cells operate both on the carbon and carbon monoxide, whereas cells placed only over the carbon bed operate only on carbon monoxide. As a result of this modification, the carbon monoxide content in exhaust gases is reduced; an increase in specific power is expected at the expense of system efficiency.

Simultaneously, a similar concept was developed by Ravi Chandran of Thermochem International [100]. His power generation system is a modified carbonaceous material gasifier. His modifications include the protrusion of at least one solid oxide fuel cell element into the gasifier reaction chamber. The heat of the exothermal reaction on the SOFC anode is sufficient to gasify the carbonaceous material. The basic design comprises two sets of fuel cells, one above the bed and one directly in it. The feedstock, which can be any type of carbonaceous material, including pure carbon, is introduced into a drying zone placed above the fuel bed, where it is subjected to devolatilization. This process is supported by an electric indirect heater system.

An original DC-SOFC stack design, proposed by the China Huaneng Group, utilizes planar cells [38–41]. The cells are connected in planar series to form flat stacks. These planar stacks are used as the walls of the anodic reaction chamber containing the carbon bed. Fig. 10 presents a schematic diagram of the invention. The gaseous products of the reactions in the anodic chamber are recirculated through the distribution plate placed at the bottom of the device.

### *3.2.3. Other solutions*

Nürnberger et al. [115, 116] used the concept of a consumable anode in the form of a pellet pressed against the electrolyte. A similar idea had been introduced initially by William Jacques in 1896 in his DCFC using a molten hydroxide electrolyte with carbon rods applied as consumable anodes. Nürnberger's test stand included two different configurations of the cell. In the first, maximum power density of 100 mW/cm$^2$ was recorded using a Ni-GDC commercial anode- supported cell (C|Ni-GDC|8YSZ|LSM|Air) at 1000°C and with Vulcan conductive carbon black as fuel. In the second configuration, the authors tested a half cell consisting of cathode and electrolyte layers. A carbon pellet was utilized as a consumable anode. At a temperature of 1000°C, power density of approximately 40 mW/cm$^2$ was achieved. During the measurements, a carbon pellet was pressed against the anode by a ceramic piston (Fig. 11). Both configurations used the same system for current collection, namely, a nickel mesh placed on top of the carbon pellet between the pellet and the piston. It was claimed that this configuration enabled an increase in the fuel-electrolyte contact surface and thus acquisition of a relatively high level of performance with a simplified design. The same concept was further developed and published [115, 116]. It is worth noting that this group's results are superior to those of other published tests utilizing cells without anodic catalyst layers or Pt catalysts [53, 55, 101].

Most batch-operated systems are used for fundamental research; however, the technical simplicity of the design seems to be a factor capable of driving certain special applications. Jacobson et al. proposed a small portable power system based on a DC-SOFC designed to run on any type of biomass and to be heated on a cooking stove [143]. The system consists of a cell integrated with a fuel storage container. The fuel container includes a wall enabling heat to be

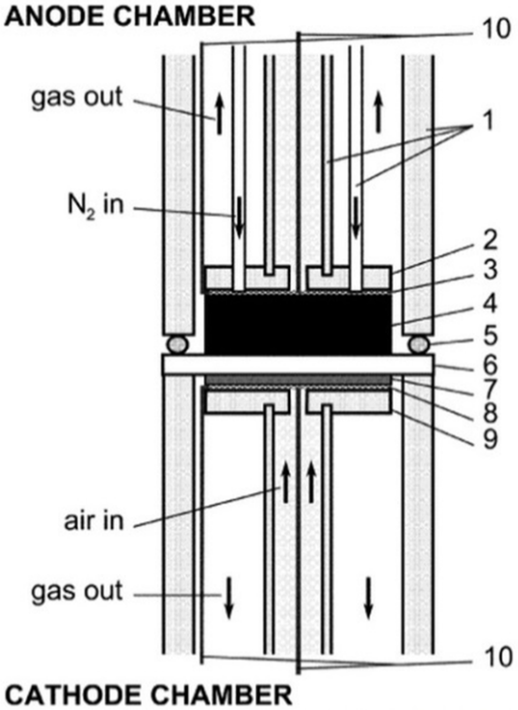

Figure 11: DC-SOFC laboratory cell [23]: 1—alumina tubes, 2—anode flow field, 3—nickel current collector mesh, 4—carbon pellet, 5—gold wire used as sealing, 6—YSZ electrolyte, 7—LSM-based cathode layer, 8—platinum current collector mesh, 9—cathode flow field, 10—current collector wires (Pt or Ni)

conducted from an outside source in order to maintain the cell's operating temperature. From time to time carbon fuel must be refilled and solid residues removed. The prospective application of the system is to provide power for small electronic devices such as cell phones or flashlights.

Cinti and Hemmes [125] performed a system-level study for integration of a concentrated solar power (CSP) with DCFC. The solution presented by the authors utilizes heat from CSP for splitting methane into hydrogen and carbon, with the latter being supplied to a highly efficient DCFC. The proposed concept utilizes renewable energy in the form of solar power to perform the endothermic methane splitting process and is a prospect for North African countries with natural gas resources and copious sun-hours per year.

## 4. Deposited carbon SOFCs (rechargeable SOFCs)

A separate type of DC-SOFC carbon fuel cells includes deposited carbon fuel cells, also called rechargeable DC-SOFCs. This type of power source runs on carbon, which is a product of the thermal decomposition of natural gas into carbon and hydrogen gas. The process of thermal decomposition ('charging') takes place on nickel particles in the cermet when natural gas is passed over a hot anode. During the charging process, the nickel particles are covered with soot and the hydrogen gas leaves the fuel cell compartment, becoming an additional, valuable product as described by Hemmes et al. [15]. When the rate of the decomposition process drops significantly, the charging process is considered to be complete. At that point, the cell is switched into power draw mode. This method of supplying carbon to the SOFC anode is a modern alternative approach to DC-SOFCs. This is a promising technology for fast-charging, high-efficiency electricity generation devices as well as a scientific method to bring solid carbon directly to the cell's TPB and its surroundings. Moreover, according to Hemmes et al., including the energy contained in the produced hydrogen gas, such systems can reach up to 88.4 % efficiency (LHV). Therefore it is considered not only for power generation applications but also for investigation of the reaction mechanisms of carbon oxidation in a DC-SOFC.

Scientists from the Toyota Motor Corporation [131] proposed a stack of DC-SOFC rechargeable cells designed for continuous operation. The cells in the stack are arranged so that electrodes of the same polarity face each other. The cells are separated by ceramic interconnects forming anodic and cathodic gas channels, and divided into two groups, those being charged and those supplying power. During the operation, the cells being charged are disconnected from the load.

Ihara et al. [127] back in 2004 demonstrated a laboratory cell operating on carbon from methane in situ decomposition. Multiple repeated power cycles were shown and 66.5 mW/cm$^2$ power density measured. The concept of deposited carbon SOFC was investigated experimentally and supported with modeling by Zhao et al. [65]. The authors conclude from their experimentally validated modeling efforts that better cell performance would be achieved in the case of 'charging' the cell with higher methane concentration and over a shorter time.

Manabu Ihara patented a SOFC [26, 27, 31] stack which generates power as a product of the oxidation of carbon and a secondary fuel, CO. The fuel cell is activated by charging it with hydrocarbon gas over a period of several minutes. After 5 minutes of charging at 800°C, the fuel cell can operate for over 11 hours at 45 mW/cm$^2$, at a load of 80 mA/cm$^2$. The power output reaches 150 mW/cm$^2$ at 800°C. The author claims that it is possible to reduce the dimensions of the anodic chamber, thus reducing the stack dimensions, through the elimination of carrier gas in the power generation mode. A similar technical solution is presented in a patent of the Japan Science and Technology Agency [96].

Another patent from Honda and the Tokyo Institute of Technology [28] describes a DC-SOFC device charged by spraying liquid hydrocarbons into the anode compartment. As a result of high-temperature cracking of the hydrocarbons, the anodic compartment interior is filled with, and utilizes, carbon fuel.

Li et al. [68] proposed a detailed mechanism of carbon oxidation in a SOFC fed by carbon deposited from $CH_4$. They concluded that carbon deposited not only on the TPB and electrolyte surface but also on the electronic conductor in the anode (i.e. nickel) can undergo electrochemical oxidation. The same authors [67] compared three configurations of the same SOFC fuel cell: fuel detached from the anode, fuel in physical contact with the anode surface, and deposited carbon fuel. In the first and second cases, the cell achieved poor performance (OCV of ca 0.7 V and MPD of 1 and 2.5 mW/cm$^2$, respectively). In the third configuration OCV reached 1.2 V and MPD reached 85 mW/cm$^2$, i.e. significantly higher values. The third cell operated for 225 minutes under a load of 30 mA/cm$^2$ until the voltage dropped to zero. The area of each of the tested cells was 1.54 cm$^2$.

A deposition of methane inside a SOFC was investigated recently by Jiao et al. [89]. The authors have shown a constant current draw with intermittent methane feeding, allowing the cell to store energy in the form of deposited carbon. The concept is called direct methane SOFC.

## 5. SOFCs integrated with external carbon dry gasification reactors (IG-SOFCs)

The idea of joining a fuel cell with a carbon fueled, dry gas generator can be divided into two main concepts. The first one is the external integrated gasification SOFC, where a carbonaceous fuel is gasified with CO$_2$ in a separate reactor (gasifier); subsequently the gas is (optionally) purified and passed to a fuel cell stack [144]. The second one is the internal gasification concept, where the fuel is gasified inside the anode chamber, without direct contact to the anode surface, or in a separate chamber within the same fuel cell reactor.

Internal gasification systems, were investigated by researchers from the USA [17, 18, 48–50, 130], China [66, 92] and Korea [71]. Gür et al. [18] proposed a system consisting of an SOFC integrated with a gasifier. The single tubular cell active area was about 24 cm$^2$ and consisted of a Ni-YSZ anode support, YSZ electrolyte (8–10$\mu$m), and perovskite-based La-Sr-Mn-O/La-Sr-Co-O composite cathode. The cell was directly connected to the gasifier, but the electric heating of both reactors was independent. Operation of the gasifier at 936°C and of the SOFC at 850°C resulted in a significant power density of 450 mW/cm$^2$ with 60% fuel utilization in the SOFC. Alaskan coal char was used as fuel, suspended in minimally fluidized bed conditions. In another article, [49] biomass-derived activated carbon was applied in the same system. The gasification process of this kind of fuel was more sluggish than coal; as a result, less spectacular performance results (175 mW/cm$^2$ at a gasifier temperature of 900°C and a SOFC temperature of 850°C) were achieved.

A similar system was constructed and tested by Li et al. [66]. The test stand comprised a gasifier and a SOFC button cell structured as follows: syngas|Ni-YSZ|Ni-ScSZ|ScSZ|LSM-ScSZ|air. The cell, with an active area of 1.5 cm$^2$, was kept at a constant temperature of 750°C. The gasification temperature was controlled within a range of 700–1000°C. Power densities were 236.6 mW/cm$^2$ for H$_2$ and 97.6, 147.3, and 154.3 mW/cm$^2$ for carbon black (Black Pearls 2000, Cabot) at gasification temperatures of 900, 950, and 1000°C, respectively.

Gür's [45] invention is a carbon-monoxide-fueled SOFC integrated with a carbon gasification reactor (Fig. 12). The system is designed to generate electrical power as the product of the electrochemical oxidation of CO, which is in turn the product of dry gasification processes of carbonaceous fuel. In the basic design, the system consists of a gasification reactor for CO production and one external SOFC for power generation. The system includes an additional SOFC cell disposed inside the conversion bed so that the anode surface contacts the carbon fuel. This setup enables the direct oxidation of carbon fuel and carbon monoxide generated in situ. The author claims that in order to maximize the power output of the system, the heat from the product stream and spent air stream is supplied to the Rankine bottoming cycle.

The laboratory-scale prototype of the system employs a fluidized bed gasification reactor which holds ca. 300 grams of pulverized, low-sulfur coal fuel. The fluidization gas is pure CO$_2$. Polarization tests showed that the cell's maximum power, 10.8 W (450 mW/cm$^2$), was achieved at $U = 0.64$ V, with carbon conversion efficiency of 35.7%. Continuous operation tests showed that for an average of 0.2 kWh of electrical energy drawn, carbon conversion exceeds 45%. Over the period of operation, only a slight degradation of voltage was observed.

Operation of an anode supported SOFC (Ni-YSZ|YSZ|GDC+Co$_3$O$_4$|LSC) on CO-CO$_2$-H$_2$-N$_2$ mixtures was investigated by Leberton et al. [124]. In particular, fuel cell performances with CO-N$_2$ and H$_2$-N$_2$ fuels were compared. For lean fuels (<27% of H$_2$ or CO in fuel-N$_2$ mixture) slightly higher maximum power was obtained at 750°C with CO than with H$_2$ in contrast to rich fuel feeds.

Zhou et al. [92] proposed a single-chamber reactor with a tubular cathode-supported SOFC and carbonaceous fuel detached from the fuel-cell anode (Fig. 13). A similar approach, but with an anode supported cell (Fig. 14), was proposed by Gong and Huang [130]. In both independent developments, steam was applied as an additional gasifying agent.

The idea of connecting tubular SOFC in a stack was scaled up by Lim et al. [71]. The Korean group achieved 29.4 W of power from a reactor comprising a compact Boudouard gasifier and a tubular SOFC stack (two serial and two parallel connections of cells) of rated power ca. 50 W. The authors present the record of 11 thermal cycles of the device.

A Japanese patent [29] describes a CO-fueled SOFC. Carbon monoxide is produced by passing the CO$_2$ which is the only product of the fuel cell through the carbon fuel chamber, which is detached from the anode. In another patent by the same authors, carbon takes the form of moulded fabricates [30].

A Korean patent [34, 35] describes a low emission SOFC power generation system running on CO gas. The carbon monoxide is a product of the Boudouard reaction (1) which takes place in the carbon monoxide generator. Due to the utilization of ultraclean carbon, the anodic product gas is almost-clean CO$_2$ and therefore can be easily sequestered

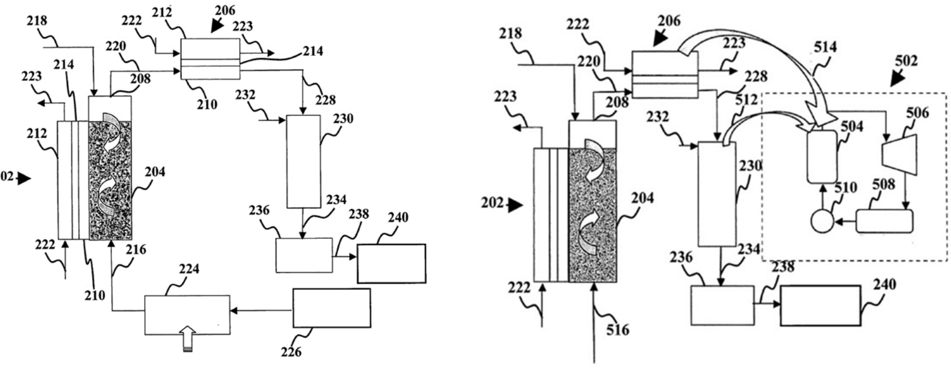

Figure 12: Integrated dry gasification fuel cell system for conversion of solid carbonaceous fuels [36]: 202—SOFC cell located in the gasification reactor, 206—carbon-monoxide-powered SOFC, 204—gasification reactor, 208—gasification reactor outlet port, 210—anode, 212—cathode, 214—electrolyte, 216—$CO_2$ inlet, 218—intake of raw coal, 220—intake of carbon monoxide, 222—air inlet, 223—air outlet, 224—heat exchanger 226—gas filter, 228—flow of SOFC products, 230—burner, 232—oxidant inlet of burner, 234—exhaust gases , 236—scrubber, 238—$CO_2$ flow from the scrubber, 240—gas filter, 502—Rankine cycle, 504—boiler, 506—steam turbine, 508—water tank, 510—water pump, 512—SOFC heat, 514—burner heat, 516—steam flow to gasification reactor [45]

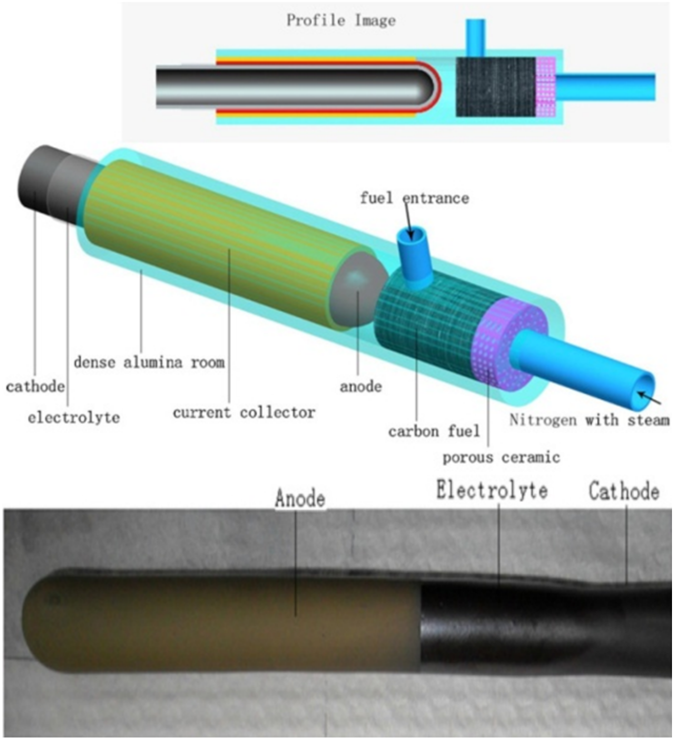

Figure 13: Detached IG-SOFC cathode-supported tubular cell by Zhou et al. [92]

and recirculated into the system.

R. D. Brost [145] invented a SOFC power system employing an enthalpy wheel for carbon monoxide sequestration and distribution. Carbon monoxide is produced in the gasification reactor as a product of the exothermic reaction between carbon and oxygen analogical to reaction (7). The product stream from the carbon gasifier is fed to the 'cold side' of the enthalpy wheel, which takes the form of a toroidal vessel filled with CO-absorbing liquid. As a result, carbon monoxide is separated from other gases. The absorbed CO is then transported to the desorption site and desorbed thermally by applying the heat of the carbon oxidation reaction to the 'hot side' of the enthalpy wheel. Carbon monoxide is collected and supplied to the anode of the fuel cell.

## 6. Summary

This review presents three directions in dry SOFC technology development involving solid-state carbon at some stage of the fuel-to-electricity conversion process. Recent achievements of science and technology were studied in order to identify the most widely developed concepts. DC-SOFC technology has the potential to enhance the efficiency of the best available coal-fired power plants. IG-SOFC technology is more mature, since, in principle, it combines two technologies that had been developed separately for years: coal gasification and syngas-fueled SOFCs. Rechargeable SOFCs are fueled with hydrocarbons and do not lend themselves to comparison with the others. Nevertheless, their working principle is based on essentially the same high-efficiency carbon electrooxidation process used in DC-SOFCs. Thus, development of these two technologies can deliver synergies for global DCFC research and development. On the other hand, IG-SOFCs are designed to efficiently utilize carbon monoxide in an electrooxidation reaction (8), which occurs to some extent in the other two technologies. Development of this technology may result in solutions that can be applied to all carbon-fueled SOFCs. The efficiency of coal-powered IG-SOFCs will be less than that of DC-SOFCs due to the thermodynamics of both coupled processes.

Although much effort has gone into basic research over the past decade, there are still many problems of a technical nature that need to be overcome in order to trigger rapid growth in DC-SOFC technology. Among these, scale-up issues regarding fuel cell stack construction, fuel and ash maintenance and long term behavior of system components as well as complete systems must be investigated

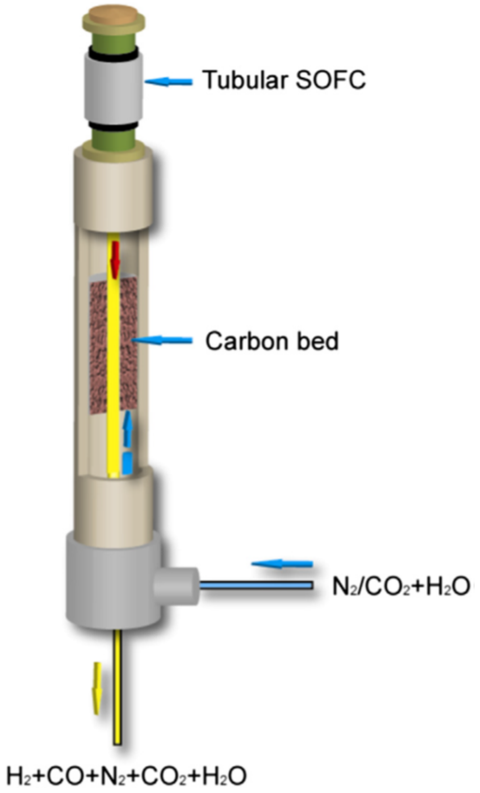

Figure 14: Detached IG-SOFC anode-supported tubular cell by Gong and Huang [130]

further. The power densities achieved in all three described technologies at the laboratory scale are already at the level of the operational point of commercial fuel cells. The stability of operation during 10..150 hour-long runs was also demonstrated. Many fuels are suitable to feed DC-/ IG-/ rechargeable- SOFCs including fossil-, biomass- and waste-sourced fuels, which opens up the applicability of these technologies to even wider vistas.

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