

Direct carbon fuel cells based on solid oxide electrolyte technology

Abstract. Direct carbon fuel cells (DCFC), developed intensively in the last decade, offer electric current generation with potentially much higher efficiency than currently achieved in coal-fired power plants. The existing planar solid oxide fuel cell technology is one of several possible fuel cell technology platforms enabling implementation of DCFC, fuelled with pulverised coal. The thermodynamic and electrochemical principles of DC-SOFC technology are summarised in the paper. The current technology development status is reviewed and future potential of technology is discussed. Key research problems influencing the development of the technology in future were stated.

Streszczenie. Węglowe ogniwa paliwowe (DCFC), intensywnie rozwijane w ostatniej dekadzie, oferują generację energii elektrycznej z potencjalnie znacznie wyższą sprawnością niż obecnie uzyskiwana w elektrowniach węglowych. Istniejąca technologia elektrolitów stałotlenkowych jest jedną z platform technologicznych umożliwiających implementację koncepcji ogniwa paliwowego zasilanego pyłem węglowym. W artykule podsumowano termodynamiczne i elektrochemiczne zasady działania technologii DC-SOFC. Dokonano przeglądu aktualnego stanu i potencjału rozwoju technologii. Wskazano kluczowe zagadnienia badawcze mające wpływ na jej rozwój w najbliższym czasie. (Węglowe ogniwa paliwowe oparte na technologii elektrolitu stałotlenkowego).

Keywords: direct carbon fuel cells (DCFC), solid oxide fuel cells (SOFC), electric power generators, electrical efficiency.

Słowa kluczowe: węglowe ogniwa paliwowe (DCFC), stałotlenkowe ogniwa paliwowe (SOFC), generatory energii elektrycznej, sprawność elektryczna.

Introduction

While most of the fuel cell types (PEMFC, PAFC, MCFC, SOFC) are classified based on the electrolyte implemented, for direct carbon fuel cells (DCFC) importance of carbon as a fuel is underlined. Carbon is especially attractive fuel for a variety of reasons. Carbon is dispersed geographically as a raw fuel (coal, lignite, natural gas, biomass, petroleum, waste material). Raw fuels can be pre-processed using well established technologies (pulverizing, pyrolysis, refining) to yield carbon in a form that can be used to fuel DCFC. Fuel cleaning or additional pre-processing (e.g., addition of catalysts) may be necessary to gain performance and durability of the DCFC system, depending on particular implementation.

Direct electrochemical oxidation of carbon is providing a unique basis for the fuel cell operation, as described by the overall reaction:



The intrinsic maximum energy conversion efficiency of this reaction, based on the first law of thermodynamics, exceeds slightly 100% as Carnot-cycle heat engine limitations are not faced for direct electrochemical energy conversion process. The positive reaction entropy of the reaction (1) indicates that external heat source is necessary for the reversible reaction to proceed in the fuel cell engine. For the DCFC operating under electric load, thermodynamic efficiency is lower, as a result of irreversible heat losses associated with ohmic losses and overpotential of electrode reactions in the fuel cell. At the DCFC system level, additional loss of efficiency is experienced due to heat and power requirements of auxiliary system components. In addition, some pre-processing of carbon containing fuel is necessary to supply carbon in a form required by DCFC. The DCFC technology can be implemented using a variety of electrolyte technologies (e.g., solid oxides, molten carbonates, hydroxides) and carbon delivery media (e.g., molten carbonates/carbon mixture, fluidized bed of carbon particles, batch of pulverized carbon). For these reasons, estimation of DCFC system efficiency is difficult and practical electric efficiency achievable in the DCFC system is to be seen. The modelling studies show that the level of 60% to 80% (LHV) electric efficiency is possible, far exceeding practical efficiencies of modern coal based power plants (~ 40% LHV).

Among various possible implementations, solid oxide

fuel cell (SOFC) technology provides attractive platform for DCFC. High electric efficiency was achieved in the existing SOFC system demonstrations using a wide range of fuels. Heat balance of DCFC based on the SOFC technology (DC-SOFC) is easier to achieve, compared to other available fuel cell platforms, with high-quality heat available in the high-temperature system, e.g. from the afterburner operation and DCFC stack operation under load. Additional gain in electric efficiency of the DCFC system comes from the absence of, otherwise required in the SOFC systems, reforming of typical fuels (natural gas), either highly endothermic steam reforming or lowering LHV of the fuel partial oxidation. Although DCFC systems are well suited for stationary power generation systems, achieving high electric efficiency in DC-SOFC systems seems also feasible for micro-scale, distributed power generation, similarly to existing natural gas fuelled SOFC/ μ -CHP system demonstrations.

Thermodynamics of DC-SOFC

At elevated temperatures solid oxide electrolytes conduct oxygen ions (O^{2-}) with almost negligible electronic conductivity present. The complete electrochemical oxidation of carbon in DC-SOFC can be described as follows:

Anode reaction:



Cathode reaction:



Overall reaction



For the reaction (4) the thermodynamic data at 25 °C is presented in table 1. On the basis of data from table 1 following calculations were done:

Open-circuit voltage (OCV):

$$E^0 = \frac{\Delta G}{n \times F} = 1.022 \text{ V}$$

Thermodynamic efficiency:

$$\eta = \frac{\Delta G}{\Delta H} = 100.22\%$$

Table 1. Thermodynamic data of reaction (4) at 25 °C

Parameter	Value	Unit
Enthalpy of reaction (ΔH)	393.51	kJ/mol
Gibbs free energy (ΔG)	394.37	kJ/mol
Entropy (Δs)	2.8.5	J/(mol*K)

Furthermore, several reaction paths are possible to occur in a direct carbon fuel cell's anode [1]:

Full-oxidation of carbon



Partial-oxidation of carbon



Oxidation of carbon monoxide



The thermodynamic data for the reaction (4) are almost temperature independent. The calculated open circuit voltage for reactions (4), (5) and (6) (thermodynamic data source: [2]) and experimental results (described later) are depicted in Fig. 1.

Additionally, a chemical process occurring in the carbon bed is described by the reverse Boudouard reaction, strongly dependent on temperature:

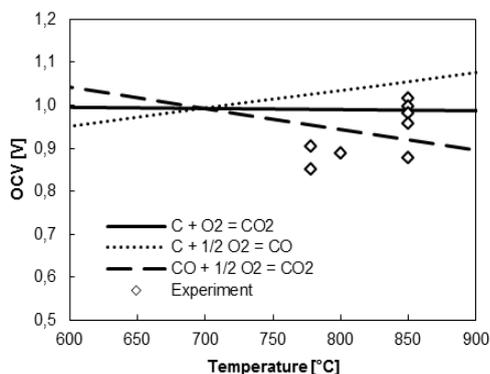


Fig.1. Theoretical open-circuit voltage [V] and experimental data for DC-SOFC (oxidant: air)

Review of recent DC-SOFC developments

Solid oxide fuel cells in both planar and tubular configurations have been extensively implemented as a technological platform for DCFC [3]. In general, tubular SOFC cells are characterised by higher operating temperature.

Planar DC-SOFC development

DC-SOFC configuration based on planar SOFC technology inherits benefits of planar technology, including possibility of lower operating temperature, easier current collection and availability of higher surface area cells (up to 1200 cm² [4]).

The planar DC-SOFC configuration is currently under development in a few research institutions worldwide. In 2006 Chuang [5] demonstrated DC-SOFC, operated at 950 °C and fuelled by raw, pulverised Ohio coal. The OCV of about 1 V and a maximum power density (MPD) of about 75 mW/cm² at 150 mA/cm² were measured for the cell with Ni-YSZ composite anode, YSZ electrolyte and LSM cathode.

Recently Nürnberg et al. [6] investigated electrolyte supported disc-shaped 7 cm² SOFC cell fuelled by cylindrical carbon pellet (diameter 3 cm, height <1 cm) prepared from carbon black (Cabot Vulcan XC72 GP3868, particle size 5-10 μm). Carbon fuel was placed directly on

the Ni-GDC (gadolinium doped ceria) anode surface of the Ni-GDC|8YSZ|LSM cell. The OCV over 0.9 V and power density of about 100 mW/cm² were measured at 1000 °C.

Desclaux et al. [7] investigated behaviour of a similar system utilising a half-cell (without anode layer). In this case, carbon pellet was placed directly on the electrolyte surface. As expected, a moderate power density of 20 mW/cm² was measured but the authors concluded that only 0.6 mW/cm² of cell's power was generated via reaction (6) (oxidation of CO) while the remaining 97% was generated in reaction 4 (direct electrochemical oxidation of solid carbon). This experiment demonstrates significance of direct electro-oxidation of carbon on the YSZ electrolyte surface. In a long-term test, almost 60% of carbon electrochemical conversion was achieved. The remaining 40% conversion was assigned to carbon utilization in Boudouard reaction.

Numerous modifications of carbon fuel have been proposed to increase power density of DC-SOFC. Wu et al. [8] proposed application of an ultra-high surface area (>1200 m²/g) catalyst-loaded (catalyst: Fe_mO_n-M_xO, m = Li, K, Ca) carbon powder fuel. The button size anode supported cell (Ni-ScSZ|10ScSZ|LSM) was operated at 850 °C yielding 286 mW/cm² power density and OCV of 0.955 V.

Dudek and Tomczyk [9] proposed composite carbon fuel as a mixture of carbon fuel (carbon black N-220) with electrolyte materials (20GDC and 8YSZ), leading to increase in the DC-SOFC performance. In comparison to operation on pure carbon black, addition of 12 wt.% of 20GDC led to 5-fold increase of MPD.

Recently Dudek et al. [10] investigated carbon black N-220 and carbonaceous fuel derived from methane RF plasma reforming in several DC-SOFC configurations. The presence of carbonates in the composite fuel leads to significant increase in DC-SOFC performance.

Tubular DC-SOFC development

DC-SOFC configuration based on tubular SOFC technology inherits benefits of this technology, easier sealing and higher mechanical strength in particular.

In the experiment performed by Lee et al. [11], the tubular Ni-YSZ|YSZ|LSM SOFC cell (MSRI) was loaded with activated carbon (Fisher Scientific) and operated at 905 °C. The power density of 220 mW/cm² was measured at 0.68V with 15 ml/min of argon flow above the carbon bed.

A similar approach was proposed in the same year by Tang et al. [12]. The tubular Ag-GDC|8YSZ|Ag cell was filled with activated carbon (specific surface area of 791.02 m²/g). The OCV of 0.9 V and MPD of 24 mW/cm² was measured at 800 °C. Similar measurements were performed with iron impregnated carbon. The OCV has increased to about 1.05 V and MPD of 45 mW/cm² was measured.

Kim et al. [13] applied pulverised graphite (99.1%) as a fuel. The authors investigated the effect of different grain sizes (<32 μm, 90-150 μm and 150-180 μm). The smaller the powder particles the higher OCVs were recorded. For the smallest particle size graphite powder OCV of 1.115 V and MPD of 16.8 mW/cm² were achieved at 950 °C with Ar flow through the anode chamber.

The results of DC-SOFC tests differ strongly, mainly because of carbonaceous fuel parameters (crystal structure, grain size and impurities: ash volatile matter, sulphur), applied temperature, SOFC cell configuration and material suppliers. Furthermore, graphite fuels usually yield lower power densities than activated carbons. The best performance is achieved with modified carbon fuels (with Fe, Ni, Ag, 8YSZ, 20GDC or molten carbonate slurry additives).

Experimental

The electrolyte supported $5 \times 5 \text{ cm}^2$ SOFC cell (Ni-YSZ|Ni-GDC|YSZ|LSM-GDC|LSM, Fuel Cell Materials) was tested in DC-SOFC configuration. The anode was pre-reduced in hydrogen. The cell was installed in the sealed housing and carbon fuel (charcoal) was placed directly on the anode surface in a fixed bed configuration. The housing was installed in the furnace and heated up to $850 \text{ }^\circ\text{C}$. After reaching operating temperature, the anode chamber was purged with nitrogen. The fuel cell was then operated under electric load until its performance has stabilized. The OCV of 0.982 V was observed and the maximum power density of 48 mW/cm^2 was measured (Fig.2). A linear current-voltage characteristics were observed for a polarization region below 0.75 V .

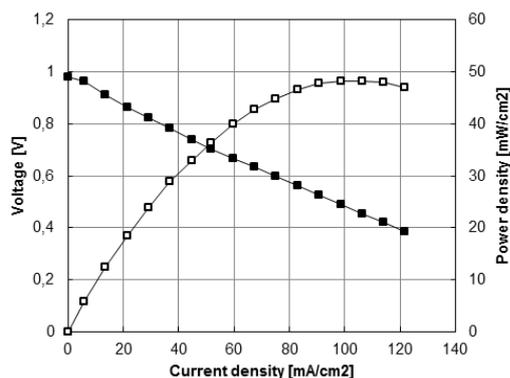


Fig. 2. Fuel cell polarisation (black squares) and power density (white squares) curves for a typical DC-SOFC cell operated at $850 \text{ }^\circ\text{C}$ with no gas feed to anode chamber (oxidant: air)

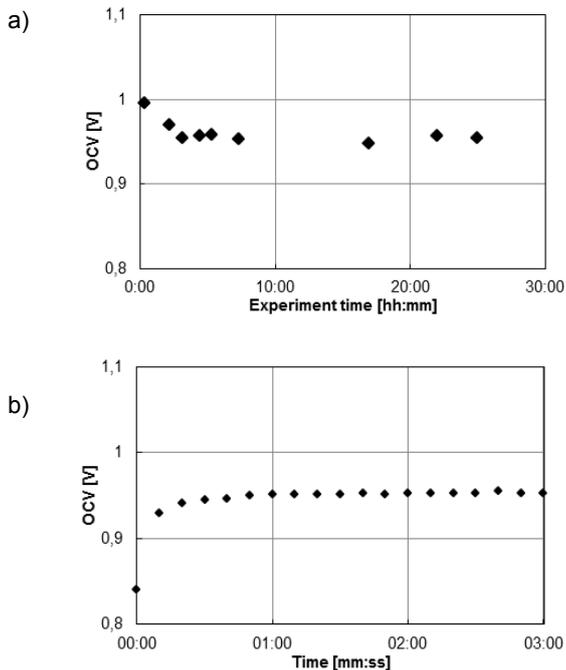


Fig.3. Open Circuit Voltage [V] in a typical DC-SOFC experiment: a) OCV-profile during 25 h of experiment, b) OCV build-up after a constant load operation at 29 mA/cm^2

Later the cell was operated under constant 29 mA/cm^2 electric load for the period of 17 hours and under varying electric load of up to 60 mA/cm^2 for the following 8 hours. In between periods of cell operation under electric load, OCV was measured for the periods of 15 minutes each time. Stabilized OCV values are presented in Fig.3a.

A typical OCV measurements are presented in Fig.3b. It can be observed that 99.2% of the final, stable OCV value is established in 60 s period following the release of 29 mA/cm^2 electric load. The observed increase in OCV (Fig.3b) is attributed to stabilization of gas composition near the anode surface following the release of current load.

Summary

The concept of the direct carbon fuel cell (DCFC) has been proven in various fuel cell configurations, including solid oxide fuel cells (SOFC). Solid oxide fuel cells as a technological platform for the implementation of DCFC seems feasible in both tubular and planar geometry configurations. At the current stage of technology development, both configurations are interesting from the implementation standpoint although planar configuration allows for the possibility of operation at the lower temperature range, more interesting from the materials standpoint.

Selected results of the open cell voltage measurements has been presented for the typical, planar DC-SOFC configuration and compared with the thermodynamic calculations. The open cell voltage measurements point to mixed potential of the cell as a result of several anodic reactions proceeding in parallel, with significant share of complete direct electrochemical oxidation of carbon.

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