

CO₂ CAPTURE IN SOFC-GT SYSTEMS

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Contribution to the Second Annual Conference on Carbon Sequestration,
Hilton Alexandria Mark Centre, Alexandria, VA, USA, 5-8 May 2003.

Revisions		
A		
B		
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Second Annual Conference on Carbon Sequestration,
May 5-8, 2003, Alexandria, Virginia, USA

ABSTRACT

A promising solution for the high penalties associated with CO₂ capture in power generation systems could be the use of Solid Oxide Fuel Cells (SOFC's), or a combination thereof with a gas turbine (GT). A novel concept has been introduced for SOFC-GT systems with CO₂ capture using a water gas shift membrane reactor burner (WGSMR-burner). Two SOFC-GT systems using this concept have been evaluated for their thermodynamic efficiency. The carbon capture penalty calculated is less than 50% of that of state-of-the-art CO₂ capture systems.

INTRODUCTION

The special property of the fuel cells in general and the SOFC specifically is that fuel conversion takes place without the dilution of the CO₂ with nitrogen. In SOFC systems a stream with a high CO₂ content is formed. Therefore, the SOFC offers the prospect of reducing the CO₂ capture penalty in terms of efficiency and costs.

Commercially available CO₂ capture technologies for power generation are in general post-combustion technologies, i.e. the CO₂ is captured from the flue gases after the conversion of fuel into power. Post-fuel cell CO₂-capture results in a significant drop in cycle efficiency, and increase in plant investment and operating costs. Typically, CO₂ capture with an amine scrubbing unit in a gas fired combined cycle results in an efficiency drop of 9%-points (16% relative), and in an investment increase of 59% and in cost of 50-70 Euro/ton CO₂ avoided.

At the Energy Research Centre of the Netherlands ECN a new program (DECAFF De-Carbonisation of Fossil Fuels) has been initiated for the development of advanced technologies for power generation with CO₂ capture. The aim is to reduce the CO₂ capture efficiency penalty with 50% and the financial penalty with 40%. The program aims at two fields of technologies: process integrated CO₂ capture in (decentralised) power production and process integrated CO₂ capture in (on-site) hydrogen production.

To reduce the efficiency and cost penalties of CO₂ capture novel concepts are required. These concepts will most likely make use of at least one but probably a combination of key technologies. The three key technologies envisaged are gas turbines, membranes and solid oxide fuel cells.

The SOFC offers high efficiency power production, even at scales suitable for distributed generation. A special property of the SOFC is that the fuel conversion takes place without the dilution of the CO₂ with nitrogen. In the SOFC a stream with a high CO₂ content is formed. However the fuel conversion (fuel utilisation) of the SOFC is limited to 85%. This means that the off-gas has to be treated to convert the unconverted fuel. Oxidation with air is not an option as the dilution with nitrogen will be too large.

SOFC WITH CO₂ CAPTURE IN LITERATURE

In earlier work an literature overview of SOFC systems with CO₂ capture has been presented (Dijkstra, 2002). The systems published can be divided into three categories:

1. *Pre-fuel cell capture.*

The result is a hydrogen fuelled SOFC

2. *Post-fuel cell capture*

Several schemes have been proposed using separation through chemical or physical absorption, cryogenic separation or pressure Swing Adsorption (PSA). A recycle of the unconverted fuel is generally required.

3. *Post-fuel-cell oxidation*

Prevent dilution of the CO₂ with nitrogen is the key issue here. Therefore, oxidation is done with pure oxygen, or a oxygen conducting membrane is used to supply oxygen, parallel to combustion. The availability of low cost oxygen is critical in his system. Systems with ultra high fuel utilisation have also placed in this category. Here the stack design is a critical issue. Even flow distribution is to be assured to prevent degradation of the stack. A promising concept is that of oxidation using a oxygen conducting membrane (OCM) reactor placed in the anode off-gas. The cathode off-gas is used as a sweep gas. Oxygen from the cathode off-gas permeates through the oxygen conducting membrane. At the permeate side unconverted fuel is oxidised with this oxygen. A variant of this concept is that of the current imposed electrochemical afterburner (CIEA) which is identical except from the current that is imposed on the membrane. Doing this can increase the flux and can prevent membrane degradation. It will however lower the system efficiency. Finally a novel system has been proposed which will be worked out further.

A NOVEL CONCEPT FOR CO₂ CAPTURE IN SOFC SYSTEMS

A novel concept has been developed for CO₂ capture at SOFC and hybrid systems (Jansen, 2002). The concept uses a water gas shift membrane reactor-burner (WGSMR-burner). This is a modified version of the membrane reactor type earlier investigated by Alderliesten (Alderliesten, 1997).

The working principle is depicted in Figure 1. Air is fed to the SOFC cathode, fuel is fed to the SOFC anode. The SOFC produces DC power. The cathode off-gas is fed to the permeate side of the membrane reactor, the anode off-gas is fed to the feed side of the membrane reactor. On the feed side the water gas shift reaction takes place producing H₂ and CO₂. The H₂ permeates through the hydrogen selective membrane in the WGSMR-burner. At the permeate side this hydrogen is burned with O₂ present in the SOFC cathode off-gas. This results in a very low hydrogen partial pressure on the permeate side, thus resulting in a high H₂ permeation rate.

The WGSMR-burner feed side products are CO₂ and H₂O, and small amounts of H₂ and CO, which can be removed by (catalytic) oxidation with air resulting in only a small dilution with nitrogen. The water can be removed easily e.g. with cooling. The resulting CO₂ can be used for sequestration without the need for further treatment. The WGSMR permeate side product is N₂, H₂O and O₂.

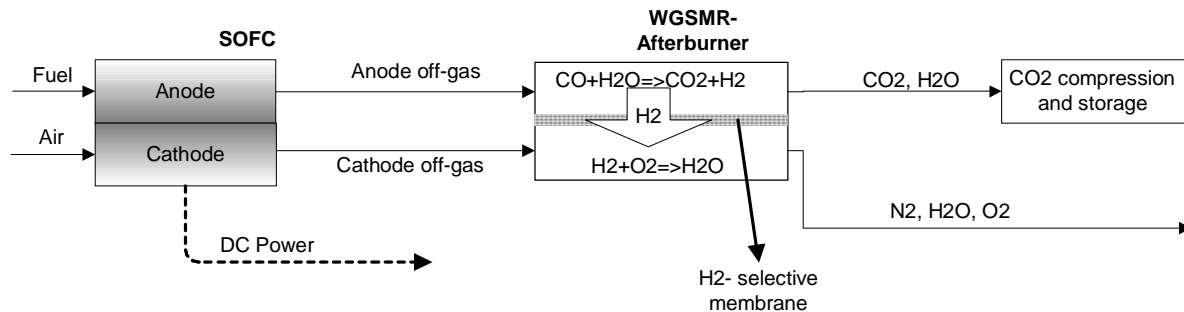


Figure 1: Working principle of the WGSMR-burner

This concept has been evaluated for implementation in SOFC-GT systems. Conceptual system designs have been made, which were evaluated for their thermodynamic efficiency using simulation in Aspen Plus. With these results, and that of a reference SOFC-GT system without CO₂ capture the carbon capture penalty was calculated, which can be compared to that of conventional systems.

STARTING POINTS

For the thermodynamic evaluation the following assumptions have been made:

- Heat losses to the environment have been neglected.
- Leakage has been neglected.
- Pressure drop of all equipment has been neglected.
- The Redlich-Kwong-Soave thermodynamic model is used.
- Reactors and reaction steps have been calculated assuming chemical equilibrium at the outlet temperature, allowing all possible reactions to take place.
- For the SOFC constant cell potential has been assumed.
- Both the SOFC and the membrane reactor assume that the outlet temperature of all streams is equal (within 1°C difference).
- Both the SOFC and WGSMR membrane are 100% selective in permeation. Leakage flows are not accounted for.
- Desulphurisation is not modelled.

For the SOFC the following approach has been used:

- The SOFC is modelled using a combination of standard unit operation models in Aspen Plus.
- The SOFC DC power production is calculated on the basis of the sum of the oxygen flows of both stacks and the cell potential.
- The fuel is pre-reformed and then equally distributed over the two stacks.
- For the first stack, the air mass flow is chosen such that the heat balance around this stack closes.
- The air from the first stack is quenched with cold air from the compressor and fed to the second stack cathode side. The quench flow rate is chosen such that the heat balance around the second stack closes.

For the membrane reactor a much-simplified approach has been used using a combination of standard Aspen Plus unit operation models.

- The model gives an approximate description of the parallel reaction and separation of hydrogen on the feed side, and combustion on the permeate side.
- The parameters have been chosen such, that an arbitrary value for the outlet hydrogen content of about 0.6 mole-% results from the calculations.
- The outlet temperature has been chosen according to the maximum allowable membrane temperature. In this case a maximum temperature of 700°C (for a palladium membrane) has been used.

Table 1 lists the process equipment specifications as used in the simulations. The SOFC data is based on the choice of using an anode supported flat plate type SOFC with internal reforming. The SOFC potential is set at a constant value of 0.7 V at 85% utilisation. An SOFC cathode side pressure of 6

bara has been chosen because this value favours recuperation above a higher pressure (e.g. 10 bara). The gas turbine pressure has not been optimised.

Table 1: *Process equipment specifications*

Type	Value	Type	Value
Desulphurisation section		Electrical equipment	
Temperature	350 °C	DC/AC converter	98 %
		Generator efficiency	98 %
Pre-reformer		WGSMR-burner	
Inlet temperature	500 °C	from Outlet temperature	700 °C
Conversion	As calculated equilibrium		
Steam to carbon ratio	2.6 (mol H ₂ O/mol CH ₄)	CO₂ compression section	
Duty	0 (adiabatic)	Isentropic efficiency η_{is}	0.85
SOFC		Number of stages	3
Inlet temperature	700 °C	Intercooler temperature	50 °C
Outlet temperature	800 °C	Heat exchangers	
Anode side pressure	6 bara	Temperature approach gas-liquid	20 °C
Cathode side pressure	6 bara	heat exchangers	
Fuel utilisation	0.85 or variable for system 1	Temperature approach gas-gas	50 °C
Cell potential	0.7 V (fixed)	heat exchangers	
Gas turbine compressor		Catalytic afterburner	
Isentropic efficiency η_{is}	0.85	Excess air	100%
Gas turbine expander		All equipment	
Inlet temperature	Max 1000 °C	Pressure drop	Negligible
Isentropic efficiency η_{is}	0.85		

SYSTEM EVALUATION

For evaluation of the novel concept three systems have been evaluated using thermodynamic modelling in the flow sheeting package Aspen Plus. The three systems evaluated are:

- System 1: the reference SOFC-GT system without CO₂ capture
- System 2: SOFC-GT with WGSRM-burner
- System 3: SOFC-GT with WGSRM-burner in counter-current configuration

Figure 2 gives a simplified schematic flow diagram of the reference SOFC-GT without CO₂-capture. This reference is used to assess the penalty associated with carbon capture in a SOFC-GT system using the WGSMR-burner. Fuel is pre-reformed (not shown), mixed with steam and fed to the SOFC anode side. Air is compressed in the gas turbine compressor, heated and fed to the SOFC cathode side. The off-gasses are mixed, resulting in combustion of the unconverted fuel. Hot off-gasses are then expanded in the gas turbine expander. The expander drives the compressor as well as a power generator. Heating and cooling of the streams is done using heat exchange, which is not shown in Figure 2.

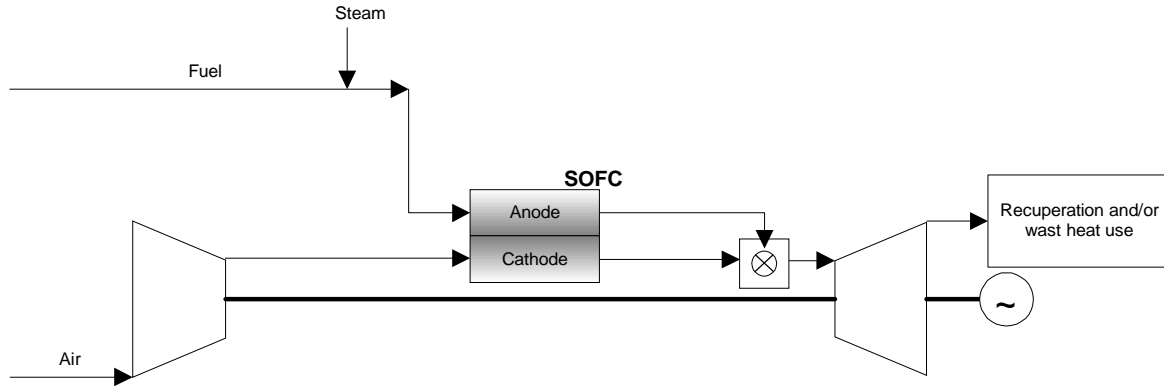


Figure 2: System 1. Reference SOFC-GT system, simplified schematic flow diagram

Figure 3 gives the simplified schematic flow diagram for an SOFC-GT cycle with an afterburner for CO₂ capture. The left part of the cycle is identical to the SOFC-GT without CO₂ capture (System 1). However anode off-gas is fed to the WGSMR-afterburner. Instead of being fed to the combustion chamber, the cathode off-gas is used as a sweep gas for the WGSMR-burner. In the burner the CO and H₂ in the anode off gas are converted. On the feed side the shift reaction takes place. Hydrogen permeates through the membrane and is burned at the permeate side of the WGSMR. The resulting CO₂ rich stream requires additional (catalytic) oxidation with air to remove the remaining small amount of unconverted fuel. It then flows to the CO₂ compression and storage section. The sweep gas stream can be used for recuperation or waste heat use. A small amount (15%) of the anode off-gas is injected in this stream and combusted to improve the efficiency. This will of course lower the CO₂-capture percentage since the CO₂ resulting from combustion is not captured.

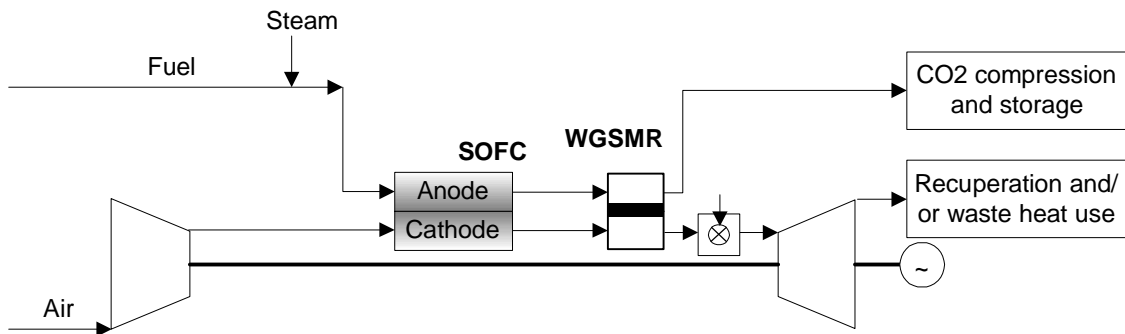


Figure 3: System (SOFC-GT with WGSMR-burner) simplified schematic flow diagram

Figure 4 depicts system 3, which is a modification of system 2. Here the airflow enters the WGSMR-burner first, before entering the SOFC. The system airflow direction is opposite of that of system 2 and is therefore depicted as the counter-current configuration. Note that the term ‘counter current’ does not refer to the flow direction inside the WGSMR-burner, but to the direction of the flows in the system it self. In the WGSMR-burner the flows can be both co-current as well as counter-current.

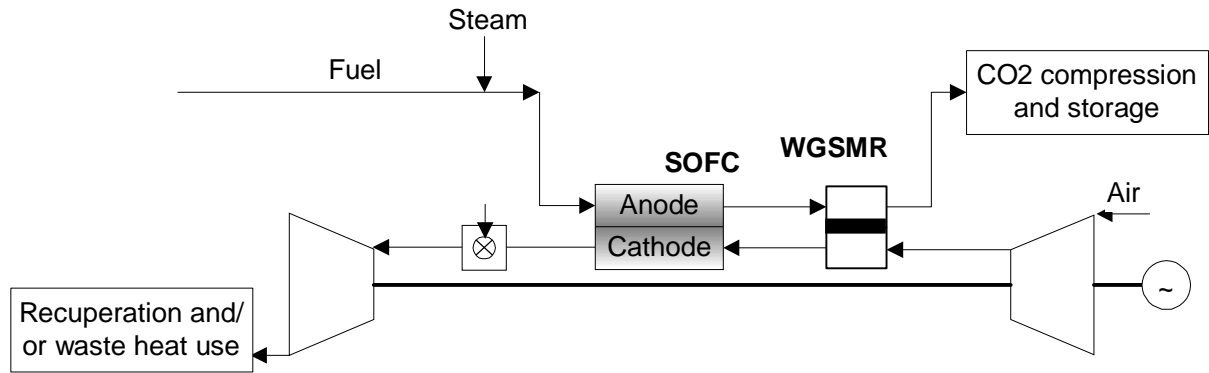


Figure 4: System 3 (SOFC-GT with WGSMR-burner in counter current system configuration) simplified schematic flow diagram

Heat integration has not been depicted in these schemes. The heat integration strategy used is that natural gas is first preheated with flue gas, the last part is heated with SOFC anode off-gas. Air is preheated with flue gas, the last part with cathode off-gas. The order of heat recuperation from the flue gas with the other streams has been chosen in accordance with the required outlet temperature (i.e. stream with the highest required outlet temperature is first recuperated, then the stream with the second highest temperature etc.)

For system 1 the SOFC fuel utilisation is chosen such that the inlet temperature of the expander is at its maximum value (1000°C). The resulting fuel utilisation is 69%. For systems 2 and 3 the fuel utilisation is fixed at its maximum value of 85% to limit the temperature increase in the WGSRM-burner. The turbine inlet temperature results from the heat integration.

RESULTS

CO₂ product quality

Table 2 gives for system 2 the composition of the retentate and that of the stream that leaves the catalytic afterburner that has been placed after the WGSMR to convert the last traces of CO and H₂. The results for system 3 are very similar. Table 2 shows that the retentate stream contains a large amount of water (75.8%). This water is to be removed in the compression section. In Table 2 it can also be seen that the retentate of the WGSMR contains 0.6% hydrogen and a small amount of CO. In the catalytic afterburner these components are combusted with 100% excess air. This results of an increase in the N₂ content of the stream of 3.3% in the retentate to 5.6% in the off-gas of the catalytic afterburner. This increase in nitrogen content in the catalytic afterburner is within acceptable limits.

Table 2: Stream data for WGSMR-burner retentate and catalytic burner off-gas (System 2)

	WGSMR retentate	Cat. burner off-gas
Temperature	699°C	726°C
Pressure	6 bara	6 bara
Composition [mol %]		
H ₂	0.6%	2*10 ⁻⁷ %
CO	920 PPM	3*10 ⁻⁸ %
CO ₂	20.3%	19.8%
H ₂ O	75.8%	74.3%
N ₂	3.3%	5.6%

System efficiency

Table 3 shows the system energy balance for a fixed fuel inlet flow of 0.1 kmol/s for all cases. The results for system 2 and 3 are almost identical, so a comparison can be made between system 1 on the one hand, and systems 2 and 3 on the other hand.

Comparing to the case without CO₂ capture (System 1), in the cases with CO₂ capture (Systems 2 and 3) the effects are observed:

- The SOFC produces more power as a result of the difference in fuel utilisation.
- The net power produced by the GT is lower. The gas turbine compressor consumes considerably more power. The expander produces a little less power.
- Additional power for CO₂ compression is required.

As a result the system power decreases from 11.79 to 10.64 MW (-9.7%) at constant fuel input. The total efficiency decrease in the SOFC-GT system amounts to 4.9%-points. The efficiency decrease due to CO₂ compression amounts to 1.7%-points. The total system efficiency decrease then amounts to 6.5%-points.

Table 3: System energy balance (LHV basis)

	Without CO ₂ capture		With CO ₂ capture	
	System 1	System 2	System 2	System 3
Natural gas in	<u>17.52 MW</u>	<u>17.52 MW</u>	<u>17.52 MW</u>	<u>17.52 MW</u>
Net SOFC power	7.96 MW	9.81 MW	9.81 MW	9.83 MW
GT compressor	-2.83 MW	-4.74 MW	-4.74 MW	-4.74 MW
expander	6.72 MW	5.87 MW	5.87 MW	5.85 MW
GT generator	3.82 MW	1.11 MW	1.11 MW	1.09 MW
CO ₂ compression	-	-0.29 MW	-0.29 MW	-0.29 MW
Net power	11.78 MW	10.63 MW	10.63 MW	10.64 MW
Efficiency (LHV)	67.2%	60.7%	60.7%	60.7%

Capture penalty

Calculation of the carbon capture penalty is done in terms of an increased heat rate rather than reduced efficiency. The increased heat rate is linked directly to the financial and energy input penalties. Furthermore, it is insensitive towards the system efficiency. (Note that a decrease in efficiency of 1%-point at a system efficiency of 70% is different to that of a 1%-point efficiency decrease a system efficiency of 50%).

Figure 5 illustrates the calculation of the carbon capture penalty. The reference carbon capture penalty is the difference in specific primary energy use in a large combined cycle unit with and without carbon capture. The reference carbon capture penalty is 0.34 [J_{prim}/J_e]. The target for the novel concept is to decrease this value with at least 50%, thus the target is to have a capture penalty below 0.17 [J_{prim}/J_e]. The carbon capture penalty for the novel concept (Systems 2 or 3, which have equal performances) is calculated through comparison with a reference SOFC-GT system (System 1). The carbon capture penalty of the novel system is 0.16 [J_{prim}/J_e], which means that the target of 0.17 [J_{prim}/J_e] is reached.

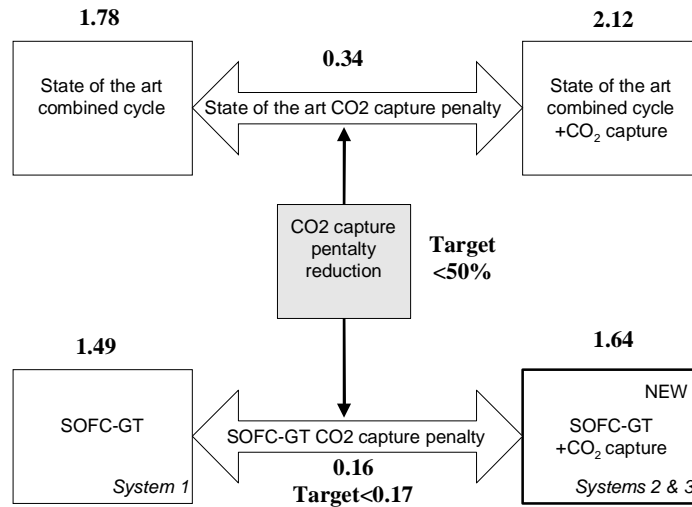


Figure 5: Carbon capture penalty calculation. (Primary energy use [J_{prim}/J_e])

The overall results for Systems 2 and 3 are almost identical. The efficiency of system 2 and 3 are lower than that of System 1. The main causes for this lower efficiency are losses in output power due to:

- Power required for compression of CO₂.
- A higher air mass flow.
- Withdrawal of mass flow before the expander. This stream is then not available for expansion.
- A lower water content in the expander inlet gas resulting in a lower Cp.
- A lower expander inlet temperature.

However, these losses are only partly compensated by positive effects to the system power i.e. a higher SOFC output power as a result of the increased fuel utilisation.

Through further optimisation and improvement of the system design, further reduction of the carbon capture could be possible.

CONCLUSIONS

A novel concept for CO₂ capture in SOFC-GT systems has been proposed. The concept makes use of a WGSMR-burner. Two promising implementation schemes for the concept are presented. The first one is the most simple form implementation in an SOFC-GT system (System 2). The second one is a modification of this scheme with a counter-current configuration of the unit operations (System 3). These two schemes are compared to the reference SOFC-GT scheme (System 1).

Thermodynamic simulation of the systems showed that system 2 and 3 have equal overall efficiencies. The carbon capture penalty of the novel concept is less than 50% of that of state-of-the are CO₂ capture technologies.

ACKNOWLEDGEMENT

The Dutch Ministry of Economic Affairs (EZ) has financed the work presented.

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