Collected Extended Abstracts of ECN Contributions to the 2002 Fuel Cell Seminar in Palm Springs

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REMOVAL OF SULPHUR-CONTAINING ODORANTS FROM NATURAL GAS FOR PEMFC-BASED MICRO-COMBINED HEAT AND POWER APPLICATIONS

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INTRODUCTION
Natural gas is an important feedstock for the production of hydrogen for Polymer Electrolyte (or Proton Exchange) Membrane Fuel Cells (PEMFC’s) for residential applications. Presently, much research efforts are carried out to develop small-scale catalytic fuel processors for on-site generation of hydrogen from natural gas. A typical residential power generator (RPG) may consist of several unit process steps such as fuel pretreatment (e.g. cleaning and preheating), catalytic partial oxidation, high and low temperature shift, preferential CO oxidation (PROX), PEMFC and off-gas treatment in the afterburner. In cases where the natural gas is to be used for residential purposes, naturally occurring sulphur compounds are first removed, and then sulphur containing odorants are added to odorise the otherwise odourless natural gas. Typical sulphur containing odorants are tetrahydrothiophene (THT), mercaptans, organic sulphides or mixtures thereof. In the Netherlands, and most of Europe, tetrahydrothiophene is used. Sulphur containing components present in the fuel processor fuel, are likely to be converted to H2S in the fuel processor section of the hydrogen generating system. To prevent detrimental effects on the catalysts in a typical PEMFC-based micro combined heat and power installation, sulphur removal from the natural gas feedstock is mandatory.

SENSITIVITY OF PEMFC FOR HYDROGEN SULFIDE
Information from open literature on the sulphur tolerance of (noble metal based) CPO and ATR, Water Gas shift, PROX, and PEMFC catalysts is scarce.
As the temperature level in the whole system is the lowest in the PEMFC itself and due to its catalytic composition, the influence of H2S is expected to be largest of the PEMFC. Uribe and Zawodzinski of Los Alamos National Laboratory assessed the effect of fuel impurities on PEM fuel cell performance (1) using a PEMFC with a Pt/C anode. They found that concentrations as low as 0.2 ppmv H2S adversely affect the performance of the fuel cell. The effect appears to be cumulative and causes severe deterioration of the fuel cells’ performance. Regardless H2S concentration and running time, replacing the contaminated fuel stream with pure H2 does not allow any recovery.
To make this picture more complete, the effect of 0.2 and 2 ppm H2S in H2 on the performance of a PEMFC with a 1:1 Pt:Ru containing anode has been investigated. Taking into account the dilution in the fuel processor, a feed containing 5 ppm of THT would lead to approximately 1-2 ppm of H2S in the fuel cell when no sulfur is scavenged in the fuel processor itself.
Figure 1 shows that exposing the fuel cell to the 2 ppm H2S containing anode gas leads to an almost instantaneous - and drastic decrease in performance. In about 15 hours the performance of the fuel cell dropped to 50% of the original value. Recovery of the performance with pure hydrogen appeared to be impossible, while exposing the anodes to air during several minutes caused a significant restoration of the original performance (> 90%). Anode gas containing 0.2 ppm H2S does not lead to such a drastic performance loss during an exposure time of 100 hours. Comparing these results to those presented by Uribe and Zawodzinski (1) on Pt/C leads to the conclusion that the use of PtRu anodes does not lead to a lower sensitivity for H2S, although it might be helpful for catalysing the recovery.
Considering the composition of PROX catalysts and new generation WGS catalysts, it seems reasonable to assume that they will be poisoned by low levels of sulphur as well.
Figure 1: PEMFC voltage at a constant current density of 0.4 A/cm² upon exposure to 0.2 and 2 ppm H₂S in H₂. Anode: 0.4 mg/cm² PtRu; Cathode: 0.4 mg/cm² Pt. Nafion 112. T_{cell} = 65°C. P = 1.5 bara. Anode not humidified; cathode humidified at 65 °C. Exposure to H₂S starts at 24 hrs.

BENCH-MARKING STUDY AMBIENT TEMPERATURE ADSORBENTS FOR THT

Ambient temperature technology based on the use of porous adsorbents such as active carbons, zeolites or molecular sieves seems to be a good choice for the removal of sulphur containing odorants from natural gas because of its simplicity when compared to elevated temperature technology like hydrodesulphurisation, combined with H₂S scavenging by ZnO. However, an important drawback of ambient temperature adsorbents is the fact that their sulphur uptake capacity is generally low (< 1 g THT per liter of adsorbent). In case of the yearly heat demand of an average Dutch family approximately 1200 m³ of natural gas has to be desulphurised for the 1 kWₑ RPG with at least 22 liter of adsorbent. This amount probably precludes its use as THT filter material because of size, weight and economic (material costs) constraints (total size of a residential power generator will probably be less than 250 liter).

To identify potential adsorbent candidates for the removal of THT from natural gas at ambient temperature, an experimental bench-marking study of several commercially available materials has been conducted. All adsorbents have been tested with commercial Dutch (North-Sea) natural gas of pipe-line quality under ambient conditions. Table 1 presents an overview of the tested adsorbent materials, the general test conditions that have been applied and the composition of the natural gas. THT adsorption tests were carried out in a manually operated flow rig. The flowrate of the natural gas of 3 l/min is representative for the actual situation in a 1 Kwₑ residential power generator (1200 m³/yr is approximately 2.2 l/min). Figure 2 presents an overview of the breakthrough curves for the tested samples. The residual THT concentration in the purified natural gas has been plotted as a function of filtered natural gas per liter of the adsorbent material in the reactor. This amount is directly proportional to the uptake of THT by the adsorbent.
Table 1: *Tested adsorbent samples and general test conditions*

<table>
<thead>
<tr>
<th>Tested adsorbent samples</th>
<th>Shape and size of tested particles</th>
<th>Total surface area (m²/g)</th>
<th>Pore volume (ml/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-impregnated active carbon</td>
<td>Extrudate, 1 mm</td>
<td>1100</td>
<td>0.5</td>
</tr>
<tr>
<td>Transition metal impregnated active carbon</td>
<td>Extrudate, 1 mm</td>
<td>1300</td>
<td>0.7</td>
</tr>
<tr>
<td>CuO / ZnO / alumina</td>
<td>Pellets, 3 mm</td>
<td>125</td>
<td>0.3</td>
</tr>
<tr>
<td>Promoted nickel on oxide carrier</td>
<td>Extrudate, 1 mm</td>
<td>280</td>
<td>0.4</td>
</tr>
<tr>
<td>Natural mineral based material</td>
<td>Particles 1–2 mm</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Molecular sieve</td>
<td>Extrudate, 1 mm</td>
<td>540</td>
<td>0.3</td>
</tr>
<tr>
<td>Zeolite</td>
<td>Extrudate, 1.5 mm</td>
<td>700</td>
<td>0.4</td>
</tr>
</tbody>
</table>

**General test conditions**

- Natural gas flow (l/min 0 °C, 1 atm.) | 3
- Natural gas composition (vol.%) |
  - 78.4 CH₄, 4.13 C₂H₆, 0.95 C₃H₈, 0.3 C₄H₁₀, 0.04 C₅H₁₂
  - 0.05 C₆H₁₄, 13.8 N₂, 2.21 CO₂, dewpoint –20 °C
- THT content (mg/m³) | 18, (approx. 5 ppmv)
- Inlet pressure (mbarg) | 100
- Temperature (°C) | Ambient (16 – 25)
- Packed-bed reactor dimensions |
  - Volume 70 ml, int. diam. 25 mm, bed height 150 mm
- Sample weight (g) | 30 – 35
- Gas analysis | GC – FPD and electrochemical THT sensor

In general, an arbitrary - but low- THT breakthrough criterion is set (0.1 ppmv) instead of using the full sulphur uptake capacity of the adsorbent. When the sulphur slip exceeds this criterion, replacement of the filter is necessary to prevent the downstream located fuel processing catalysts from exposure to even low sulphur levels.

![Figure 2: THT adsorption breakthrough curves of selected adsorbents. Conditions as in Table 1.](image-url)

For all samples that have been tested, the pre-breakthrough concentration of THT appeared to be below the detection limit of the flame photometric detector of the GC (< 20 ppbv). From Figure 2 it is obvious that the zeolite, the molecular sieve and the natural mineral based material
perform better than the active carbons and the metal / metal oxide based materials, with the active carbons showing the smallest THT uptake. The rather flat and irregular slope of the breakthrough curves for the zeolite and the molecular sieve might be due to micro-pore diffusion limitations for these materials. Among the active carbons, the transition metal impregnated carbon performs better than the non-impregnated sample.

A significant increase in weight has been observed for all samples after THT breakthrough (4%-10%). This might be due to the co-adsorption of higher hydrocarbons in the natural gas as indicated by an exothermic temperature effect at the beginning of the adsorption test. Especially for the zeolite a large temperature rise of more than 40 °C was observed at the beginning of the adsorption test. The commercial application of a material for a THT-filter is dependent on THT removal efficiency (i.e. residual THT concentrations in the filtered natural gas) and THT uptake capacity. The latter determines size and weight of the filter, that should be as small as possible in order to make the filter cost-effective for commercial applications. In Table 2 THT uptake capacities at 0.1 ppmv THT breakthrough are presented. It should be noted that these effective capacities are in general lower than the maximum obtainable THT uptakes. Consequently, from Figure 2, it follows that the zeolite G has the highest THT uptake, but using the breakthrough criterion of 0.1 ppmv, the capacity of E, F and G are similar. Table 2 also contains the yearly volume of the adsorbents, needed for the amount of THT that has to be removed in an RPG.

Table 2: Sulphur capacities of selected adsorbent samples for THT removal from natural gas

<table>
<thead>
<tr>
<th>Adsorbent material</th>
<th>g THT per liter adsorbent</th>
<th>As wt% S</th>
<th>Yearly volume of adsorbent for an RPG (l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-impregnated active carbon</td>
<td>1</td>
<td>0.1</td>
<td>22</td>
</tr>
<tr>
<td>Transition metal impregnated active carbon</td>
<td>2</td>
<td>0.2</td>
<td>11</td>
</tr>
<tr>
<td>CuO / ZnO / alumina</td>
<td>2</td>
<td>0.1</td>
<td>11</td>
</tr>
<tr>
<td>Promoted nickel on carrier</td>
<td>7</td>
<td>0.3</td>
<td>3.1</td>
</tr>
<tr>
<td>Natural mineral based material</td>
<td>9</td>
<td>0.5</td>
<td>2.4</td>
</tr>
<tr>
<td>Molecular sieve</td>
<td>10</td>
<td>0.5</td>
<td>2.2</td>
</tr>
<tr>
<td>Zeolite</td>
<td>11</td>
<td>0.6</td>
<td>2</td>
</tr>
</tbody>
</table>

From Table 2 it is obvious that the promoted nickel adsorbent, the molecular sieve, the zeolite and the natural material are potential candidates for application within an RPG. However, the strong temperature rise at the beginning of the adsorption test with the zeolite is an important drawback for commercial application. Also, the high nickel load on the promoted nickel adsorbent is a serious disadvantage from a labour-hygienic point of view and because spent material might be difficult to dispose of. The natural material has been identified as a new adsorbent for THT. The material is environmentally safe, easy to use and possesses good activity (low residual sulphur levels) and sufficient capacity. In addition, the material is easily available at much lower costs than all other candidates. This is especially important, because the development of a micro combined heat and power generator is aimed at large scale residential use. For a successful market penetration the cost aspect is of utmost importance.

ACKNOWLEDGEMENTS
Ing. Michiel P. de Heer of the ECN PEMFC & Supercaps department is gratefully acknowledged for the PEMFC H2S tolerance tests.

REFERENCES
PEMFC SYSTEMS: THE NEED FOR HIGH TEMPERATURE POLYMERS AS A CONSEQUENCE OF PEMFC WATER AND HEAT MANAGEMENT

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INTRODUCTION
It is quite common to operate PEMFC systems at pressures of 2-3 bar(a) and at or below 80°C. Pressurised operation requires that the system includes a compressor, possibly an intercooler and an expander to reclaim part of the energy that was required for compression. This paper addresses why PEMFC systems usually are not operated at lower pressure, and/or somewhat higher temperature. A typical air management system is given in Figure 1. The relevant components are:

- A compressor or blower,
- The humidifier, which may be integrated with the cooling circuit,
- The stack(cathode),
- A water separator,
- A pressure release device (backpressure controller or expander),
- A cooling circuit: pump, buffer and heat exchanger.

In case of pressurisation above about 1.6 bar an air cooler is required. Cooling of the inlet air can also be done by injection of water into the compressor. This option is not considered here.

EXPERIMENTAL
To assess the effect of pressure and temperature on cell performance, a 7 cm² cell was operated at 1, 1.5 and 2.5 bar(a), and at temperatures of 65 and 80 °C. An air stoichiometry of 2 was maintained by continuously adjusting the cathode flow rate as function of current density. The MEA was made using E-Tek electrodes and a membrane prepared by filling a 50 µm 85% porous substrate (Solupor) with Nafion ionomer(1). Both anode and cathode gases were fully humidified. Polarisation curves obtained with this cell under various P,T conditions are given in Figure 2. Although the PEMFC can be operated over a wide range of the displayed curves, it should be noted that cell efficiency is proportional to cell potential, in first approximation given by $\eta=0.8-V$ (V in Volts, $\eta$ is with respect to LHV, at 100% H₂ utilisation). For that reason, operation at a potential lower than 0.6-0.7 V hardly is attractive. Power density curves are...
given in Figure 3. Opting for the highest power density is tempting in order to reduce the power specific size, weight and cost of the stack. However, compression of air takes energy, and these losses should be accounted for. The amount of air required by a fuel cell depends on the operating conditions. At an individual cell potential of 0.675 V and air stoichiometry of 2, a 50 kW system uses 150 Nm³/hr of air. A 70% efficient compressor uses 8.6 kW for compressing this amount to 3 bar(2), that is 17% of the power produced by the fuel cell. For systems in the order of a few kW or less, the power penalty associated with the use of a compressor is even bigger. Taking into account the losses for compression, one can calculate the net power density, as represented in Figure 4. From this and from what was stated above on efficiency, it is concluded that the net effect of pressurisation is negligible at preferred operating conditions, that is, at current densities of less than about 0.6 A/cm². Only at high current density, a net power gain remains. So, if for reasons of efficiency, high cell potential/low cell current density operation is preferred, and if no net system power gain is achieved under such conditions, then why would one prefer pressurised operation? The reason is that at pressurised conditions, the water vapour pressure has less effect on water balance, gas flow rates and gas composition. In the following, this will be shown for the air system only.

**EFFECTS OF HIGH RELATIVE HUMIDITY**

The performance of the PEMFC strongly depends on the conductivity of the polymer(3), which is strongly related to the relative humidity of the gas the cell is in contact with. The requirement of working at saturated gas conditions may perhaps not make it impossible to operate the PEMFC at low P and relatively high T, but such conditions require an adapted design of stack and system. High water vapour pressures lead to strong dilution of reactants by water vapour and large heat exchange surfaces.

In terms of water management, the following occurs in the cathode line:

![Figure 4 Net power density derived from Figure 3](image)

![Figure 5 The calculated wet gas volume at various temperatures and pressures. The original dry gas flow rate used in this calculation is 150 Nm³/hr, or 0.042 Nm³/s](image)
**Humidifier.** The air is humidified and heats up to stack temperature. Using saturation vapour pressure data found in literature[4], the consequences of working at 100% R.H. are analysed. First of all, the addition of water vapour increases the volume of gas flowing through the system (when pressure is kept constant). Especially at high $T$ and low $P$, the increase in gas volume is substantial (Figure 5). The hydraulic implications have to be taken into consideration in the design of the fuel cell stack and the system. This leads to an increase in the diameters of fuel cell flow channels and system piping. This will however result in increased system volume and weight.

A trivial consequence of humidification is that water is consumed (Figure 6). This will particularly become of relevance if the water that is produced in the stack is not sufficient to compensate for the water used in the evaporator.

The evaporation of water takes energy (Figure 7). This energy can be taken from the cooling circuit, in which case no extra energy is required. The waste heat of a 50 kW fuel cell stack operating at 0.675 V individual cell potential (the basis for these calculations) under condensing conditions is 61 kW. Comparing this number with the values given in Figure 7, it can be concluded that there should generally be no problem to fulfil this heat demand.

**Cathode:** The addition of water vapour results in a dilution of the oxygen present in air (Figure 8). The concentration shown here is that at the cathode inlet. It can be concluded that working at low $P$, high $T$ conditions leads to high oxygen dilution, which decreases cell performance. Since oxygen is used in the fuel cell reaction, the downstream part of each cell is exposed to substantially lower concentrations.

Under the conditions assumed here (50% oxygen utilisation), half of the oxygen is used by the electrochemical reaction taking place in the fuel cell. Since this reduces the volume of gas, some of the water originally present in the vapour phase will condense out to form liquid water. This produces heat, which has to be removed by the stack coolant circuit. Also, some water is produced, in addition of the
water produced by the electrochemical reaction. So, in the cathode, a two-phase flow is established.

**Water separator**: The liquid water is separated from the cathode exit gas by a water separator. The amount of water that is collected should match the amount needed for humidification. Figure 9 shows the water surplus of a system as function of $P$ and $T$. Negative numbers indicate a net water loss from the system. One way to prevent a system from turning into a net water consumer is to cool the water separator, such that it now becomes a condenser. This may seem unattractive since it apparently increases the amount of heat that has to be discarded to the surroundings, which is very undesirable for automotive applications. Theoretically, this is not the case however since under these conditions a large amount of heat is taken from the stack coolant flow, to provide the heat required for evaporation of the large amount of water for humidification. So, there is merely a shift of the heat removal problem.

**Overall heat management**: One can try to match heat sources and sinks, to avoid the need for external heating and to reduce the amount of heat that has to be discarded by a radiator. Even if such matching could be done perfectly, a net cooling duty is still necessary. This is shown in Figure 10. At low temperatures, the water content of the cathode exit gas is low. Little heat is removed in the form of latent heat, but as sensible heat instead. As temperature increases, cathode exit gas humidity increases, and the net sensible heat removal from the system is reduced. At even higher temperatures the water separator has to be cooled in order to become a condenser, e.g. at 60°C for the 1 bar situation. For high operating pressures, the heat removal by latent heat is relatively low, since most water is in the liquid form. In addition, a significant cooling duty is required for the inter cooler.

**DISCUSSION**

From Figure 10 it seems logical to conclude that working at low $P$ and high $T$ is most attractive. A compressor is not required, and heat rejection to the surroundings is minimised. However, to make such a system work, huge amounts of water have to be evaporated in the humidifier, requiring large amounts of heat. The water condenser has to make up for the water used in the humidifier and therefore has to withdraw large quantities of heat from the humid cathode exit flow. In the calculations used to produce Figure 10, the heat sources and sinks are coupled. This is however, not realistic at high $T$, low $P$ combinations, as can be deduced from Figure 11. Here, the sum of the duties of the air cooler after the compressor, the humidifier, the condenser and the external heat exchanger (e.g. car radiator) is presented. From Figure 11, it can be concluded that working at high $T$ and low $P$ will lead to huge heat duties (hence sizes) for the heat exchanging components. In combination with the large wet gas volumes (Figure 5), there will be a large effect on system size.

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**Figure 9** Water surplus for the system shown in Figure 1

**Figure 10** The calculated amount of sensible heat that has to be discarded to the surroundings

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It seems that the use of a compressor is inevitable if heat rejection to the surroundings demands for operating temperatures of close to 80 °C. For many applications a different parameter setting would be much more attractive though. Preferably, the temperature should be even higher. That is, close to or above 100 °C. The pressure should be close to atmospheric to avoid compressors. For cars, the higher operating temperature helps to alleviate the problem of heat rejection to the surroundings. For stationary applications, the benefit of a higher operating temperature would be in the more versatile use of the waste heat for space heating and hot tap water.

It will be clear that as long as Nafion type polymers are used in the PEMFC, the problems of pressurisation, heat and water management will not be solved. This will only be the case if a new type of proton conductor is found, allowing for operation at higher temperatures and low relative humidity. Preferably, such a polymer should still have the good properties of Nafion type polymers: cold start capabilities, toughness and good proton conductivity.

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INTRODUCTION
In January 2002 the project "FRESCO", Fuel-Cell Reduced-Emission Scooter, partially funded by the European Commission through the 5th framework program, has been started. In this project a prototype fuel cell driven scooter will be developed, built and circuit-tested by the end of 2004. The European consortium carrying out this project consists of Piaggio & C Spa responsible for the overall vehicles system, building and circuit testing, Selin Sistemi Spa for developing the electric rotating machine and traction converter, ECN for the fuel-cell stack and supercapacitor module, and CEA responsible for the development and fabrication of the high-pressure hydrogen storage tank. The scooter will be a modified, modern mass-production type, will have a maximum speed of 75 km/hrs, a range $\geq 100$ km and further state-of-the-art characteristics. A supercapacitor module will support the fuel-cell stack to optimize system behavior and to facilitate for regenerative breaking. An advanced system concept is chosen, aiming at reduction of electronic hardware, simplicity in system control and high system stability.

MODELING AND SYSTEM CONCEPT
Models of FCEV systems have been built in Matlab / Simulink. The basic model blocks for the system components are obtained from the QSS-Toolbox by the ETH Zürich and from NREL's ADVISOR. These blocks are customized to the actual needs and complemented with a control algorithm. The resulting tool is a quasi-static, back-wards-facing model. A quasi-static model assumes the system to be at equilibrium at each simulation time-step. This approach is chosen because this kind of simulations typically precedes the component development stage. Hence it is not always possible to obtain sufficient data to feed a dynamical model. The main goal of the simulations is to perform component scaling of the FC stack, the EC module and the traction motor, based on performance requirements in the form of a drive-cycle. In a backwards-facing model the cause and effect relationship are reversed by providing the
drive-cycle to be complied with as input, and calculate the power output each component must achieve in order to meet the performance requirements. After the component scaling is done, the model is used to estimate performance indicators like fuel consumption, carbon dioxide and other emissions. Subsequently the geometrical size of the system components is estimated and at Piaggio a 3D-CAD approach is used to fit the components in the frame of the scooter. Piaggio field data of a large-type scooter for urban use have been analyzed. Drive-cycles based on this analysis have been used in the modeling.

Various system concepts have been evaluated using the modeling approach described. A common concept is to maintain a quite constant rail voltage in the system and to couple the fuel-cell stack, the supercapacitor module and the electric rotating machine all via their own converter device. In the case of a small vehicle like an electric scooter, using a relatively low rail voltage, it turns out that another approach is more advantageous. Allowing a relatively large voltage swing on the rail, the supercapacitor module can be coupled directly to the rail thus eliminating a converter device. In addition, this concept facilitates a very simple system control via the two remaining electronic devices, i.e. the current pump between the fuel-cell stack and the bidirectional traction converter. Also, because of the low-pass filter characteristic of the rail with directly coupled supercapacitor module, the system stability is significantly improved as compared to a common layout.

The result of the modeling, system evaluation and 3d-analysis is shown in Figure 1, indicating the feasibility of the FC + EC system for this small city vehicle. In this particular case the use of an EC module has a significant weight advantage over a battery, because weights are in a range ≥ 10 % of the total vehicle weight. The volume advantage is even larger and for this type of vehicle very important.

**SUPERCAPACITOR DEVELOPMENT**

Currently available supercapacitor technologies often have two high-surface-area carbon electrodes and thus rely on pure double-layer capacitance. From the model analysis explained above, it turns out that these technologies have too low energy densities for an optimal sizing of the device regarding performance, volume and weight. In the same way, battery technologies suffer from too low power density. Also it turns out that for this particular case the improvement of energy density of supercapacitor technology is the strategy to be preferred over the one of power density increase of batteries. The increase of energy content of supercapacitors is pursued by the use of so-called pseudo-capacitance. A well known material showing this property in KOH electrolyte is Ni(OH)₂. However, this electrode material has a number of disadvantages limiting the effect of this approach, i.e. a limited usable voltage window and a low and state-of-charge dependent electrical conductivity. In addition, as a nickel compound it has environmental and health drawbacks. At ECN a well-defined screening strategy has resulted in the identification of two new classes of materials with very promising properties for the application in supercapacitors. The classes have been named EMX and EMZ. The materials do not contain any precious elements and are therefore low cost. Some of the relevant properties of EMX-1 are shown in Table 1 in comparison with known electrode materials.

| Table 1. Comparison of the main properties of supercapacitor electrode materials. |
|-------------------------------|------------------|----------|----------|----------|
| Sp. Area (m²/g)                | AC   | RuOₓ  | NiOOH    | EMX-1    |
| Capacity (mAh/g)               | 1500 | 120   | 120      | ≤ 50     |
| Conduct. (S/cm)                | 14   | 98    | 90       | ≤ 170    |
| Price (Euro/kg)                | 2.0  | 3000  | > 6.0    | < 20     |

Using a simple geometrical model for the EMX-1 / KOH / AC technology, the attainable energy for cells and modules has been estimated. Energy densities up to ca. 20 Wh/kg may be obtained, where presently available technologies are limited to ca. 5 Wh/kg. The development of a prototype supercapacitor module based on EMX material is also part of the FRESCO project.

**ACKNOWLEDGEMENT**

The European Commission and the Netherlands Ministry of Economic affairs (SENTER agency) are gratefully acknowledged for partially funding the project. UMICORE s.a. (Belgium) is thanked for support of the material powder development.
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ABSTRACT
In this study the possibilities are explored for a trigeneration system combining a PEMFC or SOFC based CHP system with a sorption cooler. A priori, the usefulness of such an integrated system for the production of cold, heat and power is largely determined by the extend in which CHP waste heat can be used for the production of cold. Based on evaluation of three different fuel cell systems it appears that in case of PEMFC and other humidified fuel cell systems only minor fractions of the available heat is present at temperatures required to operate sorption coolers. A dry system based on catalytic partial oxidation (CPO) fuel pre-treatment and SOFC shows the best results. About 80% of the heat can be used for cold production, resulting in an overall net cooling efficiency for the trigeneration system of 25%. Evaluation of the environmental and economic performance of this trigeneration system in a grid connected setting in the Netherlands, shows diverse results: trigeneration does not result in primary energy saving and it is questionable whether or not it leads to CO2 emission reduction. Energy costs reduction largely depends on tariff structure which appears unfavourable for small scale application (up to a few hundred kW). It appears that, in addition to a good thermal match, an adequate electrical and overall efficiency of the fuel cell CHP system is essential to obtain a profitable trigeneration system.

INTRODUCTION
In periods when there is little demand for heat, for instance during the summer the benefits of small scale combined heat and power (CHP) cannot fully be employed. Combining CHP systems with heat-driven cooling technologies may extend and enhance the applicability of small scale CHP systems by providing an additional possibility to effectively use the heat produced. Furthermore, it offers the possibility to optimise the economics of the system.

To explore the potential of trigeneration for fuel cell based CHP systems, ECN and Shell have jointly carried out a feasibility study. Shell is currently involved in development of a CPO fuel processor for fossil fuelled fuel cell systems. ECN is involved both in development of PEM and Solid Oxide fuel cell technology for small scale CHP application as well as in development of technologies for waste heat utilisation. The latter comprises amongst other the so-called Salt Water Energy Accumulation and Transformation technology (SWEAT), which is a solid sorption heat pump based on the pair Na2S.xH2O/H2O [de Boer et al., 2002]. A specific feature of this technology is its energy storage ability which is advantageous in situations of mismatch between energy supply and demand. The main characteristics of the technology are presented in table 1, together with some alternative technologies.
### Table 1: Main characteristics of sorption coolers

<table>
<thead>
<tr>
<th>Sorption Cooler</th>
<th>T-supply °C</th>
<th>COPth range</th>
<th>Capacity range</th>
<th>T-cool °C</th>
<th>T-sink °C</th>
<th>Thermal storage capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>SWEAT (Na$_2$S/H$_2$O)</td>
<td>90-95</td>
<td>0.5-0.55</td>
<td>2-500 kW$_{th}$</td>
<td>28-30</td>
<td>9-14</td>
<td>yes</td>
</tr>
<tr>
<td>Mycom (Silica/H$_2$O)</td>
<td>70-80</td>
<td>0.6</td>
<td>50-350 kW$_{th}$</td>
<td>28-30</td>
<td>9-14</td>
<td>no</td>
</tr>
<tr>
<td>LiBr-H$_2$O</td>
<td>70-90</td>
<td>0.6-0.7</td>
<td>0.4-10 MW$_{th}$</td>
<td>28-30</td>
<td>9-14</td>
<td>no</td>
</tr>
</tbody>
</table>

### APPROACH

Figure 1 shows the layout of the CPO-PEMFC/SWEAT trigeneration system. The main question in combining a CHP system with a heat driven cooler is whether, and to what extent, the quality of the heat produced by the CHP system matches the quality of the heat required by the sorption cooler. This aspect has been investigated by matching temperature-duty profiles of heat available from CHP systems and the temperature profile of the heat needed by the cooler, using pinch analysis (Odessy Pro). Three different atmospheric, natural gas fuelled fuel cell systems are evaluated. Temperature duty profiles for these systems are obtained through simulation of the fuel cell systems with a flowsheeting programme (AspenPlus). A summary of the parameters used for simulation of the fuel cell system is given in table 2.

### Table 2: Some characteristics of simulated fuel cell systems

<table>
<thead>
<tr>
<th>System</th>
<th>Tcell °C</th>
<th>Vcell</th>
<th>Ufuel</th>
<th>Uoxid</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPO-PEMFC</td>
<td>70</td>
<td>0.7</td>
<td>80%</td>
<td>50%</td>
</tr>
<tr>
<td>SR-SOFC</td>
<td>700 → 800</td>
<td>0.7</td>
<td>80%</td>
<td>7.1%</td>
</tr>
<tr>
<td>CPO-SOFC</td>
<td>700 → 800</td>
<td>0.7</td>
<td>80%</td>
<td>6.7%</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

In figures 2, 3 and 4 calculated temperature duty profiles are shown for the different fuel cell systems. In these figures the temperature profile of the heat needed by the SWEAT cooler is depicted as the cold composite curve in the lower right-hand corner. System efficiencies based on simulation and pinch analysis results are summarised in table 3. In this table the heat pump supply fraction is the fraction of the net thermal efficiency which can be used by the sorption cooler. The net cooling efficiency is the cooling duty as fraction of the heating value of the natural gas input.
Table 3 Comparison of the three different fuel cell systems (LHV)

<table>
<thead>
<tr>
<th></th>
<th>CFO PEMFC</th>
<th>SR SOFC</th>
<th>CFO SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>net electrical efficiency</td>
<td>0.32</td>
<td>0.45</td>
<td>0.28</td>
</tr>
<tr>
<td>net thermal efficiency</td>
<td>0.64</td>
<td>0.49</td>
<td>0.62</td>
</tr>
<tr>
<td>net total efficiency</td>
<td>0.96</td>
<td>0.93</td>
<td>0.91</td>
</tr>
<tr>
<td>heat pump supply fraction</td>
<td>0.23</td>
<td>0.22</td>
<td>0.77</td>
</tr>
<tr>
<td>net cooling efficiency</td>
<td>0.08</td>
<td>0.06</td>
<td>0.25</td>
</tr>
</tbody>
</table>

The results show that in case of the CPO-SOFC system about 80% of the available heat can be used by the SWEAT sorption cooler. In the other cases only a minor fraction of the heat can be used, because most of the heat is available at too low temperatures. Partly this is explained by a low fuel cell operating temperature (PEMFC, 70°C), and partly because a considerable amount of heat is present in the form of latent heat which can only be recovered by condensation of the water vapour at low temperatures (CPO-PEMFC and SR-SOFC).

Opposite to the large fraction of usable heat for cold production, the electrical efficiency of the CPO-SOFC system is rather low. Part of the heating value is lost in fuel processing. Furthermore, a large part of the gross electric power of this system is used for ventilator energy, due to a high air demand for cell stack cooling. The high air factor also causes the water vapour to be diluted, so that there is no contribution of condensation heat to the thermal efficiency. As a result also the overall efficiency is relatively low.

With respect to electrical and overall efficiency, the steam reforming SOFC system is to be preferred. The cooling performance of a trigeneration system based on SR-SOFC can be improved by combining this system with a sorption cooler technology that enables the use of lower quality heat. Silica gel/water (Mycoc), or LiBr-H\(_2\)O based sorption coolers, therefore, offer a better perspective for a practical trigeneration system than the SWEAT sorption cooler.

Potential for reduction of energy use, CO\(_2\)-emission and energy costs
Because electricity is the preferred product, and otherwise the heat is dumped, in stand-alone operation, the use of available CHP heat for cooling always leads to savings and reductions with respect to primary energy, CO\(_2\), and energy costs. In grid connected situations, where there are alternatives to fulfill the energy demands, this will not always be the case. Whether or not trigeneration is beneficial, will, amongst others, depend on central power plant efficiencies, the central power plant fuel or fuel mix, and the tariffs and tariff structure of the CHP fuel and the electricity of the grid. Primary energy saving, CO\(_2\) emission reduction and energy cost savings are obtained if the following criteria are fulfilled:
Criterion for primary energy saving:

$$\eta_{CPP} \leq \eta_{dCHP} \left( 1 + \left( \frac{\eta_{bCHP}}{\eta_{dCHP}} \right) \left( \frac{F_{supp} \cdot COP_{sc}}{COP_{cc}} \right) \right)$$

Criterion for CO₂ emission reductions:

$$\frac{\eta_{CPP}}{EF_{CPP}} \leq \frac{\eta_{dCHP}}{EF_{NG}} \left( 1 + \left( \frac{\eta_{bCHP}}{\eta_{dCHP}} \right) \left( \frac{F_{supp} \cdot COP_{sc}}{COP_{cc}} \right) \right)$$

Criterion for fuel cost saving:

$$\frac{F_{price}}{E_{price}} \leq \left( 1 + \left( \frac{\eta_{bCHP}}{\eta_{dCHP}} \right) \left( \frac{F_{supp} \cdot COP_{sc}}{COP_{cc}} \right) \right)$$

Where:

- $\eta_{CPP}$ = average efficiency of the central power production
- $\eta_{dCHP}$ = electric efficiency of the CHP unit
- $\eta_{bCHP}$ = thermal efficiency of the CHP unit
- $F_{supp}$ = CHP thermal output fraction used by the sorption cooler
- $COP_{sc}$ = Coefficient of performance of the sorption cooler
- $COP_{cc}$ = Coefficient of performance of the compression cooler
- $EF_{CPP}$ = Central power production CO₂ emission factor [kg CO₂/GJ]
- $EF_{NG}$ = CHP fuel CO₂ emission factor [kg CO₂/GJ]
- $F_{price}$ = Average CHP fuel price [€/GJ]
- $E_{price}$ = Average electricity price [€/GJ]

Using these criteria a number of case studies are considered for grid connected settings in the Netherlands [Weeda et al., 2002]. The case studies were performed for trigeneration systems consisting of a fuel cell CHP system and a SWEAT sorption cooler. The average central power plant efficiency and the coefficient of performance (COP) of conventional compression coolers are assumed 42% and 4, respectively. Natural gas is used as CHP fuel with an CO₂ emission factor of 56 kg/GJ. The emission factor for the average central power plant is 77 kg/GJ. Natural gas and electricity tariffs for the Dutch 2002 situation are used.

Under the above assumptions, only in case of the SR-SOFC system a primary energy reduction is found. However, this is due more to the relatively high electrical efficiency of the system, than to savings as a result of trigeneration. In general, significant CO₂ emission reductions were obtained. This is explained by the substitution of average central power plant fuel mix by less carbon intensive natural gas. However, if the CHP system replaces natural gas fired central power production, instead of an ‘average’ power plant than it becomes questionable whether or not CO₂ emission reduction is obtained. Finally, for the Dutch situation it appears that energy cost reduction resulting from the application of trigeneration, largely depends on the energy tariff structure. At small scale, up to about 300 kW, gas is relatively expensive compared to electricity, and energy cost savings appear marginal. It appears that, in addition to a good thermal match, an adequate electrical and overall efficiency of the CHP system is essential to obtain a profitable trigeneration system.

**CONCLUSIONS**

1. The Solid Oxide Fuel Cell system with a CPO-based fuel processor show the highest fraction of heat available for cooling purposes. Most of the heat supplied by the PEMFC and
SR-SOFC system considered is too low in quality to be used for cold production by sorption coolers.
2. In addition to a good thermal match, an adequate electrical and overall efficiency of the fuel cell CHP system is essential to obtain a profitable trigeneration system.

ACKNOWLEDGEMENT
We gratefully acknowledge the Dutch Ministry of Economic Affairs and the SENTER Agency for funding the research.

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1. R. de Boer, W.G. Haije, J.B.J. Veldhuis " determination of structural, thermodynamic and phase properties in the Na2S-H2O system for application in a chemical heat pump, ECN-RX--02-009
SOLID OXIDE FUEL CELL DEVELOPMENT AT ECN
AND PRODUCTION AT INDEC

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INTRODUCTION
The Energy research Centre of the Netherlands (ECN) works on the development of Solid Oxide Fuel Cell technology since 1991. Although many aspects related to the development and evaluation of SOFC stacks and systems have been and are addressed, the development of cell designs, cell materials and cell manufacturing procedures have been the core activity throughout this period. In 1999 the spin-off company InDEC B.V. has been established for the commercial exploitation of the R&D developments achieved by ECN. The electrolyte and anode supported cell types are currently routinely produced by InDEC, while ECN continuously works on their further improvement. Recently the development of what is called the ‘third generation cell’ type has been started. Since low system costs are essential for the commercial introduction of SOFC based systems into society (1), cost efficient manufacturing procedures have always been an important issue even at the earliest development stages of SOFC cells. Therefore, all developments are based on essentially two manufacturing processes: i.e. tape casting for the relatively thick mechanically supporting component and screen printing for all the thin layers. These processes were selected because they are considered to be scalable relatively straightforward to high volume and low cost production.

R&D AND ROUTINE MANUFACTURING
The ECN spin-off company InDEC (Innovative Dutch Electro Ceramics) is a pilot production plant for the manufacturing and sales of SOFC cells. Presently InDEC is fully owned by ECN. However, InDEC is close to a minority participation by a venture capital fund and discussions are running on a major participation of an industrial organisation providing added value for the technology, the production and the business development. The participations will enable InDEC to grow from the pilot production stage to a fully automated industrial production plant as soon as the market starts pulling for real large numbers of cells. The existing production capacity of InDEC is 2 MW_e.

Figure 1. The relationship between R&D at ECN and manufacturing at InDEC
The relationship between ECN and InDEC is depicted by Figure 1. Essentially, all R&D on cells and manufacturing processes is done by ECN. Validated manufacturing protocols are exclusively licensed to InDEC. In return ECN receives a royalty fee from InDEC. The mission of InDEC is the routinely manufacturing of cells according to these protocols and the sales to non-exclusive customers.

**STATUS OF ELECTROLYTE SUPPORTED CELL**

The electrolyte supported cell type, for high temperature (900-1100°C) operation, has been under development from 1991, first in collaboration with Siemens and later also with Sulzer-Hexis. It is therefore the most mature cell type. The mechanical support is provided by an approximately 120 μm thick, 3 mol% yttria doped fully stabilised zirconia (3YSZ), which is tape casted. The cathode consists of two screen printed layers: adjacent to the substrate a 25 μm composite layer of La0.75Sr0.2MnO3 (LSM) and 3YSZ and on top of that a 25 μm current collecting of LSM only. Up to the year 2000 the anode consisted of a dual phase Ni/8YSZ layer. The stationary performance of this anode was according to customer requirements, however the resistance against oxidation reduction cycling appeared to be poor: performance decay was from 50% to complete die out after only one or two cycles. A novel anode type was developed which consists of a 25 μm layer composed of Ni and gadolinium doped ceria (GDC), connected to the electrolyte through an approximately 5 μm intermediate layer of GDC. On top of the Ni/GDC functional layer is again a 10 μm current collecting layer of Ni with an improved microstructure. The typical performance of such an anode type is shown in Figure 2. A five cell stack of the Sulzer-Hexsis type was cycled three times. After 170, 310 and 380 hours of operation the fuel flow is cut off for 24 hours while the stack is kept on its operating temperature of 950°C. The surrounding air that leaks into the stack oxidises the nickel of the anode. On recovering the fuel flow, the cells recuperate completely after the first and second cycle. Only after the third cycle there is some loss, which is mainly attributed to the high efficiency operation at a fuel utilisation of 87%, under which this cycle was performed. The stack was operated on pre-reformed Dutch natural gas with a steam to carbon ratio of 2.5.

Figure 3 shows a similar stack test, however now with three thermal cycles down to room temperature imposed. After each of the cycles full performance recovery occurs. This stack has been operated at 950°C with H2-3%H2O at a utilisation of 50%, except for the first 500 hours, during which the fuel was gasified willow wood from one of ECN’s in house gasifiers. Apart from the improved oxidation reduction resistance, the performance of the Ni/GCO anode is about 15% higher compared to its Ni/8YSZ predecessor.

Reducing manufacturing costs is a continuous activity. Most significant achievement in this respect has been the development of a process that allows for high volume sintering of the 3YSZ electrolytes, which reduced electrolyte costs by almost 30%. The manufacturing process for the earliest Ni/GCO anodes required additional screen printing and sintering steps, which increased the costs compared to the previously standard Ni/8YSZ anode. Recently the manufacturing pro-
cess was economised and the number of fabrication steps, and consequently the costs, cut back again.

The Ni/GCO electrolyte supported cell type is a regular product of InDEC that can be supplied in many customer specified shapes and sizes.

**STATUS OF ANODE SUPPORTED CELL**

Typically the standard ECN/InDEC anode supported cell (ASC) is composed of a 0.6 mm thick support structure of Ni/8YSZ, a 10 μm anode functional layer Ni/8YSZ, a 5 μm 8YSZ electrolyte and a two layer cathode: 25 μm LSM/8YSZ adjacent to the electrolyte and 25 μm LSM at the outside for current collecting, Figure 4. This type of cell offers high and stable performance at operating temperatures around 800°C, Figure 5. However, at lowering the cell temperatures cathode polarisation losses become increasingly dominant. Cathodes based on the mixed conducting $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) show a considerable lower temperature dependence of their electrochemical performance. Because this compound is known to form low conducting phases when sintered on YSZ electrolyte (2,3) an intermediate $Ce_{0.9}Y_{0.1}O_{1.95}$ (YDC) layer is applied, Figure 6. Manufacturing processes for anode supported cells with this type of cathode have been developed two years ago, but only recently systematic investigations on the degradation behaviour were started. Figure 7 shows the performance of this type of cell up to 2400 hours of operation. The performance degradation during this period was 0.7 % / 1000 hrs. This value is considered close enough to the world wide accepted target of 0.5% / 1000 hrs to incorporate this type of cell into the range of InDEC products.

Beside improvement on electrochemical properties, considerable effort has been put into the improvement of cell warpage. Anode supported cells tend to become curved when cooled down from the sintering temperature due to the differences of thermal expansion coefficients of the applied materials (4). This curvature is generally homogenous and along a large radius. A cell with only this type of curvature can be pressed flat with only small forces and without breaking it. Nevertheless it may complicate the assembly of stacks and therefore procedures have been developed that reduce this type of curvature from 1.6 mm deflection of the centre of a 120 mm cell to 0.6 mm. A second type of curvature is due to heterogeneous sintering. This type of warpage is manifested by relatively small bending radii along the edges of the cells. Flattening the cell requires high pressures and the probability of cracking the cell is unacceptably high. By adjustments of the manufacturing process the edge curvature has been eliminated completely.

**Figure 4. SEM-SEI image of the anode supported cell with an LSM cathode.**

**Figure 5. Endurance behaviour of ASC with an LSM cathode. Fuel is $H_2-3\%H_2O, T=800^\circ C, j=0.55 \text{ A/cm}^2$.**

**Figure 6. SEM-SEI image of the anode supported cell with an LSCF cathode.**
Anode supported cells with either LSM or LSCF based cathodes with improved flatness characteristics as described above are currently routinely manufactured by InDEC and can be supplied in relatively large numbers.

Particularly for industrial CHP of higher power classes, increasing the cell size from the current state of art 100 cm$^2$ range to the 400 or even 900 cm$^2$ range is essential for meeting the stack and system cost targets. On the laboratory scale small series of 400 cm$^2$ cells have been produced yet. However further product improvements with regard to flatness and yield has to be achieved before the manufacturing procedures will be handed over to InDEC for routine manufacturing. For the next years, up-scaling the cell size will be one of the major ASC related development issues.

Reduction of cell manufacturing costs has been the leading principle throughout the ASC development. Through the years batch sizes for preparing pastes and suspensions have been increased, manufacturing steps combined and eliminated, and the yield of the individual process steps improved. By these achievements the manufacturing costs, within the InDEC environment, has been reduced to 18% (for 500 pieces of 100 cm$^2$ ASC-LSM type cells) with respect to the status on January 1999. Further significant cost reductions should be realised by industrial automation of the presently labour intensive batch wise manufacturing at InDEC.

**THIRD GENERATION CELL DEVELOPMENT**

The development of this new type of cell is still entirely within the R&D phase. Instead of successive improvements of ESC and ASC for meeting functional system requirements, this development line works on a redesigned cell type that provides optimal opportunities to meet these requirements. Mechanical integrity for reducing risks of cracking during cell manufacturing, stack building and clamping, and of course enduring thermal cycling, is considered a major prerequisite. Further cell properties required are sulphur tolerance (5), oxidation reduction resistance and suitability for dry internal reforming and/or direct oxidation of methane (6,7).

The mechanical integrity requirement implies strength and ductility of the cell substrate. The alloy group of ferritic (because of the required TEC match) stainless steels offers potentially suitable candidates. However, these alloys do not have sufficient corrosion resistance to the fuel environment and therefore the substrate has to be on the cathode side. Equally decisive to focus the work on a cathode side substrate is the fact that all other cell requirements are related to the anode. An anode substrate would enforce many constraints on the anode that impede development towards the desired properties, while a free anode offers the required freedom for engineering its composition and microstructure.

The operating temperature of the cell should be in the range of 600 to 700°C to minimise the chances on carbon deposition and for reducing the corrosion rate of the stainless steel substrate. Provisionally, the LSCF type of cathode is selected for this development. For mechanical reasons 3YSZ (2-4 μm) is the preferred electrolyte, although ceria is still considered as an alternative (8). Certainly, the biggest challenge is provided by the anode. It has to be an (almost) full oxide anode to meet the requirement on oxidation reduction resistance. However, up to now no single oxide compound providing the necessary electronic and ionic conductivity at the operating conditions has been identified. Therefore, the anode development at ECN focuses on multi layer anodes of mixed compounds. Small additions of ruthenium and rhodium are considered for catalytic activity.

Substantial development of manufacturing processes is required for making the described type of cell. State of the art SOFC manufacturing processes depend on sintering temperatures in the 1300-1500°C range and a co-shrinking substrate for achieving a dense electrolyte. However, because of the stainless steel substrate, sintering temperatures for all components of the third generation cell have to be lower than 1100°C, and the candidate substrate structures considered up
to now have only limited shrinking capacity at this temperature. For that reason alternative deposition and firing processes using nano-sized powders and sol-gel solutions are currently evaluated and elaborated.

REFERENCES
HYDROGEN FOR RESIDENTIAL COMBINED HEAT AND POWER

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Abstract
The use of hydrogen as an energy carrier for residential areas is investigated. The required hydrogen for the district is produced on-site from natural gas and is subsequently distributed by a hydrogen grid to the houses. The main issue for the system is whether the high end-use efficiency of hydrogen for distributed power generation compensates the extra losses and costs for the conversion step from natural gas to hydrogen. A comparison is made with other advanced energy supply systems for residential areas.

As a part of the IEA-hydrogen implementing agreement Annex 13, Design and optimisation of integrated systems, a study [1] has been carried out to evaluate the use of hydrogen as a future energy carrier in residential districts. Using hydrogen offers several advantages. Hydrogen can be a clean and renewable energy carrier and can strongly reduce local emissions (NOₓ, particulates). Furthermore it is a potential storage medium for excess electricity from renewable sources and the appropriate fuel for fuel cells, in particular PEMFC's.

This study has investigated potential benefits of using hydrogen as an energy carrier for a 1300-house residential area (City of the Sun in Heerhugowaard, the Netherlands). Because the Netherlands has an energy system that is dominated by natural gas, much attention is devoted to the development of combined heat and power systems (CHP) for residential areas. In this study the CHP systems use hydrogen. The required hydrogen for the district is produced in a decentralised plant inside the district. Consequently, the gas is transported via a hydrogen grid to the houses for the production of electricity and heat. In the houses hydrogen is primarily fed to a PEMFC. Depending on the size of the fuel cell, additional heating and electricity is required. For the production of heat either a hydrogen burner or an electric heat pump can be used. The electricity grid can be used to buffer excess or supply extra electricity.

The hydrogen-based system is not the only conceivable system with the potential to reduce energy consumption and emissions. As such, the hydrogen-based system has to compete with several other systems, using other energy carrier, for example on natural gas or electricity (see table 1).

- System A is the conventional system, which is present in most of the Dutch houses.
- In system B, a solid oxide fuel cell (SOFC) is used to supply a part of the heat and electricity in the district using natural gas as an energy carrier. Similar to the hydrogen case, extra heat is supplied by a heater and extra electricity from the grid.
- System C is all-electric and an electric heat pump converts electricity to the required amount of heat for the district.

In the study various configurations for the hydrogen-based systems have been considered, using time dependent patterns for heat and electricity demand [2]. Amongst others, the influence of fuel cell size, control strategy and the buffer sizes on the system performance have been evaluated.

Table 1 Reference systems

<table>
<thead>
<tr>
<th>System</th>
<th>Energy carrier</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Natural gas</td>
<td>NG heater/ electricity grid</td>
</tr>
<tr>
<td>B</td>
<td>Natural gas</td>
<td>SOFC/ NG heater/ electricity grid</td>
</tr>
<tr>
<td>C</td>
<td>Electricity</td>
<td>Electric heat pump/ electrical heater</td>
</tr>
</tbody>
</table>
In the hydrogen system, the hydrogen production in a steam methane reformer has a large influence on the total system efficiency. Here, natural gas is reformed to hydrogen with an assumed efficiency of 75% (LHV). This means that a large part of the input energy (25%) is lost in this step. The efficiency of the PEMFC should therefore be high enough to make up for the losses. In theory the efficiency of the fuel cell operating on hydrogen (50-60%) is sufficiently high to compensate for losses in the hydrogen production step. However, in the actual system, where fluctuating electricity and heat demand must be satisfied at all times, achieving the high efficiency is more difficult. Fuel cells supply both heat and power in a ratio, which depends on the efficiency of the fuel cell. However, this heat to power ratio is not equal to the required heat to power ratio of the district. The households in the district on average demand more heat than electricity. The fuel cell produces more electricity than heat. Sizing the fuel cell for the heat demand results in a large excess production of electricity. Sizing the fuel cell for the electricity demand means that a substantial part of the heat must come from another source. The imbalance between heat and electricity demand is already apparent in the average heat and electricity demand and production, but becomes even more relevant if the heat and demand patterns are taken into account.

Figure 1: Systems considered for supplying heat and electricity to the residential system

The performance for the different systems in this study is characterised by the cost (total annual cost to the consumer) and CO₂ emissions. A more detailed analysis of the environmental impact (CO₂, NOₓ, SO₂, etc.) of the reference system using a natural gas boiler and the environmental impact of one of the hydrogen-based systems is discussed in [3]. As all systems studied use natural gas as the primary energy carrier, the efficiency and CO₂ emissions are not independent numbers in this case. For each system the results for a representative configuration are shown in table 2.
Table 2 shows that the calculated CO$_2$ emissions and annual cost for the hydrogen system, the conventional natural gas (NG) system with heater, the natural gas fuelled SOFC system and the electrical heat pump (EHP). The data indicate that the reduction in emissions (and primary energy) in the SOFC and EHP system amount to 10%, while the hydrogen based system reduces primary energy consumption by 6%. The major cost components are the investments for the reformer, the fuel cell and, if present, the heat pump. Because of the complexity (a large number of conversion steps), the hydrogen systems are more expensive. However, the study identifies a number of possibilities to improve the general performance of the system: reducing CO$_2$ emission by 10…15% is feasible.

One of the main issues identified as critical is the efficiency of the steam reformer for the hydrogen production. Evidently, the hydrogen route requires an additional conversion step, from natural gas to hydrogen, which introduces substantial losses. Because of the higher efficiency with which hydrogen can be converted into electricity compared to natural gas, these losses can be compensated. However, the system is very sensitive to the efficiency of the reformer. The calculations show, that a five-percent (point) higher efficiency (from 75% to 80% LHV) already leads to higher CO$_2$-reduction than the all-electric EHP system. A high reforming efficiency is therefore a critical factor for the hydrogen-based system.

Table 2 $CO_2$-emissions and annual costs per house for four main systems

<table>
<thead>
<tr>
<th>System</th>
<th>CO$_2$-emissions kg/a per house</th>
<th>Total annual cost $/a per house</th>
</tr>
</thead>
<tbody>
<tr>
<td>NG/Heater</td>
<td>2422</td>
<td>893</td>
</tr>
<tr>
<td>NG/SOFC</td>
<td>2185</td>
<td>824</td>
</tr>
<tr>
<td>Electrical heat pump (EHP)</td>
<td>2201</td>
<td>1712</td>
</tr>
<tr>
<td>Hydrogen/PEMFC</td>
<td>2280</td>
<td>2174</td>
</tr>
</tbody>
</table>

Figure 2: Sankey diagram for the cumulative annual energy flows (MWh/a) in the residential district for one of the hydrogen based cases (0.35 kW/house PEMFC in base load)

For all configurations the complete energy balances have been determined, taking into account the fluctuation in heat and electricity demand [4]. Figure 2 shows a typical energy balance for the residential district. Matching heat and electricity demand and production simultaneously turns out to be the main challenge for the hydrogen systems taken into account in this study. On one hand, a large fuel cell, although it is able to cover a large part of the heat demand, leads to a
large excess production of electricity. The electricity can be sold to the central grid, but returns are relatively small (in our study, the price paid for electricity sold to the grid is assumed to be half the purchasing price).

On the other hand, minimising excess electricity production with the fuel cell means that additional heating units are required to supply the remaining part using the available energy carriers. For the hydrogen districts a hydrogen burner and an electric heat pump are considered. Combusting hydrogen is not attractive because of the relative low chain conversion (due to the reforming step). The electric heat pump on the other hand has a high efficiency and can cause a high reduction in the CO2-production. At this moment however, the costs for such units are high. In both cases, supplying additional heat with a burner and with a heat pump, the efficiency is determined by the design of the system: size of the fuel cell, control strategy, etc. The design of the system, in particular with respect to the heat production, is identified as a second critical factor.

An option to improve the efficiency of the system is to utilise the heat that is produced in the reformer. Two configurations have been considered which use the heat of the reformer to heat a part of the district. Two different types of houses exist in these configurations. Part of the houses is equipped with a fuel cell and part is connected to a local heat grid that utilises (in part) the heat from the reformer. Electricity produced in excess by the fuel cell in one part is exported to the other part where it covers the electricity demand. These split-districts have lower CO2-emissions than the all-electric system indicated above, even taking into account the substantial losses in the heat grid. A configuration combining a hydrogen grid for part of the district and a central heat pump, achieves reductions which are substantially higher than those indicated for the SOFC system.

The costs calculated for the hydrogen systems in this study are prohibitive. It should be noted however, that these cost calculations are based on non-dedicated equipment. For example the cost for the small heat pumps, as required for the hydrogen FC/heat pump systems are based on the cost of much larger systems. Similarly for the reformer, the costs are based on downscaled industrial type reformers. In general development of dedicated equipment, including stationary fuel cell systems for hydrogen may change the economic perspective.

Based on this analysis, the focus of research with respect to hydrogen systems for residential applications should be on:
- The improvement of the reformer efficiency;
- Improved balancing heat production and heat consumption (both total as in time);
- More detailed assessment of cost and potential cost reduction by development of dedicated equipment.

The relevance of the concept of hydrogen for residential applications for a more sustainable energy system, for example in combination with CO2 capture and sequestration or renewable concepts for residential systems, should be further developed.

REFERENCES


This work is part of the Dutch participation in Annex 13 of the Hydrogen Implementing Agreement of the IEA and was sponsored and supported by Dr. Antoon Kipperman and Dr. Henk Bartten of the Dutch organisation for Energy and Environment (NOVEM).