A transient investigation on the plate-wall heat-exchange methane steam reformer assisted with methane combustion using electrically heated alumite catalyst

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ABSTRACT:

The start-up behavior of a methane steam reformer is a crucial issue for the design of the domestic fuel cell. However, start-up times of the reformers are reported to be more than 1 hour. In this contribution, start-up acceleration strategies for the reformer are discussed using a novel alumite catalyst, i.e. electrically heated alumite catalyst (EHAC). The reformer is designed as a heat exchange plate reactor with methane combustion adopted as a heat source for methane reforming reaction. Simulation studies based on 2-D steady-state and dynamic multiphase models for heat and mass transfer coupling with velocity distribution were carried out.

Results from the steady-state simulation suggest that the inlet temperature and gas flow directions play important roles on the ignition of methane combustion. Dynamic simulation results show that the start-up process takes 45 mins without any acceleration strategies, while it takes no more than just 10 mins with electrically heating at the beginning of the process.

KEYWORDS: Methane Steam Reformer, Methane Combustion, Electrically Heated Alumite Catalyst, Simulation

Introduction

Fuel cells are anticipated to be highly efficient clean power generation devices. Recently, Polymer Electrolyte Fuel Cell (PEFC) systems have been developed for transportation and residential applications. From a feasibility study of residential energy demand in Japan, there has been extensive development 0.25-1kW class PEFCs, where methane steam reforming is regarded as a major route for the generation of H₂ rich gas for the accompanying fuel stack (Nakata, et al., 2001; Echigo, et al., 2004). Various reviews of steam reformers have discussed the conventional process, which is carried on supported Ni catalysts in multi-tubular reactors operated at temperature varied for 773 K (inlet) to 1073 K (outlet), pressure ranging from 20 to 40 bar and S/C in the feed 2-4. (Van Hook, 1980; M. Zanfir, 2003). However, this process suffers from a number of limitations; such as, diffusion and thermodynamic limitation, great pressure drop and large size. Further, for residential utilization, start-up time presents a problem that affects the performance of the fuel cell. Until now, the start-up time of the methane steam reformers has been reported to be more than one hour (Nakata, et al., 2001).

To address the above problems, from a viewpoint different from that of a conventional fixed-bed reactor, a heat-exchange plate reformer using electrically heated alumite catalyst (EHAC) is proposed in this paper. Differing from conventional coating methods, anodization technology is utilized in the catalyst preparation. A commercial Al/Cr-Alloy/Al clad plate was anodized in 4 wt% oxalic acid solution to form alumina films on both sides, which is then used as the supporter for the reforming and combustion catalyst (Zhang, et al., 2006). The results of thermal endurance test at 1073 K showed the catalyst a high thermal resistance, and no Al₂O₃ layer was found to shell from the alloy layer since the alumina film is derived form
the Al layer (Zhang et al., 2004). The most attractive aspect of EHAC would be its electrically heated character of that can provide prompt heat supplementation to the reactions. The catalyst is electrically heated at the beginning of the process to simultaneously warm up the reactor and ignite the combustion. By this way, the start-up time is expected to be shortened to within just a few minutes.

In respect to the research on a heat-exchange plate reactor, Hunter and McGuire (1980) were among the first to suggest the coupling of endothermic and exothermic reactions by means of indirect heat transfer. The approach shares a similar mechanism with that of heat exchange equipment, which is often found in large-scale process such as hydrocarbon cracking, steam reforming and dehydrogenation. Reay (1993) explained the benefits of such approach in the context of the catalytic plate reactor (CPR), which is comprised of closely spaced catalytically coated metal plates, such as it proceeds at lower temperature that poses less constraints for materials of the reactor.

Simulations are an important part of research today, before and during the design of reactors; they enable the optimization of design parameters and can predict reactor performance. Zanfir and Gavriilidis (2003) reported a steady-state simulation of methane steam reforming coupled with methane catalytic combustion in a CPR ignoring the velocity distribution, to discuss the design parameters for design a heat-exchange reformer. However, few papers presenting the dynamic performance of a reformer have focused on the start-up behaviors.

The present paper aimed to model a coupled heat-exchange methane steam reformer in order to accumulate relevant information before designing the reactor. Based on the results of a steady-state simulation, the effects of inlet temperature, and comparison of countercurrent and co-current flows are discussed to simplify the assessment of the dynamic situation. Then considering the dynamic behavior of the reformer without electrically heating, start-up acceleration strategies are proposed.

1. Electrically heated character of EHAC

An electrically heating experiment was carried out in a quartz tube in an N₂ atmosphere. The catalyst was connected to electrodes with 10 cm long and 0.5 cm wide. The electrical current was controlled to 12 A, and the surface temperature of the catalyst detected by a radiate thermocouple. Figure 1 shows the EHAC's surface temperature profile as a function of the electrically heating time. It can be seen, that $T_{\text{cat.}}$ takes just 22 seconds to reach 1263 K from 298 K. The electrically heating experiment was carried out continuously 40000 times, and no $\text{Al}_2\text{O}_3$ layer was found to shell from the alloy layer, showing the excellent thermal resistance character of the catalyst. The results of the electrically heating experiments demonstrate the promise of utilizing a heat-exchange reformer for fast start-ups.

![Fig. 1 Profile of EHAC temperature from electrical heating in an N₂ atmosphere (catalyst width: 1 cm; catalyst length: 10 cm; catalyst resistance: 0.9 Ω, electrical current: 12A)](image)

2. Modeling

2.1 Heat exchange reforming reactor

Figure 2 shows cross-section views of the heat-exchange reforming reactor. The upper and lower channels are of methane combustion and the middle channel involves methane reforming. According to the symmetry of conditions at the centerline of the reactor, half of the reactor as shown in Figure 2 (b) is disused in the models. Thus, five different domains could be identified: a reforming channel, a catalyst layer for reforming, an alloy layer, a catalyst layer for combustion and a combustion channel. Both ends of the catalysts are connected to the electrodes (Figure 2 (c)). At the very beginning of the process, catalysts are electrically heated to start the methane combustion and steam reforming reactions.

![Diagram](image)
Fig. 2 (a) r-direction cross-section view of heat-exchange reactor (b)-direction cross-section view of heat-exchange reactor (c) three domains remained in the EHAC( for a clarity, the scheme is not drawn in real scale). (1) an insulation layer (2) a reforming channel (3)a combustion channel (4) electrically heating catalyst (including: (5) a catalyst layer for reforming (6) an alloy layer (7) a catalyst layer for combustion ). δ₁=5 mm, δ₂=2.5 mm, δ_cat=40 µm, δ_alloy=50 µm

2.2 Kinetics

The reaction kinetics for methane steam reforming and combustion were derived from our experimental results. In this work, Ni was selected as the active metal for the methane reforming reactions, and Pt for the methane combustion reaction. The kinetic characteristics for EHAC were obtained using a differential reactor, avoiding concentration and temperature gradients by adopting the kinetic mechanism cited by Numaguchi and Kikuchi (1988).

$$\begin{align*}
\text{CH}_4 + 2\text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad (\Delta H)_1 = 227 \text{ kJ/mol} \quad (1) \\
\text{CO} + \text{H}_2\text{O} & \rightarrow \text{CO}_2 + \text{H}_2 \quad (\Delta H)_2 = -33.2 \text{ kJ/mol} \quad (2) \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad (\Delta H)_3 = -837 \text{ kJ/mol} \quad (3)
\end{align*}$$

$$\begin{align*}
w_1 & = k_1 \frac{P_{\text{CH}_4} - P_{\text{CO}_2}P_{\text{H}_2}\vr}{P_{\text{H}_2}\vr} \\
w_2 & = k_2 \frac{\Delta H_{\text{CH}_4}}{P_{\text{H}_2}^2} \\
k_1 & = 1.14 \times 10^6 \exp(-163000/(R_yT)) \\
k_2 & = 1.87 \times 10^5 \exp(-66000/(R_yT))
\end{align*}$$

$$K_2 = \exp(-22430/T + 26.078)$$

For catalytic combustion using a Pt catalyst, the order in methane is usually about unity, while the reaction order in oxygen tends towards zero (Trimm, et al.,1980, Zanfir, et al., 2003). The kinetic parameters were obtained using an integral reactor. In this simulation a first-order kinetic expression with respect to methane is utilized in the calculation along with an activation energy of 83.3 kJ/mol. The heat of reaction, $(\Delta H)_m$ was determined at 1160 K. The equilibrium constant, $K_m$ was estimated from thermodynamic data.

2.3 Model development

Several assumptions are made:

1. The gases are assumed as ideal gasses and as suitable for ideal gas law;
2. The chemical reactions take place only on the catalyst layer
3. The pressure drop is neglected in all runs.
4. Heat loss of the reformer is neglected.

Partial differential equations (PDEs) are given in Table 1, where catalyst surfaces, alloy surfaces are regarded as the interior boundaries in this model. The PDEs were solved using FEMLAB, a PDE solver tool from COMSOL Inc., which uses a finite element method. We used quadratic triangular elements and a non-uniform mesh, with small elements located at the gas-solid interface and solid phase.

In this work, we simulate the reformer with the capability to provide enough H₂ for a 250W domestic fuel cell. In the case of steam to carbon ratio (S/C) =3, assuming the conversion of methane steam reforming of 95% and fuel cell efficiency of 40%, the necessary methane flow rate should be 0.049 mol/s. The conditions used in the simulation in the base case are shown in Table 2. In the following sections, the calculation conditions are accordance with those of the base case unless otherwise stated.

<table>
<thead>
<tr>
<th>Table 1 Model equations</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Gas phase</strong></td>
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<tr>
<td><strong>Mass transfer</strong></td>
</tr>
<tr>
<td>$\frac{\partial \rho_{ji}}{\partial t} + \rho_{ji} \frac{\partial u_{ji}}{\partial r} = \frac{\partial \rho_{ji} \theta_{ji}}{\partial r} + \rho_{ji} \frac{\partial \theta_{ji}}{\partial t}$</td>
</tr>
<tr>
<td><strong>Heat transfer</strong></td>
</tr>
<tr>
<td>$\rho_{ji} \frac{\partial \theta_{ji}}{\partial t} + \rho_{ji} \frac{\partial u_{ji}}{\partial r} = \frac{\partial}{\partial r} (\lambda_{ji} \frac{\partial \theta_{ji}}{\partial r}) + \frac{\partial}{\partial \theta} (\lambda_{ji} \frac{\partial \theta_{ji}}{\partial \theta})$</td>
</tr>
<tr>
<td><strong>Navier-Stokes velocity equation</strong></td>
</tr>
<tr>
<td>$\rho \frac{\partial u_j}{\partial t} + \rho (u_j \frac{\partial u_j}{\partial r} + \frac{\partial p}{\partial r}) = -\frac{\partial p}{\partial r} + \rho (\frac{\partial^2 u_j}{\partial r^2} + \frac{\partial^2 u_j}{\partial \theta^2})$</td>
</tr>
<tr>
<td><strong>Catalyst layer</strong></td>
</tr>
<tr>
<td><strong>Mass transfer0</strong></td>
</tr>
<tr>
<td>$\frac{\partial \rho_{ji}}{\partial t} + \frac{\partial}{\partial r} (\rho_{ji} \frac{\partial u_{ji}}{\partial r}) = -\Sigma (w_{ji} M_{ji}) \cdot \rho_{iw}$</td>
</tr>
<tr>
<td><strong>Heat transfer</strong></td>
</tr>
</tbody>
</table>
In case of electrical heating
Center conditions
\[ \text{Reactor wall conditions} \]

Internal conditions
\[ y_{i,j} = y^0_i \quad T_j = T_{in} \]

Center conditions
\[ \forall l, \ r = 0 \]

(Central line of the reforming channel)
\[ \frac{\partial T_{i,j=1}}{\partial l} = 0 \quad \frac{\partial y_{i,j=1}}{\partial l} = 0 \]

Reactor wall conditions
\[ \forall l, \ r = -(\delta_1 + \delta_2 + 2\delta_{\text{cat}} + \delta_{\text{alloy}}) \]

(wall of the combustion channel)
\[ \frac{\partial T_{i,j=2}}{\partial l} = 0 \quad \frac{\partial y_{i,j=2}}{\partial l} = 0 \]

Initial conditions
\[ T \big|_{l=0} = 298 \text{ K} \quad y_{i,j} \big|_{l=0} = 0 \]

3. Discussions and results
3.1 Results of a steady-state simulation of the reformer

Steady-state simulations of the methane steam reformer are first discussed to simplify the assessment of the dynamic situation in the following sections. Temperatures profiles of the reforming channel, combustion channel and catalyst are shown in Figure 3. A distinct temperature maximum is found near the inlet of the reformer due to CH₄ combustion being a fast exothermic oxidation reaction. The subsequent decrease in the temperature can be attributed to the endothermic effect of steam reforming reactions. Further, the temperatures of the gas phases approach the catalyst layer temperature by heat transfer within the first 2.5 cm and the outlet temperature keeps more than 1050 K which can maintain a high conversion in the reforming reaction. The mole fraction in the reforming channel is also shown in Figure 3. Outlet CH₄-concentration is 0.88%. CO-concentration reaches 13.2% and H₂-concentration is formed to 43%. For ignition of the combustion so that the steam reforming conversion can be sustained, Tₘ is a very important parameter to be discussed. Figure 4 shows the temperature and conversion profiles of the reforming channel along the reformer length for various inlet temperatures, i.e. 673 K, 723 K, 773 K. It can be seen, that when Tₘ is as low as 673 K, it will take a half of the reformer length for the gas temperature to reach a reasonable ignition point; whereas, when Tₘ reaches 723 K, the temperature increases sharply meaning that 723 K should be a sufficient ignition temperature. Furthermore, there isn’t a distinct difference of temperature within the first 0.09 m of the reformer when Tₘ varies from 723 to 773 K, which is possible because of the endothermic effects of the reforming reaction that promptly moves the heat generated by combustion. However, a marked difference is found subsequently due to the endothermic reaction rate getting slower and the reaction heat accordingly getting smaller. Since the redundant heat in case of Tₘ=773 K is greater than that of Tₘ=723 K, the reacted gas in the reforming channel is warmed up, which cause another temperature increase as shown in Figure 4.

### Table 2 Data used for base case calculation

<table>
<thead>
<tr>
<th></th>
<th>Reforming</th>
<th>Combustion</th>
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</thead>
<tbody>
<tr>
<td>Reactor Length (mm)</td>
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<td></td>
</tr>
<tr>
<td>Channel height (mm)</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Initial temperature (K)</td>
<td>298</td>
<td>(cold start)</td>
</tr>
<tr>
<td>Inlet condition</td>
<td></td>
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</tr>
<tr>
<td>Mole fraction S/C=3</td>
<td>CH₄/Air=1/10</td>
<td></td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>723</td>
<td>723</td>
</tr>
<tr>
<td>Flow rate (mol/s)</td>
<td>0.197</td>
<td>0.079</td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>101.3</td>
<td>101.3</td>
</tr>
</tbody>
</table>

**EHAC**

<table>
<thead>
<tr>
<th>Thickness (µm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina layer</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Alloy layer</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Catalyst loading Ni</td>
<td>13 wt %</td>
<td>Pt 0.14 wt %</td>
</tr>
</tbody>
</table>

\[ - \rho \frac{\partial}{\partial t} \left( \frac{\partial T_{\text{ele}}}{\partial t} \right) + \frac{\partial}{\partial r} \left( \frac{\partial T_{\text{ele}}}{\partial r} \right) + \frac{\partial}{\partial l} \left( \frac{\partial T_{\text{ele}}}{\partial l} \right) = \sum \left( H_{\text{n,l},X_{\text{n,l}}} \cdot \rho \right) \]
Fig. 3 Temperature and mole fraction profiles along the reformer length.

Fig. 4 Profiles of CH\textsubscript{4} reforming conversion and temperature in the combustion channel for different inlet temperatures (T\textsubscript{in} = 673 K, 723 K, 773 K).

To investigate the effect of the heat transfer, co-current flow and countercurrent flows are discussed in this section. For countercurrent flows, the effects of reactor length are considered. A countercurrent flow gets a surprisingly lower methane steam conversion than does a concurrent flow, as shown in Figure 5(a). To investigate the performance in all cases of co-current and countercurrent flows, a dimensionless reformer length is employed as:

\[ l^* = \frac{l}{L} \tag{4} \]

It is found that in all cases of countercurrent flow, methane steam reaction start from nearly 40\% of the reformer length, while for a concurrent flow, the reaction start at just near the inlet of the reformer. Compared with conversional heat transfer concepts, for a heat exchange reformer coupled with reactions, it demonstrates that the heat generated by an exothermic reaction plays more important role in starting up the endothermic reaction than the conversional convective heat transfer. Herein, the reaction heat flux is employed to explain the phenomena, defined as:

\[ \text{Reaction heat flux} = \sum_m (-\Delta H_m) \int_{\text{in}}^{\text{out}} w_m \, dr \tag{5} \]

The reaction heat fluxes in case of concurrent flow are shown in Figure 5(b). Since methane combustion is a fast exothermal oxidation reaction, the maxima in the reaction heat fluxes for both reforming and combustion are located near the inlet, namely, at 0.015 m. The generated heat flux is larger than the consumed heat flux, which implies that the combustion channel can provide the necessary heat to heat-up the both the reaction mixes and to drive the endothermic reaction at the same time. However, in the case of countercurrent flow, the inlet for the reforming gases is the outlet of the combustion gases where the combustion reaction is almost completed, and the generated heat flux is too small to provide the necessary heat supply to the
3.2 Start-up results of the reformer without electrically heating

Based on the discussion of the steady-state cases, dynamic combustion and reforming behaviors are presented in this section. Figure 6 shows profiles of CH$_4$ mole fraction in the reforming channel and the temperatures along the reformer with different reaction times. Considering the actual operation situation of the domestic fuel cell system, the reformer is started from room temperature (T=298 K) with 723 K combustion gases and reforming gases simultaneously conducted in. The results show that within the first 20 mins, the temperature increase gently resulting in just a small amount of methane reforming conversion in the reformer. However, when t=20 min, a sharp temperature peak is found in the first half of the reformer, which suggests that the combustion reaction is ignited and methane steam reforming reaction is started accordingly. After 40 mins of operation, the temperature approaches stability and the outlet methane mole fraction reaches 0.8%. By defining start-up time as the time needed for getting a stable methane steam conversion, it can be seen that for a plate heat-exchange reformer under base case conditions, the start-up time is 40 mins, in contrast to 60~75 mins start-up time reported in the commercial methane steam reformers (Nagata, et al., 2001, Oohara, et al., 2003), thus the plate reformer shows excellent heat transfer performance (Kameyama et al., 1995, Zhang et al., 2006). Furthermore, the time for warming up the reformer from a cold start situation (T=298 K) to a temperature driving the combustion reaction is nearly 15 mins. Thus, how to shorten the warm-up time is an important strategy for accelerating the start-up of the process. 3.3 Start-up acceleration with electrically heating strategies

According to the discussion of the above section, for shorting the warm-up time from a cold start situation and mass an acceleration of the start-up, increasing the heat input into the system is the only possibility. Heat can be inputted into the process by two tragedies as follows:

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**Fig. 6** Start-up behavior: (a) dynamic profile of CH$_4$ mole fraction in the reforming channel (b) dynamic profile of temperature in the reforming channel
Strategy 1: heating up the inlet combustion gas phase electrically at the beginning of the process; and Strategy 2: electrically heating the catalyst directly at the beginning of the process.

To confirm if the reformer is warmed up wholly and the combustion is ignited, outlet temperature of the combustion gas phase is employed as an efficient parameter in the discussion. Figure 7 shows the comparison of the outlet temperature of combustion channel between the two heat-up strategies by keeping the input heat, $Q$, as a constant of 30 kJ. For the strategy 1, $Q$ is calculated as:

$$Q = C_{p,\text{comb}} \cdot \Delta T \cdot F_{\text{comb}} \cdot t$$

(6)

where, $\Delta T$ means the inlet temperature difference increased by electrically heating and $t$ means the electrically heating time.

For the strategy 2, $Q$ is calculated as

$$Q = I \times I \times R \times t$$

(7)

where, the electrical current is set as 20 A and the electrical resistance is 0.4 $\Omega$.

A breaking point at 10 min can be found in the results of the strategy of gas heated up, which can divide the heat-up process into two stages as warm-up stage and reaction stage with the character of

$$dT_{\text{outlet}} / dt \big|_{\text{reaction stage}} > dT_{\text{outlet}} / dt \big|_{\text{warmup stage}}.$$

It can be seen that, in case of strategy 1, it takes nearly 10 mins to warm up the reformer and 15 mins for the reaction stage; whereas, for strategy 2, the stages are both dramatically shortened and no distinct separation of the stages can be found in process attributed to the prompt and efficient heat supply to the catalyst, which drives the two stages simultaneously. Therefore, heating the catalyst directly should be a better measurement to start-up the reformer since it can provide the whole reformer a well-distributed heat input and a directly heat supply to the catalyst surface.

Figure 8 shows the transient behaviors of reforming gas phase temperature with an electrical power of 170 W for 3-minute catalyst electrical heat-up. As expected the electrical heat-up of the catalyst requires as little as 2 mins for igniting the combustion reaction, and it takes just 6 mins to achieve a stable operation. When $t=3$ min, it can be seen that the temperature peak is higher than in the stable situation ($t=40$ min), which can be attribute to that the supplementing heat by electricity is great enough to transiently break the heat balance between endothermic and exothermic reactions. However, after heat-up electrically has finished, the situation returns to a balance within 2 mins, which shows that the extra heat does not make the situation deviate too far from a balance.

From the simulation results of methane distribution in the reforming channel (Figure 9), it can be seen that after 2 mins, there is a distinct concentration distribution appearing in the channel. Especially, between 0.02~0.06 m in the reformer, the $\text{CH}_4$ mole fraction is relatively lower near the catalyst layer because a distinct local temperature peak appears as shown in Figure 8. After 6 mins, $\text{CH}_4$ is found to have almost completely reacted.

As addressed above, the amount of input heat will affect the operation situation of the reformer. Figure 10 shows transient profiles of outlet temperatures with different heat input $Q$, by keeping flow rates and electrical power as constants. It can be seen that if the $Q$ is not sufficient, the exit temperature increase slowly indicating that the start-up time will not be efficiently shortened, while when $Q$ is excessively great, it will take a long time to return to a balanced state and an extreme high temperature will inevitably cause damage to the catalyst. In the case of 250 W-scale reformer, heat input of 30.24 kJ should be the optimum, according to the simulation results. The heating rate is also an essential parameter to affecting the warm-up time, which in this work can be described as electrical power. Figure 11 shows the effects of electrical power on the behavior of the $\text{CH}_4$ combustion by keeping the input heat as a constant of 30.24 kJ. As expected that the larger electrical power leads to a faster combustion start-up and a shorter warm-up time. As the electrical resistance of the catalyst applied in the reformer is no

<table>
<thead>
<tr>
<th>Company</th>
<th>Scale</th>
<th>Reformer type</th>
<th>Start situation</th>
<th>Start-up time [min]</th>
</tr>
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<tbody>
<tr>
<td>SANYO Electric. +OOSAKA Gas</td>
<td>750W</td>
<td>Plate reactor</td>
<td>Cold start (298 K)</td>
<td>45</td>
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<tr>
<td>IHI.</td>
<td>5 kW</td>
<td>Fixed bed reactor</td>
<td>Warm start (583 K)</td>
<td>72</td>
</tr>
<tr>
<td>Toshiba</td>
<td>1 kW</td>
<td>Fixed bed reactor</td>
<td>Cold start (298 K)</td>
<td>80</td>
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<tr>
<td>Present work</td>
<td>250 W</td>
<td>Plate reactor using EHAC</td>
<td>Cold start (298 K)</td>
<td>6</td>
</tr>
</tbody>
</table>
Fig. 9 Methane mole fraction profile in the reforming channel varied with different time

Fig. 10 Outlet temperature profiles over time affected by input heat

Fig. 11 Exit CH₄ mole fraction profile over time for varied electrical power inputs

more than 0.4 Ω, considering the application range of electrical current, 0.17 kW should be a reasonable electrical power to start-up the process. On the other hand, how to increase the resistance of the catalyst should be another issue for further developing the reformer in the future.

Conclusion and outlook
A simulation study was carried out as the first step in the development of a heat-exchange reformer for domestic fuel cells. The results of the steady-state models demonstrated that inlet temperature and flow directions are important to ignite the combustion. As methane combustion is a fast exothermic reaction, contrasting with conventional viewpoint of heat transfer, a co-current flow shows a better performance than a countercurrent flow. The results of dynamic models of the heat exchange reformer demonstrated that it is a fast and efficient start-up strategy to electrically heat-up the alumite clad catalyst with 6-minute start-up time.

Table 3 summaries the reported methane reformer utilized for domestic fuel cell with various scales. Compared with the commercial reformers cited in the lectures, two pointes can be concluded as:
(1) Since a plate reactor has a better heat transfer performance than a fix-bed reactor, a faster start-up can be obtained by plate reformer;
(2) Since the electrical heat up by EHAC can provide a well-distributed heat input, the warm-up time can be dramatically shortened lead to much faster start-up of the process.

Therefore, the developing plate heat-exchange reformer using EHAC indicts more promising in the utilization of domestic fuel cells with a satisfying start-up time.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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</thead>
<tbody>
<tr>
<td>C_p</td>
<td>heat capacity</td>
<td>J·kg⁻¹·K⁻¹</td>
</tr>
<tr>
<td>D_eff</td>
<td>effective diffusion coefficient</td>
<td>m²·s⁻¹</td>
</tr>
<tr>
<td>H</td>
<td>heat of reaction</td>
<td>kJ·mol⁻¹</td>
</tr>
<tr>
<td>I</td>
<td>electrical current</td>
<td>A</td>
</tr>
<tr>
<td>k</td>
<td>reaction rate constant</td>
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<td>K</td>
<td>equilibrium constant</td>
<td></td>
</tr>
<tr>
<td>l</td>
<td>axial co-ordinate</td>
<td>m</td>
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<tr>
<td>l'</td>
<td>dimensionless length</td>
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<tr>
<td>L</td>
<td>reformer length</td>
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<tr>
<td>P</td>
<td>pressure</td>
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<td>P_elec</td>
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<td>u</td>
<td>velocity</td>
<td>m·s⁻¹</td>
</tr>
<tr>
<td>w</td>
<td>reaction rate</td>
<td>mol·kg⁻¹·cat⁻¹·s⁻¹</td>
</tr>
<tr>
<td>y</td>
<td>mole fraction</td>
<td>-</td>
</tr>
</tbody>
</table>
\( \lambda_r = \text{gas thermal conductivity} \quad [\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}] \)

\( \rho = \text{density} \quad [\text{kg} \cdot \text{m}^{-3}] \)

\( \delta = \text{thickness of the layer} \quad [\text{m}] \)

\( \nu = \text{kinematical viscosity} \quad [\text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-1}] \)

\( \text{alloy} = \text{alloy layer} \)

\( \text{cat} = \text{catalyst} \)

\( \text{gas}, g = \text{gas phase} \)

\( i = \text{component of the reactions} \)

\( \text{in} = \text{inlet} \)

\( j = \text{reaction system} (j=1, \text{steam reforming} ; j=2, \text{water gas shift}) \)

\( m = \text{reactions} (m=1 \text{ steam reforming reaction} \) 

\( m=2 \text{ water shift reaction} \) 

\( m=3 \text{ methane combustion reaction} \)

**Appendix**

**Heat capacity:**

\[ C_p = a + bT + cT^2 \]

**Thermal conductivity:**

\[ \lambda_r = \lambda_0 \left( \frac{T}{T_0} \right)^{0.75} \]

**Diffusion coefficient:**

\[ D_{r,i} = D_{r,0} \left( \frac{T}{T_0} \right)^{0.75} \]

The \( D_{r,i} \) is calculated for a binary mixture between \( i \) component species and \( \text{H}_2 \) (for reforming) and \( \text{N}_2 \) (for combustion).

The effective diffusion number:

\[ D_{\text{eff},i} = \left[ \frac{e}{7} \cdot \frac{\rho_p}{T} \cdot \frac{T}{M_i} \cdot r^{-1} \cdot \frac{1}{D_{r,i}} \right] \]

**Idea gas law**

\[ \frac{\rho_j}{RT} \left[ \frac{\nu_j}{M_{i,j}} \right] \]

**Reference**


Hunter, J.B. and G. McGuire; Method and apparatus for catalytic heat exchange. US patent 4 214 867


