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Microchannel Reactor for Methanol Autothermal Reforming

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Automotive exhaust is currently one of the major pollution sources. As a pollution-free and energy-saving power supply for electric vehicles, the fuel cell is the best candidate because of its high energy conversion efficiency (50 %～70 %) and zero or nearly zero emission. Hydrogen is the fuel for the proton exchange membrane fuel cell (PEMFC). The on-board generation of hydrogen using liquid alcohols and hydrocarbons is the most practical way for PEMFC vehicles. Nowadays, PEMFC technology has been well developed, and is gradually in the stage of commercial application, while the hydrogen-generating technology has become the bottleneck for the practical utilization of fuel cells. The miniaturization of the hydrogen source is prerequisite for its practical application.[1,2].

Microchemical technology (MCT) is a new direction originating in the early 1990s. This technology focuses on the study of chemical engineering process properties and principles of micro devices and systems whose dimensions are less than hundreds of microns. Owing to the small dimensions, the specific area increases, the surface effect is enhanced, and the entrance effect of transport processes (flow, heat and mass transfer) leads to a remarkable increase of transfer rates, which exceed those of conventional-sized devices by 2～3 orders of magnitude. The application of MCT can improve greatly the efficiency of systems and diminish their volume and weight. The integration of a microchannel reactor system and a heat exchanger system is the main technique of the MCT. Further study of it will provide important theoretical directions for the miniaturization of a fuel cell hydrogen source to accelerate its commercialization[3～5].

An on-board fuel processor will require novel catalysts and reactor configurations. This paper mainly focuses on the performance of the methanol autothermal reforming (MATR) in microchannel reactors. MATR, in principle, is a combination of partial oxidation and steam reforming on the same catalyst particles, the overall reaction rate is thus quite fast and the catalyst bed can be small. This combination has a net reaction enthalpy change of zero, thus the reactor for this process does not require any extra external heat transfer after having reached the reaction temperature. The molar ratio of H_2 to MeOH, β, varies with the reaction temperatures. It can be seen in Table 1, that β increases with the reaction temperatures under stoichiometric ratio and adiabatic conditions.

$$CH_3OH + (1 - 2\beta)\,H_2O + \beta O_2 \longrightarrow CO_2 + (3 - 2\beta)\,H_2$$

Table 1 Effect of reaction temperature on β

θ /℃	300	400	500	600	700
β	0.123	0.129	0.133	0.137	0.140

Fig 1 shows a chip of the microchannel reactor made by a chemical etching method. The chip is made of stainless steel. Table 2 shows its structure parameters.

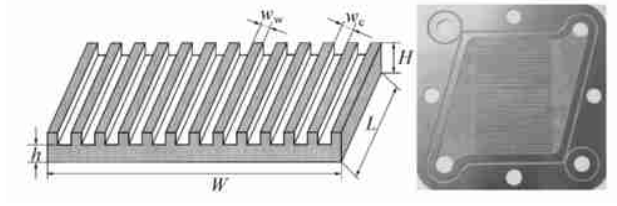

Fig 1 Chip of microchannel reactor

The catalyst on the chips was prepared as follows. First, the metal substrates were cleaned by Na_2SiO_3 solution to remove any oily substances, then rinsed with distilled water, and dried at 110 ℃

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Table 2 Parameters of the structure of the chip

H	h	L	w_c	w_w	W	n_1	n_2	V/ml
0.34	0.17	30	0.5	0.5	45	48	5	1.1

H — Thickness of chip, h — Depth of channel, L — Length of channel, w_c — Width of channel, w_w — Wall thickness between channels, W — Width of total channels, n_1 — Number of channel per chip, n_2 — Number of chip, V — Volume of microreactor
The unit of H, h, L, W, w_c and w_w is mm.

for 2 h. Second, a wash-coat on the stainless steel was made by a CeO_2-ZrO_2 solid solution[6]. Finally, the main active component, Pt, was added by Pt $(NH_3)_4 \cdot (OH)_2$ solution (0.1 g/ml) *via* dip-coating, and dried at 120 ℃, then calcined at 400 ℃ for 3 h, and reduced with 10 %H_2-90 %N_2 at 400 ℃ for 2 h.

The molar ratios of H_2O and O_2 to MeOH in the feed were 1.2 and 0.3, respectively, and air was used as oxidant. Methanol and water were prevaporized at 150 ℃, then mixed with air and entered the microreactor which was placed in an oven. Water and methanol were removed from the exit gas by a cold trap, while the dry gas entered a GC and soap bubble flowmeter for composition analysis and flow-rate measurement respectively. The reaction was carried out at 450 ℃.

From Fig 2, it is clear that the methanol conversion in the monolith reactor is rapidly reduced to lower than 80 % at 20 000 h^{-1}, while it is still higher than 93 % in the microchannel reactor even at 186 000 h^{-1}, which is about 10 times higher than that in the monolith reactor. The reason is that the intrinsic rate of MATR is very high, so the apparent reaction rate is heavily limited by mass and heat transport. While the reaction rate increased remarkably and the conversion is still high even at high GHSV in the microchannel reactor, owing to its rapid heat and mass transfer with its small dimensions.

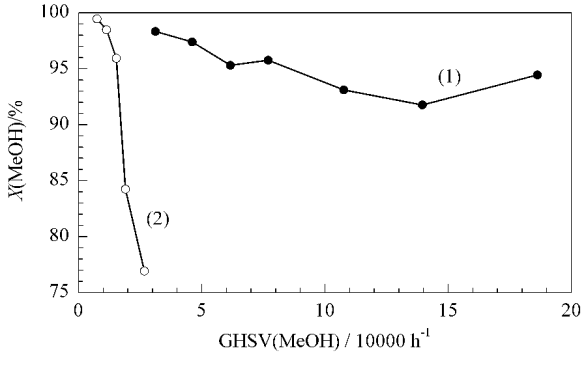

Fig 2 MeOH conversion vs GHSV(MeOH) in different reactors
(1) Microchannel reactor, (2) Ceramic monolith reactor
(Reaction condition: $n(O_2)/n(MeOH) = 0.304$, $\theta = 450$ ℃)

Fig 3 shows the composition of the dry product gas of MATR. H_2 has a high value of 43 % and CH_4 is lower than 0.5 %, while CO is higher than 15 % under the reaction condition. CO is the main poison of the electrode catalyst (Pt) of the PEMFC, so it must be reduced to less than 1×10^{-5}. To attain that, supplementary reactions, such as gas-water shift reaction and preferential oxidation, have to be applied. Meanwhile, novel catalyst for MATR with high hydrogen selectivity should be developed to reach this low CO concentration level.

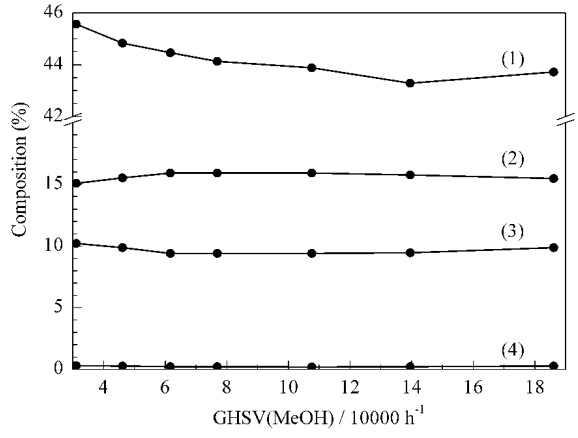

Fig 3 Product composition vs GHSV(MeOH) in microchannel reactor
(1) H_2, (2) CO, (3) CO_2, (4) CH_4
(The reaction condition is the same as in Fig 2)

In conclusion, owing to the small characteristic dimensions of the microchannel reactor, the effect of heat and mass transport is increased remarkably. The reaction rate increases and the methanol conversion remains high at very high GHSV. The miniaturization of the hydrogen generation system can be achieved with a microchannel reactor.

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