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Methanol decomposition fuel processor for portable power applications

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ARTICLE INFO

Article history:
Received 8 January 2009
Received in revised form
2 February 2009
Accepted 3 February 2009
Available online 28 February 2009

Keywords:
Portable power
Fuel processor
Hydrogen generator
Fuel cell
Methanol decomposition
Membrane reactor

ABSTRACT

A new fuel processor approach for portable fuel cell power sources significantly improves upon microreformers by overcoming the difficulties with heat deficiencies and contaminants in the product hydrogen. Instead of reforming, the processor uses methanol decomposition to enable the byproduct, carbon monoxide (CO), to be used as the heat source. A hydrogen permselective membrane segregates the CO for combustion in an integrated burner, maximizes the decomposition conversion, and provides pure hydrogen for a fuel cell. Discharging the CO-rich retentate through an ejector to draw combustion air into the burner greatly simplifies the system. High and stable hydrogen yields are attained with optimized catalysts and fuel compositions. The resultant simple, efficient, and self-heating processor produces 85% of the hydrogen content of the fuel. A 20 W autonomous power source based on this novel fuel processor demonstrates a fuel energy density $>1.5\ \mathrm{Wh\ g^{-1}}_{(\mathrm{electrical})}$, nearly twice as high as microreformer power sources.

1. Introduction

Difficulties with hydrogen storage have hindered the use of hydrogen fuel cells (FCs) for portable power applications (loosely defined as <50 W). A promising alternative to hydrogen storage is to use a fuel processor to convert a fuel into hydrogen for the FC. The fuel is ideally an easy-to-store liquid such as a hydrocarbon, alcohol, or even ammonia. Typically, elevated temperatures and catalysts are used to drive a chemical reaction that liberates the hydrogen from the fuel. For example, ammonia can be decomposed at ~600 °C over a cracking catalyst to produce hydrogen [1,2]. Far more common, however, is the steam reforming of organic compounds to produce the hydrogen as well as a CO_2 byproduct. In fact, steam reforming is the primary industrial source of hydrogen [3]. Thus, it is a natural first step to use reforming[1] to generate hydrogen for fuel cells in portable power sources. Since it is the easiest fuel to reform, the majority of these "microreformers" use methanol (see very extensive reviews by Holladay et al. [1] and Palo et al. [2] plus [4–6]). However, while reformers dominate industrial-level applications, miniaturization introduces difficulties that complicate their use on very small scales. Due to the challenges, very few complete and autonomous portable power sources based on microreformers have been realized, despite extensive effort in the area (notable exceptions are UltraCell and Casio). In contrast, a fuel processor that utilizes methanol decomposition instead of reforming has distinct advantages in overcoming the difficulties to easily enable an efficient complete portable power source.

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[1] The term "reforming" is also used to describe a refinery process for increasing octane ratings. Here, the term and its variants refer exclusively to steam reforming.

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doi:10.1016/j.ijhydene.2009.02.005

2. Methanol reforming vs. decomposition

2.1. *Reforming*

The reforming of methanol is an endothermic reaction typically performed at 200–300 °C over a reforming catalyst:

$$CH_3OH_{(l)} + H_2O_{(l)} \rightarrow CO_2 + 3H_2 \qquad \Delta H^{\circ}_{298} = 132\ \text{kJ mole}^{-1} \tag{1}$$

This steam reforming reaction is a two-step process, the first of which is methanol decomposition:

$$CH_3OH_{(l)} \rightarrow CO + 2H_2 \qquad \Delta H^{\circ}_{298} = 128\ \text{kJ mole}^{-1}\ {}^{2} \tag{2}$$

Full completion of the reforming reaction then proceeds via the water–gas-shift (WGS) reaction:

$$CO + H_2O_{(l)} \rightarrow CO_2 + H_2 \qquad \Delta H^{\circ}_{298} = 4\ \text{kJ mole}^{-1} \tag{3}$$

Water is needed for steam reforming, but if the fuel processor is paired with a fuel cell, then product water from the fuel cell can be recovered and blended into the reactor feed for use in the reforming reaction. This allows neat methanol (100%) to be the stored fuel, which can also be combusted to supply the heat for the endothermic reforming reaction. Such an approach is common in larger scale systems, but the required balance-of-plant (BOP) is problematic for portable systems. The use of a water/methanol mixture eliminates the water recovery subsystem, but the mixture has a lower energy density and is not an optimal burner fuel.

Further complicating a fuel processor/fuel cell system is that the carbon monoxide (CO) reforming byproduct needs to be almost completely removed for use in conventional polymer electrolyte fuel cells (PEFC), as they are quickly poisoned by the contaminant [7]. Typically, the CO levels are lowered to parts-per-million (ppm) using high steam-to-methanol ratios and additional WGS and preferential oxidation reactors, however this series of reactors results in a complex system with challenging process control. Consequently, recent efforts using fuel processors in portable power systems have taken an alternative approach to the CO problem. In these cases, no attempt is made to remove the carbon monoxide; rather, a fuel cell technology is used that operates at higher temperatures (150–200 °C) that are more tolerant of CO poisoning. The most common higher temperature portable fuel cell technology utilizes the phosphoric acid imbibed polybenzimidazole (PBI) membranes originally developed by Case Western University [8], and now used by companies such as Motorola and UltraCell for portable power. A 25 W UltraCell power source using this approach operating on a stoichiometric 1:1 methanol/water fuel achieves a fuel energy density of 0.82 Wh $g^{-1}{}_{\text{(electrical)}}$ [9]. This appears to be the highest performance attained by a fully self-sufficient microreformer based power source. Here, the fuel energy density is used as the metric for comparing fuel cell power sources, as it is independent of fuel type (unlike efficiencies) and duration of operation (unlike system energy densities), and is most relevant to the user that carries the power source. Higher values than 0.82 Wh g^{-1} are inferred in the literature, but these are typically projections based on reformer yield and tend to neglect or underestimate factors that negatively impact the efficiency of the complete power source (such as providing the process heat, heat losses, cleaning up CO, or the parasitic power requirements of the BOP). On the other hand, the 0.82 Wh g^{-1} fuel energy density is only about 23% of the 3.5 Wh g^{-1} lower heating value (LHV) energy content of the 1:1 fuel, possibly due to the need to consume extra fuel to provide the necessary heat.

Indeed, a substantial amount of heat is required to heat and vaporize the reactants, drive the reaction, and overcome heat losses from the reactor and the effluent streams. Compared to large industrial units, heat losses are also substantially greater with portable systems. As a device becomes smaller, the surface area per unit volume of the device increases inversely proportional to the characteristic length. Consequently, a device one-tenth as large as the original will have a tenfold greater heat loss (surface area) per unit capacity (volume), all else being equal (insulation thickness, heat transfer coefficients, etc.). Thus, the smaller the processor, the greater the heat requirements, and at some point the heat losses exceed the process heat load.

Substantial extra sources of heat are then required for portable and microreformers. Electrical heating is typically used [1,2,4,5,10–13], but is viable only for research purposes, as supplying sufficient electrical power severely decreases the efficiency of a complete system. The methanol/water reforming mixture can be directly combusted in a burner to supply the heat, although it is an inefficient fuel due to the water content. It is also possible to combust product hydrogen in a catalytic burner, and in this case it is beneficial to first pass the hydrogen through the fuel cell, as the fuel cell performance improves with the higher hydrogen content. However, to provide the extra hydrogen, not only is more fuel required, but it is inherently inefficient to carry water to produce hydrogen and then burn hydrogen to produce water. Yet another option is to carry a separate source of heat, such as a different fuel mixture for the burner [6,14–17], or even hydrogen peroxide for its decomposition heat [18], but these require managing a second fuel, greatly increasing complexity. In general, all these approaches significantly decrease the overall efficiencies and energy densities of the systems.

The primary system features or improvements needed to realize effective portable fuel processor/fuel cell systems are then (1) an efficient source of substantial heat for the fuel processor, (2) a solution to the problem of CO contamination of the fuel cell, and (3) simplicity. These are to a large degree interconnected. For example, a source of ample heat simplifies the system, as extensive heat recuperation and

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[2] Because of the heat loss difficulties with small systems, the enthalpies of the liquid forms of the reactants are used (the subscript (*l*)). Otherwise, using the vapor enthalpies, as is common in the literature, assumes that there are no difficulties in obtaining the heat necessary to vaporize the reactants, which is not the case in small systems. On the other hand, the thermodynamic values are for standard conditions, while in fact the reactants need to be heated to elevated temperatures, so the use of standard values effectively does allow for this limited amount of heat recovery.