SOFC-type microreactors that generate hydrogen for PEFC applications

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Portable power generation technologies with fuel cells are attractive alternatives to batteries. Although direct methanol fuel cells (DMFCs) are a promising candidate for such applications[1], there are two major problems, namely, the poor kinetic of methanol oxidation at the anodes and the phenomenon of methanol crossover through the electrolyte. The resulting low power densities prevent broad commercialization of this technology. Alternatively, polymer electrolyte fuel cells (PEFCs) with small-size reformers have been developed[2], where hydrogen is produced from liquid fuels by the reformers. However, since the reforming reaction is endothermic, the overall system efficiencies are not significantly improved as was expected.

Here, we propose a new solid oxide fuel cell (SOFC)-type microreactor that can produce hydrogen rich gases from dry butane for PEFCs. This microreactor is more practical than usual hydrocarbon reformers because it generates not only hydrogen but also electrical power. One of the most important issues for the above applications is the development of anode materials capable of producing hydrogen rich gases with as low a CO concentration as possible, which reduces a load on water gas shift reactors and preferential CO oxidation reactor. The anode materials are also required to operate on hydrocarbon fuels without carbon deposition. Although the addition of excess steam to the fuels prevents coking, it causes systematic complexity and high fabrication cost. Moreover, the anode materials must show good stability to redox cycling when the microreactors are stopped and re-started. It is desirable to develop metal-oxide anodes that show little or no volume change upon the repeated redox cycling.

The commonly used anodes for SOFCs are Ni/yttria-stabilized zirconia (YSZ) cermets; however, these anodes show instability to redox cycling and low tolerance to carbon deposition[3]. In recent papers, alternative anode materials such as Cu/ceria[4] and $LaCrO_3$-based oxides[5,6] were reported; however, these anodes promote complete oxidation of hydrocarbons during cell discharge. Unlike these anodes, the Fe_2O_3/Cr_2O_3 composite anode developed here demonstrated that the primary carbon-containing product was CO_2 when synthesizing hydrogen rich gases from dry butane. Furthermore, this anode showed small polarization resistances for butane oxidation without carbon deposition. As a result, a microreactor with the Fe_2O_3/Cr_2O_3 composite anode could generate hydrogen rich gases with a low concentration of CO together with reasonable power densities from dry butane around 700 ^oC (Figs. 1 and 2). The present microreactor would enhance the position of PEFCs as the preferred portable power sources.

References

1. X. Ren, M. S. Wilson, and S. Gottesfeld, High performance direct methanol polymer electrolyte fuel cells. *J. Electrochem. Soc.* **143**, L12-L15 (1996).
2. Y. Kawamura, N. Ogura, T. Katsumata, and A. Igarashi, Hydrogen production system by methanol reforming with microreactor. *Catalysts & Catalysis* **45**, 120-122 (2003).
3. B. C. H. Steele and A. Heinzel, Materials for fuel-cell technologies. *Nature* **414**, 345-352 (2001).
4. S. Park, J. M. Vohs, and R. J. Gorte, Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature* **404**, 265-267 (2000).
5. J. Liu, B. D. Madsen, Z. Ji, and A. A. Barnett, A fuel-flexible ceramic-based anode for solid oxide fuel cells. *Electrochem. Solid State Lett.* **5**, A122-A124 (2002).
6. S. Tao and J. T. S. Irvine, A redox-stable efficient anode for solid-oxide fuel cells. *Nat. Mater.* **2**, 320-323 (2003).

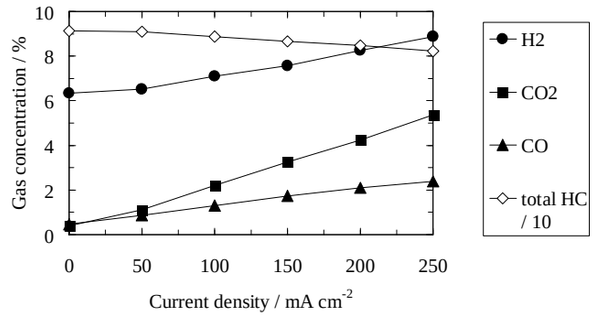

Fig. 1 Gas concentration versus current density for a Fe_2O_3/Cr_2O_3 anode. The SOFC was operated at 700 ^oC with dry butane. The electrolyte thickness was 0.50 mm. Total HC/10 means one-tenth the total concentrations of the decomposed hydrocarbons (methane, ethane, ethylene, propane, propylene etc.) and butane.

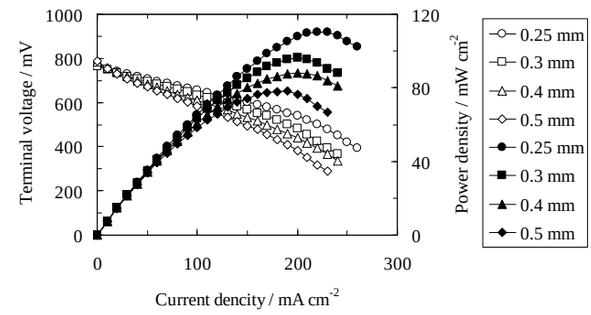

Fig. 2 Discharge properties of a SOFC with a Fe_2O_3/Cr_2O_3 anode at different electrolyte thickness. The SOFC was operated with dry butane at 700 ^oC.