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Hydrogen production from methane and water by lattice oxygen transfer with $Ce_{0.70}Zr_{0.25}Tb_{0.05}O_{2-x}$

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Abstract

Hydrogen is a prime prospect for an alternative fuel. In this paper a cyclical method of production of hydrogen is proposed. The method consists of hydrogen production from methane reduction of fluorite-type $Ce_{0.70}Zr_{0.25}Tb_{0.05}O_2$ to $Ce_{0.70}Zr_{0.25}Tb_{0.05}O_{2-x}$ followed by reduction of water by $Ce_{0.70}Zr_{0.25}Tb_{0.05}O_{2-x}$ to $Ce_{0.70}Zr_{0.25}Tb_{0.05}O_2$.

Keywords: Hydrogen production; Fluorite-related quaternary oxides; Water reduction; Decomposition of methane

1. Introduction

Hydrogen is a desirable alternative fuel to reduce atmospheric pollution. The greatest barriers for hydrogen usage are storage, transportation, and economic production. If hydrogen can be produced at the point of use the problems of storage and transportation can be minimized and it could become a universal clean fuel.

Otsuka et al. [1] have demonstrated that methane can be decomposed to hydrogen and either carbon or carbon monoxide while reducing CeO_2 to CeO_{2-x} and that the latter can subsequently reduce water to produce hydrogen. In these reactions oxygen is transferred from or to CeO_{2-x}.

In this paper a cyclic process is described for hydrogen production from methane and water by the lattice oxygen transfer with fluorite-type oxides containing Ce, Pr, and Tb [2].

2. Experiments

The $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ was prepared by co-precipitation from an appropriate mixture of $Ce(NO_3)_3$, $ZrO(NO_3)_2$, and $Tb(NO_3)_3$ solutions, using NH_4OH. The precipitated powder was heated at 800°C in air for 1 h, then cooled to room temperature.

A thermogravimetric-system (TGA) is contained in a gas-flow apparatus illustrated in Fig. 1. The reaction gas can be selected as desired from a valve manifold. An argon carrier containing 15% methane was used for reduction of the oxide and the production of hydrogen. Water vapor carried by helium gas flowing through liquid water was used for oxidation of the reduced oxide to form hydrogen. A 1.8498 g sample of oxide powder loaded into a platinum container was suspended from one arm of a Cahn microthermobalance enclosed in a quartz envelope. A temperature programmable furnace was raised to surround the quartz reaction tube containing the suspended sample. The exit gas was passed through a fuel cell (Warsitz Enterprises, Inc), consisting of a single stack of the proton exchange membrane (PEM). A voltage generated in the fuel cell indicates the presence of hydrogen in the exit gas. The temperature and weight of the sample and any voltage produced in the fuel cell were measured every 10 s and the values stored on a computer by means of a Pico multichannel *a* to *d* converter [3].

3. Results and discussion

Using this system the thermogravimetric-analysis (TGA) of the sample, and the voltage of the fuel cell under different temperature programs and different gas-flows were monitored. Specifically, methane reduction of the oxide is followed by recording TGA data, which includes the weight change of the sample as a function of the temperature. Any hydrogen produced was detected in the exit gas by a voltage generated in the fuel cell. In the succeeding run the reduction of H_2O by the reduced oxide is quantitatively determined by the weight gain of the oxide due to the oxygen transfer. The hydrogen released is qualitatively indicated by the voltage output of the fuel

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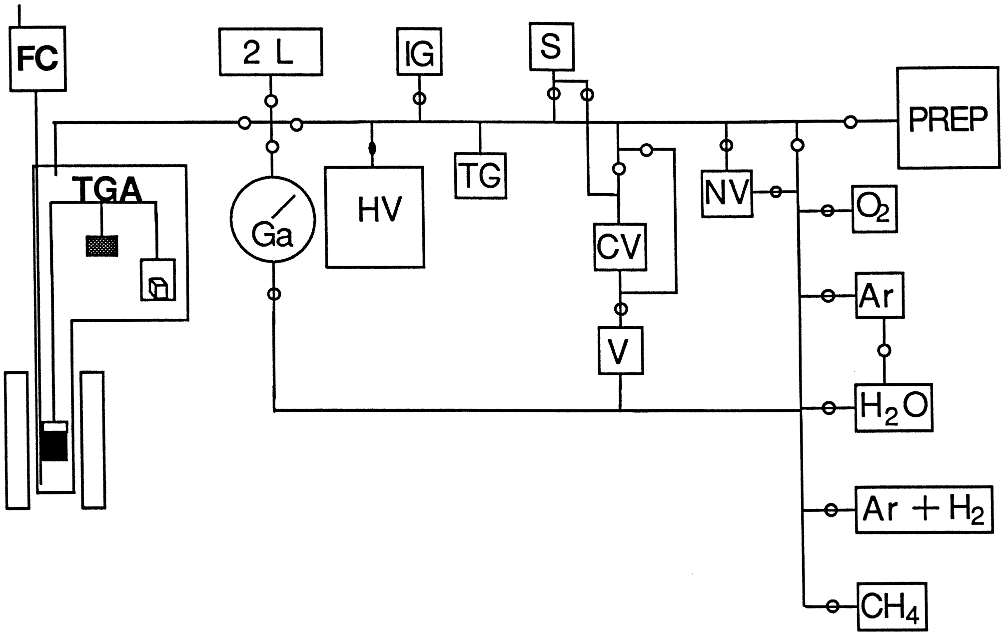

Fig. 1. Diagram of the experimental set-up.

cell. Fig. 1 diagrams the glass-enclosed apparatus used and Table 1 identifies the functional parts of the system from right to left.

3.1. Hydrogen produced from methane

Fig. 2 shows the experimental data using $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$. Fig. 2a shows that 15% methane reduces the sample around 700°C. The oxygen released by the oxide is determined by the weight loss. Fig. 2b shows the voltage variation of the fuel cell during this process. The voltage increase around 700°C confirms hydrogen production.

3.2. Hydrogen produced from water

The temperature of the oxide is controlled at 300°C following reduction by methane. He gas saturated with H_2O flows over the reduced oxide. Fig. 3a shows the results as the reduced $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ absorbs oxygen from H_2O as a function of time. Fig. 3b shows the voltage produced by the fuel cell during the flow of water vapor. Notice that while the sample absorbs oxygen and

Table 1
The functional elements of the experimental apparatus shown in Fig. 1

PREP	An enclosed quartz reaction volume allowing a specimen to be treated at a programmed, controlled temperature in any desired gaseous atmosphere
O_2, Ar, etc.	Gases or gas mixtures accessible by means of a manifold
NV	Needle valve
V	Rotary vacuum pump
CV	Control valve
S	A capacitance manometer enabling electronic control of the system gas pressure
TG	Thermocouple gauge
IG	Ionization gauge
HV	High-vacuum oil diffusion pump system
Ga	High sensitivity Bourdon gauge (0.1 mmHg)
2L	Calibrated volume to enable system component calibration
TGA	Thermogravimetric-analysis apparatus consisting of a Cahn-micro-electrobalance with a temperature controlled specimen chamber including controls and read-out
FC	Fuel cell hydrogen detector

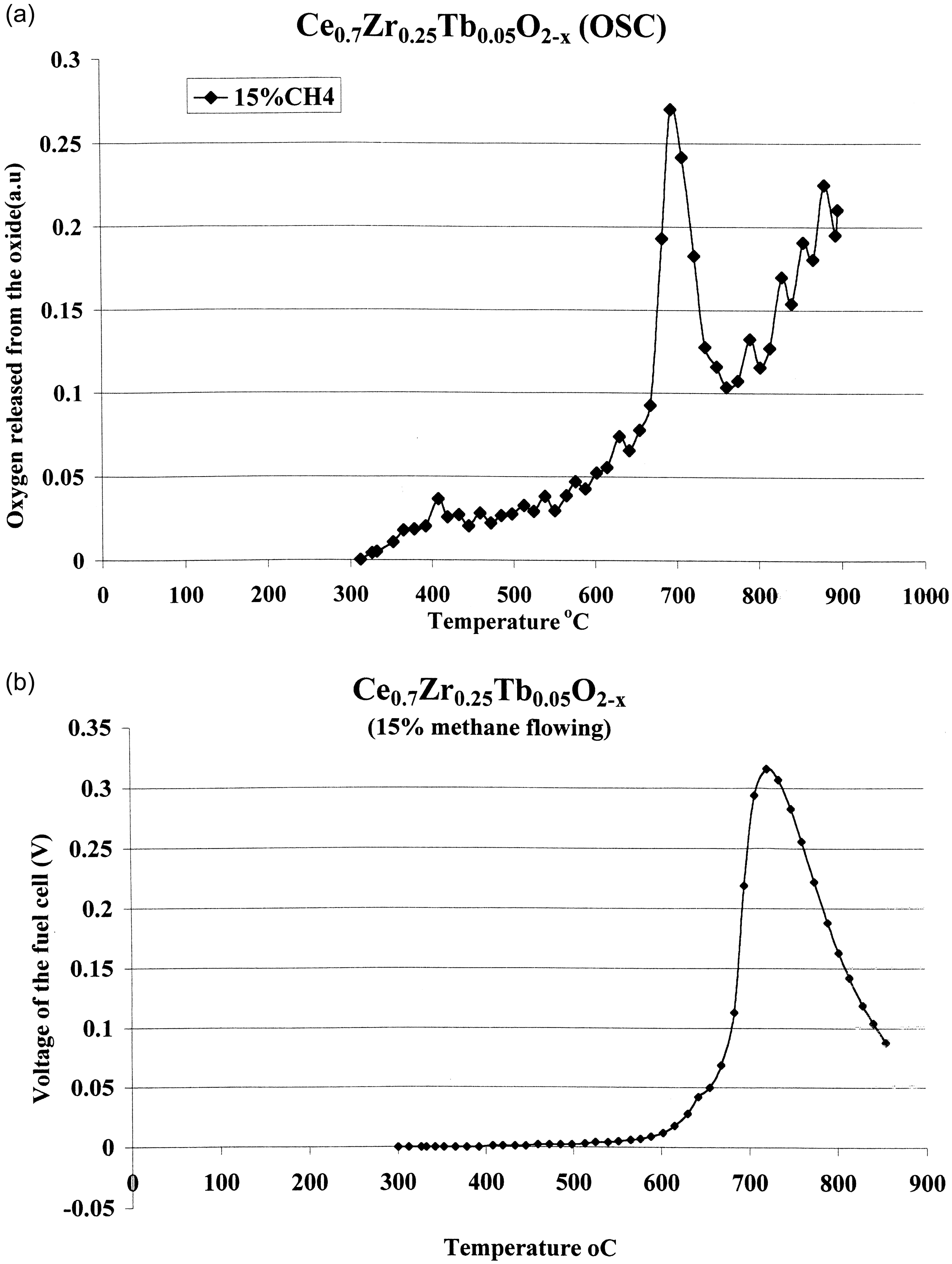

Fig. 2. (a) Oxygen released by $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ under 15% CH_4 flow as a function of temperature; (b) the voltage developed on the fuel cell during methane reduction with temperature increase.

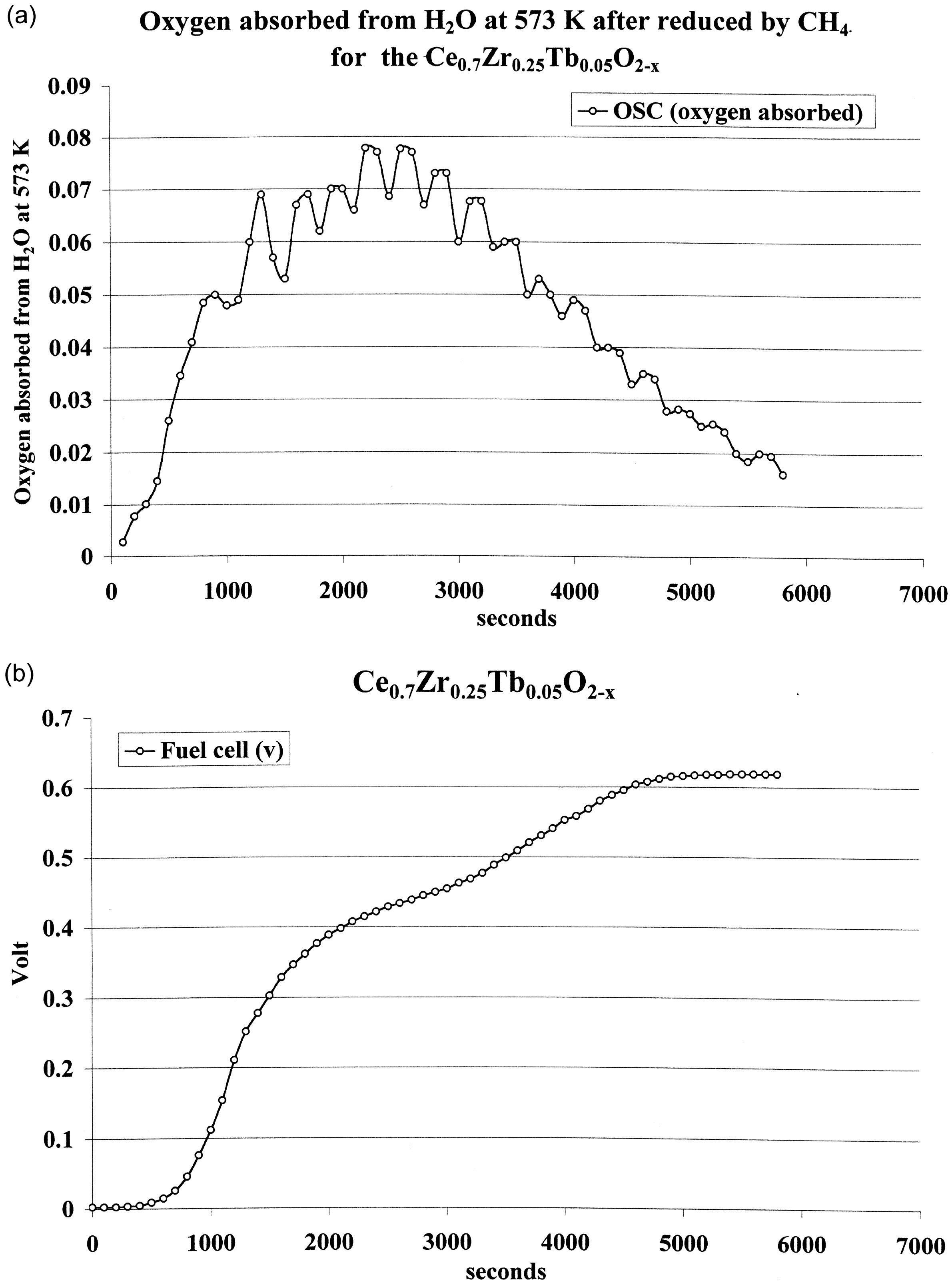

Fig. 3. (a) Oxygen absorption by $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ from H_2O vapor, and (b) voltage developed by the fuel cell as hydrogen is produced.

gains weight the voltage on the fuel cell is simultaneously increased. This records the transfer of the oxygen in water to the $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ as hydrogen is liberated.

4. Conclusion

These data show that methane can produce $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ and yield hydrogen and CO around 700°C. H_2O can oxidize the $Ce_{0.7}Zr_{0.25}Tb_{0.05}O_{2-x}$ to produce hydrogen at 300°C. Temperature (700–300°C) and gas (methane and water vapor) mediated cycles can produce hydrogen continually.

References

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