Supplementary Information

A Bifunctional Solid Oxide Electrolysis Cell for Simultaneous CO_2 Utilization and Synthesis Gas Production

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Experimental Procedure

Material preparation and cell fabrication

The $Pr_{0.5}Ba_{0.5}Mn_{0.9}Co_{0.1}O_3$ used as cathode material were prepared by a modified sol-gel method. Certain amount of dissolving Co, Pr, Ba and Mn nitrate salts were mixed and dissolved in de-ionized water with the addition of quantitative amounts of citric acid and ethylene glycol (the mol ratio of metal ion: citric acid: ethylene glycol is equal to 1:3:1.5), the PH value of the solution was carefully adjusted to ~8 by adding suitable amount of ammonium hydroxide. And then, the solution was continuously stirred on a hotplate at 60 ^{o}C overnight until the gel forms. After that, the gel was slowly decomposed at 350 ^{o}C for 2 hours and calcined in air at 950 ^{o}C for 4 hours at the rate of 2 ^{o}C min^{-1}. The prepared materials were denoted as PBMCo. The Gadolinium doped ceria (GDC) was used as buffer layer between cathode and electrode. The cathode was a mixture of equal weights of GDC and PBMCo. The anode matrix was a mixture of equal weights of YSZ powder (TOSHO Co. Ltd.) and strontium doped lanthanum manganese (LSM). The active area of electrode is equal to 1cm^2.

The Ru infiltrated LSM composites were prepared by solution impregnation of the Ruthenium(III) chloride solution into the LSM layer to reach the Ru weight ratio of 5 wt%. The infiltrated electrodes were finally fired at 700 °C for 2 h.

Electrochemical performance evaluation procedure

During SOEC test, Au paste, used as the current collectors, were brushed on the anode and cathode of the cells, respectively. The cell was then sealed on an axial alumina tube setup using a Ceramabond® 503 glass sealant (Aremco Products, Inc.). The current density-voltage (I-V) curve were obtained at different applied voltages and temperatures ranging from 800 to 900 °C. The fuel flow rate of 70%CO_2-CO to cathode chamber was carefully controlled in order to ensure the sufficient flux of oxygen ions to anode. An impedance/gain phase analyzer (Solartron 1255) and an electrochemical interface (Solartron 1287) were used to record the electrochemical performances. The stability and selectivity of the electrode catalyst for partial oxidation reaction of methane occurring in anode chamber was tested at fixed flow rate and gas composition at various temperatures. A dilute methane stream composed of CH_4 (5 vol%) was used as fuel to anode chamber.

The heterogeneous catalytic activities of the anode materials for partial oxidation of methane were also evaluated in a fixed-bed quartz reactor (5mminner diameter). 100 mg catalyst were packed in the center of the reactor using quartz wool. The reactor was kept in a tubular furnace. Before carrying out the reaction, the catalyst was reduced using 10%H_2–N_2 at 800 °C for 1 h. The mixture of $CH_4/O_2/Ar$ (ratio of 2:1:38) were injected into fix-bed reactor at a gas hourly space velocity (GHSV) of 1.0×10^5 $mL\cdot g^{-1}\cdot h^{-1}$.

The composition of the effluent gas was analysed using a gas chromatography (GC, Agilent 5890) equipment with TDX-01 molecular sieve column and Ar as carrier gas. CH_4 conversion, CO selectivity and H_2 selectivity were calculated by equations (1), (2) and (3), respectively.

$$\mathrm{Con(CH_4\ (\%))} = \frac{moles\ of\ CH_4\ converted}{moles\ of\ CH_4\ in\ feed} * 100 \quad (1)$$

$$\mathrm{Sel(CO(\%))} = \frac{moles\ of\ CO\ in\ products}{moles\ of\ CO\ in\ products + moles\ of\ CO_2\ in\ products} * 100 \ (2)$$

$$\mathrm{Sel(H_2\ (\%))} = \frac{moles\ of\ H_2\ produced}{2\times moles\ of\ CH_4\ converted} * 100 \ (3)$$

The microstructures of the cells were examined using a scanning electron microscopy (SEM, JEOL 6301F).

The temperature-programmed oxidation (TPO) method was adopted to characterize the carbon deposition using a Thermogravimetric Analysis (TGA) and the compositions of effluents were analyzed with the mass spectrometer (MS).

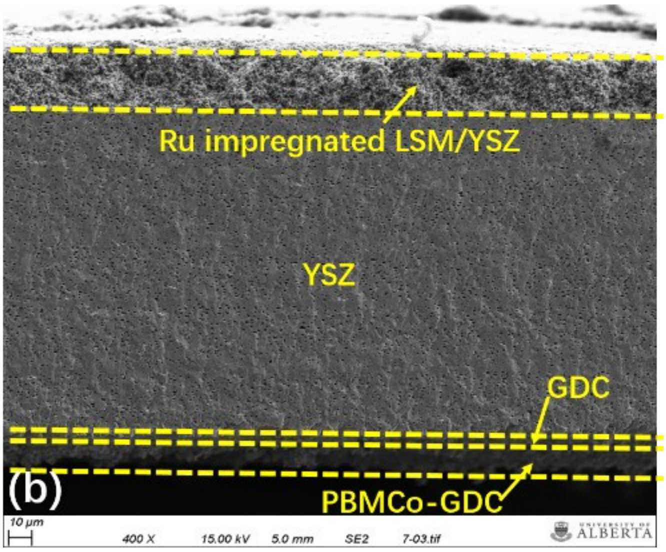

Fig. S-1. Microstructure of the Ru impregnated LSM-YSZ /YSZ/GDC/PBMCo-GDC configuration

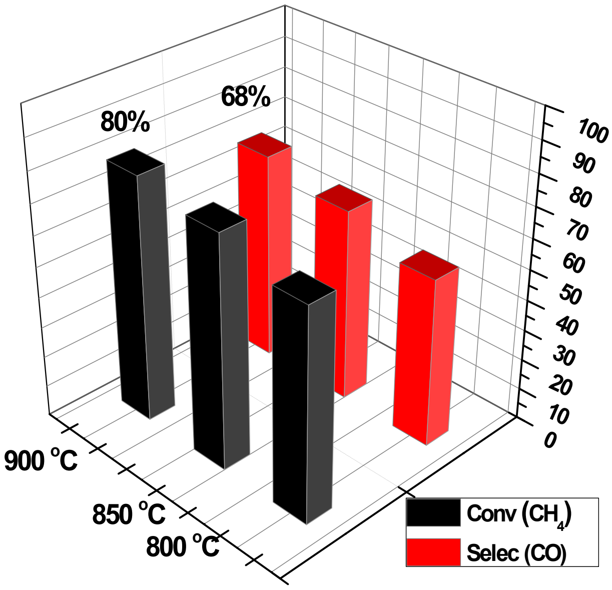

Figure S-2 CH_4 conversion and CO selectivity of LSM/YSZ catalyst as a function of temperature in a regular fixed bed

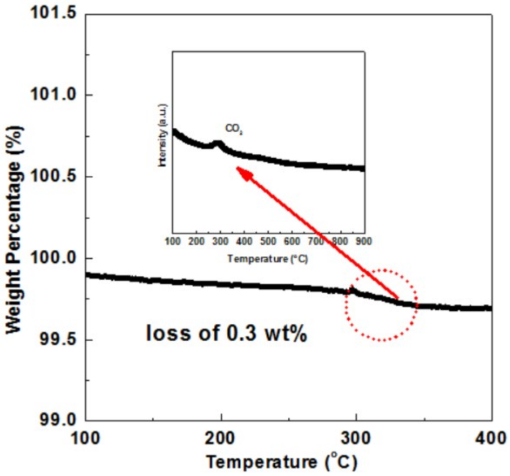

Figure S-3. The Temperature Programmed Oxidation (TPO) test for anode material after test performed on TGA-MS

(a) $CH_4 \rightarrow C + H_2$

(b) $2O^{2-} - 4e^{-} \rightarrow O_2$

(c) $2CH_4 + O_2 \rightarrow 2CO + 4H_2$

(d) $2C + O_2 \rightarrow 2CO$

(e) $2CO + O_2 \rightarrow 2CO_2$
$2CO \Leftrightarrow C + CO_2$

(f) $CH_4 + 2O_2 = 2H_2O + CO_2$

(g) $C + O_2 = CO_2$

Figure S-4 The possible reaction pathways involved on anode for the cell shown in Figure 4.