## Biogas to Syngas: flexible on-cell micro reformer and NiSn bimetallic nanoparticles implanted solid oxide fuel cells for efficient energy

## conversion

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Schematically showing the profiles of the biogas reactor.



(a) and (b) as received Ni foam; (c) Ni foam treated in H<sub>2</sub>-500 ppm H<sub>2</sub>S at 850 °C for 5h, showing no visible physical change; (d) Ni foam treated in CH<sub>4</sub>-CO<sub>2</sub> at 850 °C for 5h, and damage was observed on the Ni surface; (e) Ni foam treated in H<sub>2</sub>-500 ppm H<sub>2</sub>S at 850 °C for 5h, and then treated in CH<sub>4</sub>-CO<sub>2</sub>-200 ppm H<sub>2</sub>S at 850 °C for 24h, showing that the carbon deposition resistance of the Ni foam was enhanced via contaminating in H<sub>2</sub>S; (f) and (g) XPS spectrum of the (e): (f) Sulfur species were detected on the Ni foam, which should be responsible for the enhanced carbon deposition resistance; (g) No Ni-S compounds were observed.

Figure S2



WC before and after contaminated in  $H_2$ -500 ppm  $H_2S$  (850 °C 24 h). It is seen that no S-containing species have been detected in the WC sample (e.g., absorbed S and W-S compounds), but a small part of WC was reduced to metallic W.



WC before (a and c) and after (b and d) contaminated in  $H_2$ -500 ppm  $H_2S$ . No agglomeration was absorbed, which ensures a good durability of the WC current collector.

## Figure S4-1



Cross-sectional microstructure of the NiSn-YSZ anode, showing the NiSn nanoparticles and the regions (spots 1 and 2) for EDX analysis.

Figure S4-2



It is shown that the surface of the bulk Ni (spot 1) is alloyed with Sn.

Figure S4-3



The composition of the infiltrated nanoparticles is close to that of Ni/Sn=9/1 (spot 2).



EDX mapping shows the Sn element was well distributed.



The NiSn nanoparticles are well distributed over the  $Al_2O_3$  supports after treated in  $CH_4$ - $CO_2$ -200 ppm  $H_2S$  at 850 °C for 24 h, no surface absorbed S and C contaminations were detected.

Figure S7



The catalytic activities of NiSn-YSZ [Ni-YSZ (57-43) is pre-sintered at 1390 °C, and then is infiltrated with NiSn bimetallic NPs] and NiSn-Al<sub>2</sub>O<sub>3</sub> were compared. Catalytic activity measurements for dry reforming of biogas reaction were performed at atmospheric pressure using a compound of 0.2 g catalysts and 0.4 g catalytically inactive quartz powder, which was sieved to the particle sizes ranging from 30 to 60 mesh and packed on a bed of quartz tube. The gas mixtures of CH<sub>4</sub>-CO<sub>2</sub> were fed into the reactor at the flow rate of 20 ml min<sup>-1</sup> (gas hourly space velocity at ~2000 h<sup>-1</sup>). Compositional analysis of the effluent gases was performed with a gas chromatography (GC, Hewlett Packard Series two). The catalytic reactions took place at the temperatures ranging from 700 to 800 °C. The percentages of CH<sub>4</sub> conversion were calculated according to:

$$CH_4 \ conversion = \frac{1/2[CO]}{1/2[CO] + [CH_4]} \times 100\%$$



Voltages as a function of time for the NiSn-YSZ anode which operated in  $H_2$  and  $H_2$ -500 ppm  $H_2S$  at a constant current density of 1250 mA cm<sup>-2</sup> and 850 °C, showing the  $H_2S$  poisoning on the NiSn-YSZ anode is reversible.



Voltage as a function of time during dry reforming of biogas in a single cell with Ni-YSZ anode under 1.25 A cm<sup>-2</sup> and at 850 °C. The feeding stream during the long term test is equal amount of  $CH_4$  and  $CO_2$  balanced with 200 ppm  $H_2S$  in a total flow rate of 20 ml min<sup>-1</sup>.