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

Bin Hua a, Meng Li b, Yi-Fei Sun a, Ya-Qian Zhang a, Ning Yan c, Jian Chen d, Jian Li b, Thomas Etsell a, Partha Sarkar e, Jing-Li Luo a, *

* Corresponding author

a Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada, Tel.: +1 780 492 2232; fax: +1 780 492 2881. E-mail address: jingli.luo@ualberta.ca

b Center for Fuel Cell Innovation, School of Materials Science and Engineering, State Key Laboratory of Material Processing and Die & Mould Technology, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

c Van’t Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam, Amsterdam, 1098XH, The Netherlands

d National Institute for Nanotechnology, Edmonton, Alberta T6G 2M9, Canada

e Environment & Carbon Management Division, Alberta Innovates-Technology Futures, Edmonton, Alberta T6N 1E4, Canada
Scheme S1

Schematically showing the profiles of the biogas reactor.
(a) and (b) as received Ni foam; (c) Ni foam treated in H$_2$-500 ppm H$_2$S at 850 °C for 5h, showing no visible physical change; (d) Ni foam treated in CH$_4$-CO$_2$ at 850 °C for 5h, and damage was observed on the Ni surface; (e) Ni foam treated in H$_2$-500 ppm H$_2$S at 850 °C for 5h, and then treated in CH$_4$-CO$_2$-200 ppm H$_2$S at 850 °C for 24h, showing that the carbon deposition resistance of the Ni foam was enhanced via contaminating in H$_2$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\textsubscript{2}-500 ppm H\textsubscript{2}S (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 H₂-500 ppm H₂S. No agglomeration was absorbed, which ensures a good durability of the WC current collector.
Cross-sectional microstructure of the NiSn-YSZ anode, showing the NiSn nanoparticles and the regions (spots 1 and 2) for EDX analysis.
It is shown that the surface of the bulk Ni (spot 1) is alloyed with Sn.
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$_2$O$_3$ supports after treated in CH$_4$-CO$_2$-200 ppm H$_2$S at 850 °C for 24 h, no surface absorbed S and C contaminations were detected.
The catalytic activities of NiSn-YSZ [Ni-YSZ (57-43) is pre-sintered at 1390 ºC, and then is infiltrated with NiSn bimetallic NPs] and NiSn-Al₂O₃ 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 CH₄-CO₂ were fed into the reactor at the flow rate of 20 ml min⁻¹ (gas hourly space velocity at ~2000 h⁻¹). 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 ºC. The percentages of CH₄ conversion were calculated according to:

\[
CH_4 \text{ conversion} = \frac{1/2[CO]}{1/2[CO] + [CH_4]} \times 100\%
\]
Voltages as a function of time for the NiSn-YSZ anode which operated in H₂ and H₂-500 ppm H₂S at a constant current density of 1250 mA cm⁻² and 850 °C, showing the H₂S 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$^{-2}$ 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$_2$S in a total flow rate of 20 ml min$^{-1}$. 