Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

## **Supporting information**

## Mechanisms of methane decomposition and carbon species oxidation on

 $Pr_{0.42}Sr_{0.6}Co_{0.2}Fe_{0.7}Nb_{0.1}O_{3-\sigma}$  electrode with high catalytic activity

Peng Zhang,<sup>*a*</sup> Guoqing Guan, <sup>\**a,b*</sup> Deni S. Khaerudini,<sup>*a*</sup> Xiaogang Hao,<sup>*c*</sup> Chunfeng Xue,<sup>*c*</sup> Minfang Han,<sup>*d*</sup> Yutaka Kasai,<sup>*e*</sup> Abuliti Abudula<sup>*a,b*</sup>

<sup>a</sup> Graduate School of Science and Technology, Hirosaki University, 1-bunkyocho, Hirosaki 036-8560, Japan

<sup>b</sup>North Japan Research Institute for Sustainable Energy (NJRISE), Hirosaki University, 2-1-3 Matsubara, Aomori 030-0813, Japan

<sup>c</sup>Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China

<sup>d</sup> Department of Thermal Engineering, Tsinghua University, Beijing, 100084, PR China <sup>e</sup>Industrial Research Institute, Aomori Prefectural Industrial Technology Research Center, 4-11-6, Second Tonyamachi, Aomori 030-0113, Japan

\*Corresponding authors: Tel.: +81-17-762-7756; fax: +81-17-735-5411.

E-mail addresses: guan@hirosaki-u.ac.jp (G. Guan);

abuliti@hirosaki-u.ac.jp (A. Abudula)



Fig. S1 SEM images of PSCFN electrode after worked in  $CH_4$  at 850 °C for 30 min (a) and PSCFN anode after oxidized by O<sup>2-</sup> ions at 600 °C for 30 min (b).

TPO experiment is difficult to directly investigate the carbon species reacting with O<sup>2-</sup> ions. Here, we did addition e carbon species on PSCFN by O<sup>2-</sup> ions at 600 °C as follows: PSCFN was used as the symmetrical electrodes with LSGM as the electrolyte supported layer. Pure CH<sub>4</sub> was flown to the cell at a flow rate of 30 ml min<sup>-1</sup> at 850 °C for 30 min, then the cell was cooled to room temperature and observed the microstructure of the PSCFN by SEM. As shown in the Fig. S1a, it can be seen that the carbon fibres were formed on the surface of PSCFN, which is the same as the results in the CH<sub>4</sub>-TPCR process shown in our original manuscript. Thereafter, the cell was sealed on the top of one alumina tube, Ar was used to clean the tube at a flow rate of 100 ml min<sup>-1</sup> for 40 min at room temperature, and then the cell was heated to 600 °C, and the air and Ar were flown to cathode and anode sides of the cell, respectively, at a same flow rate of 30 ml min<sup>-1</sup> for 30 min. Finally, Ar flow was used to clean the tube of both sides so that the cell was cooled down to room temperature. When the microstructure of the anode was characterized by SEM, the result shown in Fig. S1b was obtained. It can be seen that no carbon species was formed on it, indicating that the carbon species on PSCFN can be also eliminated by the O<sup>2-</sup> ions as we thought.



Fig. S2 EDX mapping of Ni-YSZ fresh sample.



Fig. S3 EDX mapping of Ni-YSZ sample after exposed in dry CH<sub>4</sub> at 850 °C.



Fig. S4 EDX mapping of Ni-YSZ sample after O<sub>2</sub>-TPO test.



Fig. S5 EDX mapping of PSCFN sample after exposed in dry CH\_4 at 850 °C.