Mechanistic insight into catalytic conversion of methane on Sr$_2$Fe$_{1.5}$Mo$_{0.5}$O$_6$ perovskite anode: A combined EIS-DRT, DFT and TPSR investigation

Zongying Han$^{a,**}$, Hui Dong$^b$, Yuhao Wang$^c$, Yanru Yang$^a$, Hao Yu$^a$, Zhibin Yang$^d,**$

$^a$ College of Energy Storage Technology, Shandong University of Science and Technology, Qingdao 266590, China
$^b$ College of Chemical and Biological Engineering, Shandong University of Science and Technology, Qingdao 266590, China
$^c$ Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong SAR, China
$^d$ Research Center of Solid Oxide Fuel Cell, China University of Mining & Technology-Beijing, Beijing, 100083, China

* Corresponding author. Email address: hzy5315@163.com (Z.Y. Han)
** Corresponding author. Email address: yangzhbin0001@163.com (Z.B. Yang)
**Fig. S1** SFMO bulk model (a), SFMO (001) surface model (b) and potential adsorption sites (c) on SFMO (001) surface.

**Fig. S2** DRT curves of the SFM/LSGM/LSCF cell in wet hydrogen fuel.
**Fig. S3** Electron density distribution in the most stable adsorption configurations of the key species on SFMO (001) surface. Electron density is given in units of electrons per Å$^3$.

**Fig. S4** Geometry of the IS, TS and FS of methane cracking on the (Fe)-Mo-(Fe) site over SFMO surface. (a) CH$_4$ = CH$_3$ + H; (b) CH$_3$ = CH$_2$ + H; (c) CH$_2$ = CH + H; (d) CH = C + H.
**Fig. S5** Geometry of the IS, TS and FS of methane cracking on the (Mo)-Fe-(Mo) site over SFMO surface. (a) CH$_4$ = CH$_3$ + H; (b) CH$_3$ = CH$_2$ + H; (c) CH$_2$ = CH + H; (d) CH = C + H.

**Fig. S6** Geometry of the IS, TS and FS of methane cracking on the (Fe)-Fe-(Fe) site over SFMO surface. (a) CH$_4$ = CH$_3$ + H; (b) CH$_3$ = CH$_2$ + H; (c) CH$_2$ = CH + H; (d) CH = C + H.
Fig. S7 Energy profile of methane cracking on surface oxygen site of SFMO (001) surface.

Fig. S8 (a) Schematic diagram of five type of methane cracking configurations on the preferred surface (Fe)-Fe-(Fe) site of oxygen vacancy-defective SFMO surface; (b) Comparison of the energy profiles of methane cracking on the preferred surface (Fe)-Fe-(Fe) site (Fe)-Fe-(Fe) site with and without oxygen vacancy.
**Fig. S9** The CH$_4$ desorption profile over the as-synthesized SFMO perovskite.

**Fig. S10** CH$_4$-TPSR profiles corresponding to the reaction of CH$_4$ and lattice oxygen over Ni-YSZ as function of temperature.
**Fig. S11** Electron density differences as the methane molecule approaches the surface given in units of electrons per Å$^3$. In this plot a loss of electrons is indicated in blue, while electron enrichment is indicated in red. Inserted values represent the Mulliken charge of H and C atoms in CH$_4$ molecule and the beneath Mo atom on the surface.