Electronic Supplementary Information

Understanding of A-site non-stoichiometry in perovskites: promotion of exsolution

of metallic nanoparticles and hydrogen oxidation process in solid oxide fuel cells

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Fig. S1 Schematic diagram of the home-made setup for the measurement of the electrochemical performance of a single cell.



Fig. S2 Schematic diagram of the home-made setup for the measurement of the electrode polarization resistance via a symmetrical cell.



Fig. S3 XPS spectra of pristine SFNM*x* powders and reduced SFNM*x* powders (*x*=1.95, 2.00, and 2.05), a) pristine SFNM*x* powders, and b) reduced SFNM*x* powders.



Fig. S4. XPS spectrum of Fe 2p core level regions of a-b) the pristine SFNM*x* powders and c-d) the reduced SFNM*x* powders (x=1.95, 2.00, and 2.05) in the banding energy range of a) and c) 705-729 eV and b) and d) 705-708 eV.



Fig. S5 XPS of Mo 3d of the core level regions of a) pristine SFNM*x* powders and b) reduced SFNM*x* powders (*x*=1.95, 2.00, and 2.05).



Fig. S6 Cross-sectional SEM images of a) SFNM1.95 electrode, b) SFNM2.00 electrode, and

c) SFNM2.05 electrode in the symmetric cells after testing in $97\%H_2-3\%H_2O$.

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Fig. S7. a) The Nyquist plots, b) the corresponding DRT analysis results, c) resistances of the resolved peaks calculated from the DRT analysis results shown in Fig. S7b, and d) Arrhenius plots of R_ps and resistances of the resolved peaks shown in Fig. S7c of the symmetrical cell with SFMNi1.95 electrodes in 97%H₂-3%H₂O atmosphere measured at 600-800 °C.



Fig. S8 Cross-sectional SEM images of a) the single cell and b) the interface of anode/interlayer/electrolyte, and SEM images of SFNM1.95 anode c) before and b) after testing.

Anode	Cathode	Electrolyte(µm)	$R_p(\Omega cm^2)$	Ref.
SFNM1.95	LSCF-GDC	LSGM(580)	0.25	This work
Ba₂FeMoO ₆ (BFMO)	SCF	LSGM(300)	1.2	[64]
Sr ₂ FeMoO ₆ (SFMO)	SCF	LSGM(300)	0.91	[64]
Ni-YSZ	LSCF	YSZ(20)	0.81	[65]
$SrMo_{0.9}Ga_{0.1}O_{3\cdot\delta}$	SCFO	LSGM(300)	0.66	[66]
Sr _{1.9} MgMoO ₆₋₅₂	BSCF	LSGM(280)	0.31	[50]
$Sr_{2}Fe_{1.5}Mo_{0.5}O_{6-\delta}$	SFM	LSGM	0.27	[71]
$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-\delta}$	LSM	LSGM(120)	0.16	[72]
MDC infiltrated Ni-YSZ	LSM-YSZ	YSZ(30)	0.42	[69]
$La_{0.4}Sr_{0.6}Fe_{0.7}Ti_{0.1}Co_{0.2}O_{3\cdot\delta}$	LSFTC-20	LSGM(300)	1.47	[63]
(CoFe@LSFTC-20)				
La _{0.95} Fe _{0.8} Ni _{0.05} Ti _{0.15} O ₃ (Ni@LFNT	LSC	LSGM(350)	0.51	[67]
)				
$(NiO)_{0.05}$ - $(SrTi_{0.8}Nb_{0.2}O_3$ - $\delta)_{0.95}$	LSCF	LSGM(300)	0.38	[29]
(Ni@STN)				
$Pr_{0.8}Sr_{1.2}(Co,Fe)_{0.8}Nb_{0.2}O_{4+\delta}$	P-PSCFN	LSGM(30)	0.44	[68]
(CoFe@K-PSCFN-CFA)				
La _{1.2} Sr _{0.8} Mn _{0.4} Fe _{0.6} O ₄ -	LSCF-GDC	LSGM(280)	0.31	[70]
GDC(Fe@LSMF)				

Table S1 A table of cell performance comparison obtained with various hydrogen electrodes at 800°C using $97\%H_2$ -3%H₂O as the feeding gas