Supplementary information

Novel carbon and sulfur tolerant anode material $FeNi_3$ @$PrBa(Fe,Ni)_{1.9}Mo_{0.1}O_{5+\delta}$ for IT-SOFCs

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Table. S1 Rietveld refinement results for PBFMNi0.3 and $FeNi_3$@PBFMNi0.3 samples: lattice parameters and

Sample	Space group	a (Å)	b (Å)	c (Å)	R_{wp} (%)	R_P (%)	χ^2
PBFMNi0.3	Pm-3m	3.905	3.905	3.905	7.27	5.10	2.71
$FeNi_3$@PBFMNi0.3	Pm-3m	3.938	3.938	3.938	6.89	5.15	3.20

corresponding fitting errors

Table. S2 Oxygen partial pressure (P_{O2}) of humidified 5% H_2/Ar and 10% H_2/Ar at different temperatures.

Temperature (°C)	P_{O2} (atm)	
	5% H_2/Ar	10% H_2/Ar
550	7.93×10^{-27}	1.98×10^{-27}
600	4.93×10^{-25}	1.23×10^{-25}
650	1.97×10^{-23}	4.91×10^{-24}
700	5.41×10^{-22}	1.35×10^{-22}
750	1.07×10^{-20}	2.69×10^{-20}

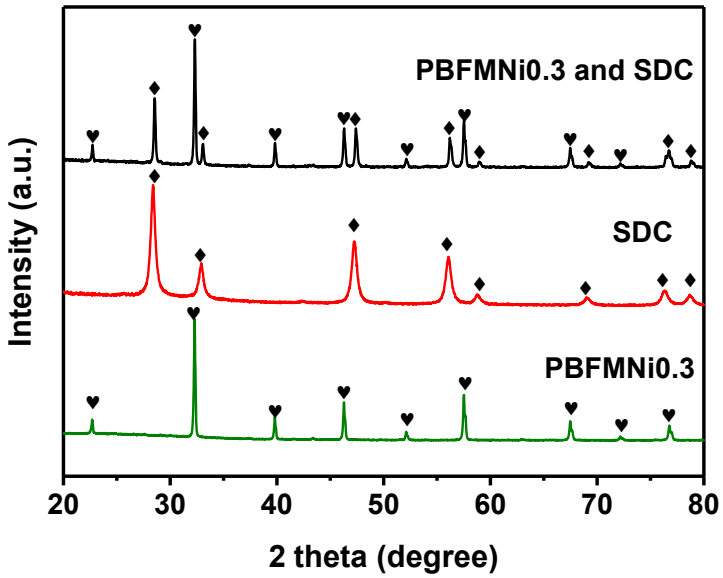

Figure. S1 RT-XRD patterns for PBFMNi0.3 powders, SDC powders and their mixtures calcined at 1000 °C in air for 2 hours.

Figure. S2 TEM image of $FeNi_3$@PBFMNi0.3

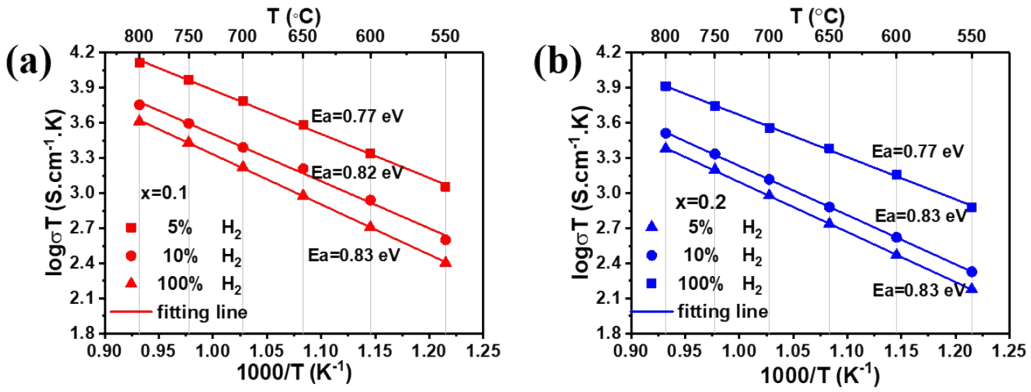

Figure. S3 Arrhenius plots of conductivities for (a) $FeNi_3$@PBFMNi0.1 and (b) $FeNi_3$@PBFMNi0.2 measured at 550-800 °C in wet 5% H_2/Ar, 10% H_2/Ar and 100% H_2, respectively.

ECR technique is based on the equilibrium relationship between the electrical conductivity and the oxygen concentration of nonstoichiometric oxide materials. The conductivity evolution of a sample after an abrupt change in P_{O2} of the ambient atmosphere is recorded as a function of time. A typical model used to estimate surface oxygen

exchange coefficient (k_{chem}) and oxygen diffusion coefficient (D_{cnem}) in ECR analysis is to solve the linear diffusion equation (Fick's second law) with linear absorbing boundary conditions. The corresponding analytical solution is given by

$$g(t) = \frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)} = \frac{c(t)-c(0)}{c(\infty)-c(0)} = 1 - \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\sum_{p=1}^{n} \frac{2L_\beta^2 exp(-\beta_m^2 Dt/x^2)}{\beta_m^2(\beta_m^2+L_\beta^2+L_\beta)} \times \frac{2L_\gamma^2 exp(-$$

Where $g(t)$ is the normalized conductivity, $\sigma(0)$ and $\sigma(\infty)$ represent the initial and final conductivities, respectively, and $c(0)$ and $c(\infty)$ are the corresponding oxygen concentrations. Parameters *x*, *y* and *z* are the sample dimensions, while β_m, γ_n, ϕ_p are the positive, non-zero roots of

$\beta_m tan\beta_m = L_\beta$; $\gamma_n tan\gamma_n = L_\gamma$; $\phi_p tan\phi_p = L_\phi$

The eigenvalues

$L_\beta = \frac{x}{L_c}$; $L_\gamma = \frac{y}{L_c}$; $L_\phi = \frac{z}{L_c}$

Where

$L_c = \frac{D_{cnem}}{k_{chem}}$

The parameters obtained from fitting are the chemical surface exchange coefficient, k_{chem} (m.s^{-1}) and the chemical diffusion coefficient, D_{cnem} (m^2.s^{-1}). When the sample is thin enough, which often means its thickness is smaller than the characteristic thickness L_c， the diffusion step is so fast that the incorporation reaction is limited only by the surface exchange. What's more，the relative change of the oxygen concentration as a function of time is

$$\frac{\partial c(t)}{\partial t} = -\frac{Sk_{chem}}{t}[c(t)-c(0)]$$

In this case, the normalized conductivity obtained in experiment is fitted with the surface exchange controlling E exponential function

$$g(t) = exp(1 - \frac{S}{V}k_{chem}t)$$

Where S (m^2) is the sample surface area and V (m^3) is the sample volume.

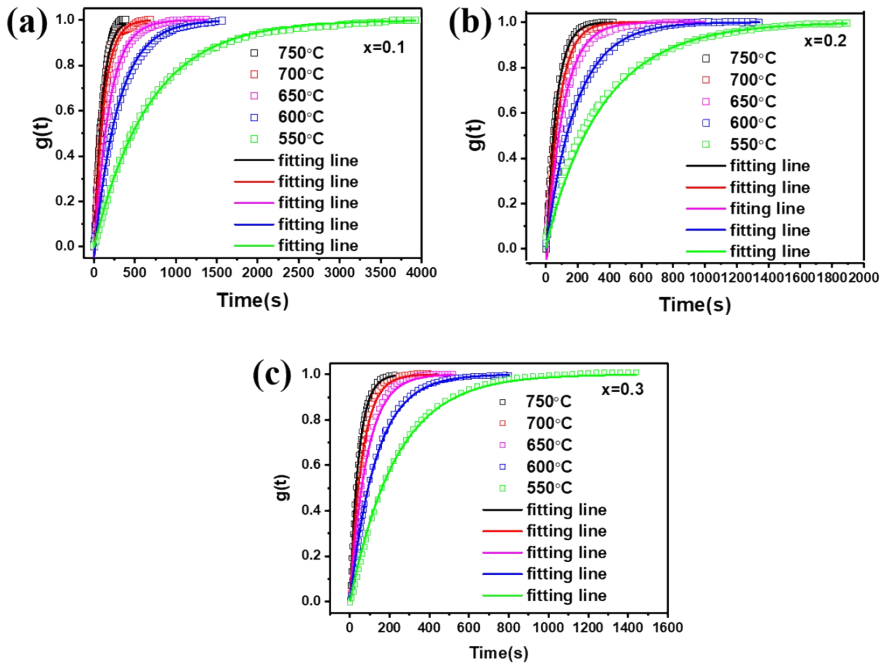

Figure. S4 Electrical conductivity relaxation curves of (a) $FeNi_3$@PBFMNi0.1, (b) $FeNi_3$@PBFMNi0.2 and (c) $FeNi_3$@PBFMNi0.3 at 550-750 °C

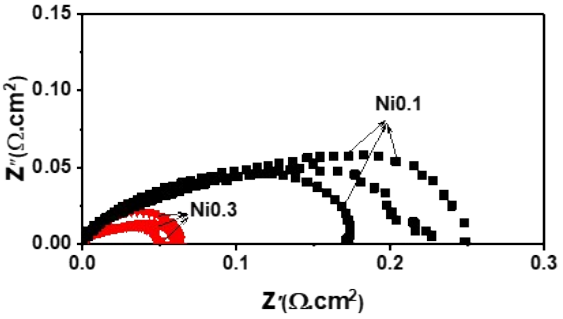

Figure. S5 EIS of button cells using PBFMNi0.1-SDC (black) and PBFMNi0.3-SDC (red) anodes, respectively, operating in wet H_2.

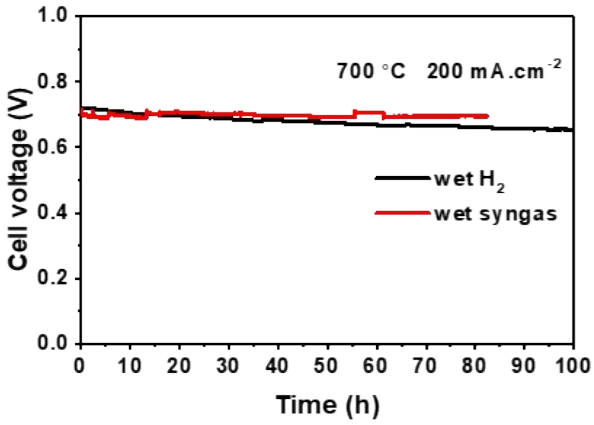

Figure. S6 Cell voltage as a function of testing time for single-cell PBFMNi0.3-SDC|SDC|LSCF-SDC operated under a constant current density of 200 mA cm^{-2} at 700 °C.

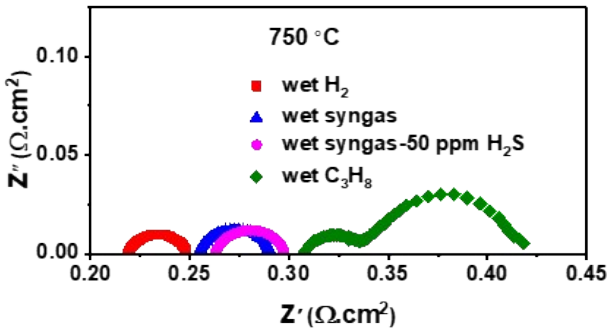

Figure. S7 EIS of SDC electrolyte-supported single-cell PBFMNi0.3-SDC|SDC|LSCF-SDC operating in wet H_2, wet propane, wet syngas and syngas-50 ppm H_2S, respectively at 750 °C.

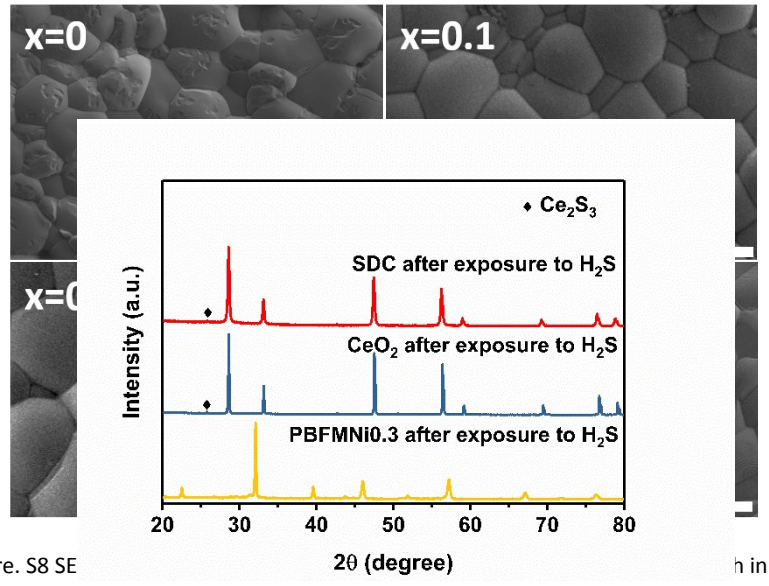

Figure. S8 SE h in air.

Figure S9 XRD patterns for PBFMNi0.3 powders, CeO_2 powders and SDC powders after exposure to H_2 with 50 ppm H_2S for 20 h at 750 ℃

Figure. S10 the SEM images: (a) Cross-sectional view of a whole cell consisting of a PBFMNi0.3-SDC anode and a LSCF-SDC cathode; (b) a PBFMNi0.3-SDC anode and a SDC dense electrolyte; (c) a PBFMNi0.3-SDC anode; (d) Cross-sectional view of a whole cell after 100 h long-term test in syngas with 50 ppm H_2S; (e) a $FeNi_3$@PBFMNi0.3-SDC anode and a SDC dense electrolyte after 100 h long-term test in syngas with 50 ppm H_2S; (f) $FeNi_3$@PBFMNi0.3-SDC anode after long term test in syngas with 50 ppm H_2S.