SUPPLEMENTARY INFORMATION

Figure S1 shows the domain for carbon formation under the experimental conditions

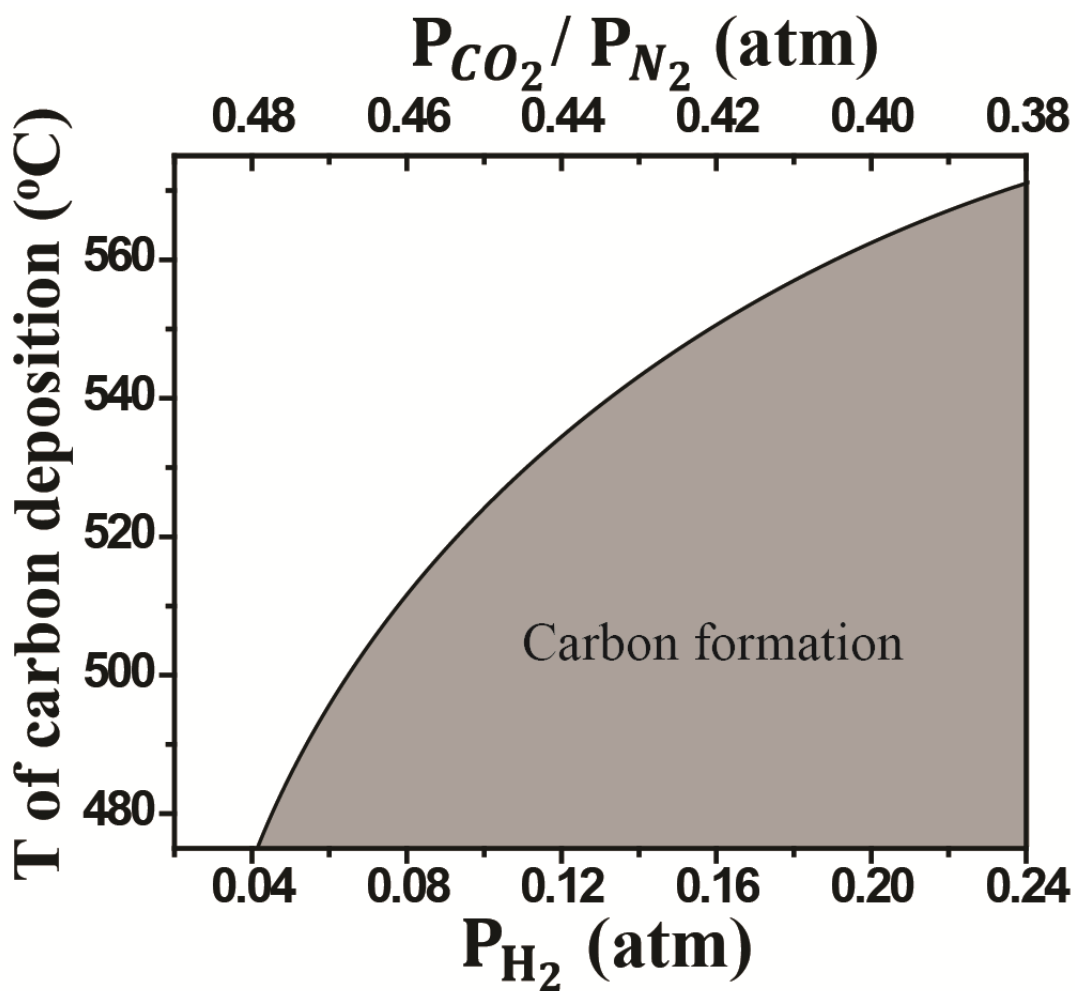employed in this study. Outotec HSC Chemistry 5.0 was used for the thermodynamic

analysis.

Figure S1 Carbon formation domain for a H_2-CO_2-N_2 system determined by

thermodynamic analysis

Derivation of CO₂ flux density equation (4)

For bulk-diffusion controlled charge transport in homogeneous mixed conductors, the classical transport theory can be used to quantify the flux density J_i of the active species i

$$J_i = -\frac{D_i C_i}{RT}\nabla\eta_i = -\frac{\sigma_i}{(z_i F)^2}\nabla\eta_i = -\frac{\sigma_i}{(z_i F)^2}\left(\nabla\mu_i + z_i F\nabla\phi\right) \tag{S1}$$

where D_i, C_i, σ_i and z_i represent the self-diffusivity, concentration, conductivity and charge of species i, respectively; η_i and μ_i are electrochemical and chemical potentials of species i; R, F and T have their usual meanings. Applying eq. (S1) to a presumed homogeneous mixed CO_3^{2-} ($CO_3^{2-}=1$) and O^{2-} ($O^{2-}=2$) conductor, we can arrive at the following flux expression

$$J_1 = -\frac{\sigma_1 \sigma_2}{z_1^2 F^2}\left(\frac{\nabla\mu_1 - z_1/z_2 \nabla\mu_2}{\sigma_1 + \sigma_2}\right) \tag{S2}$$

Considering the local chemical equilibrium $CO_2 + O^{2-} = CO_3^{2-}$, one has

$$J_1 = J_{CO_3^{2-}} = -\frac{1}{4F^2}\left(\frac{\sigma_{CO_3^{2-}}\sigma_{O^{2-}}}{\sigma_{CO_3^{2-}} + \sigma_{O^{2-}}}\right)\nabla\mu_{CO_2} = -\frac{RT}{4F^2}\left(\frac{\sigma_{CO_3^{2-}}\sigma_{O^{2-}}}{\sigma_{CO_3^{2-}} + \sigma_{O^{2-}}}\right)\nabla\ln P_{CO_2} \tag{S3}$$

Assuming that $\sigma_{CO_3^{2-}}$ and $\sigma_{O^{2-}}$ are both P_{CO2} independent, the steady-state flux $J_{CO_2} = J_{CO_3^{2-}}$ can be integrated across the thickness L of the membrane exposed to a gradient of high P_{CO2}' and low P_{CO2}''

$$J_{CO_2} = J_{CO_3^{2-}} = -\frac{RT}{4F^2}\left(\frac{\sigma_{CO_3^{2-}}\sigma_{O^{2-}}}{\sigma_{CO_3^{2-}} + \sigma_{O^{2-}}}\right)\ln\frac{P_{CO_2}''}{P_{CO_2}'} \tag{S4}$$

For dual-phase ceramic-carbonate mixed-ion conductors, the microstructural and concentration effects have to be considered in the flux equation. The microstructural factors

such as porosity ε and tortuosity τ would have a direct impact on the diffusivity of each ion.

The effective diffusivity of species i, D_i^{eff}, can be expressed by

$$D_i^{eff} = \frac{\varepsilon}{\tau} D_i \qquad (S5)$$

On the other hand, the concentration of each species would also be changed by the phase

volume ratio. The effective concentration C_i^{eff} per unit volume can be corrected by

$$C_i^{eff} = \varphi_i C_i \qquad (S6)$$

Substituting eqs. (S5) and (S6) into eqs. (S1-S4) leads to the modified flux equation shown in

eq. (4) in the main context for dual-phase mixed carbonate-ion and oxide-ion conductors

$$J_{CO_2} = -\frac{RT}{4F^2} \frac{\varepsilon}{\tau} \left(\frac{\varphi\sigma_{CO_3^{2-}}(1-\varphi)\sigma_{O^{2-}}}{\varphi\sigma_{CO_3^{2-}} + (1-\varphi)\sigma_{O^{2-}}} \right) \ln \frac{P_{CO_2}^{''}}{P_{CO_2}^{'}} \qquad (S7)$$

where φ is the volume fraction of carbonate phase.