Supporting Information

In-situ Formation of LDH Membranes of Different Microstructure with Molecular Sieve Gas Selectivity

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SI-1 EDXS measurement within the substrate pores of the

ab-oriented NiAl-CO₃ LDH membrane

Fig. S1 EDXS of the cross-section of the ab-oriented NiAl-CO₃ LDH membrane.
SI-2 Powder XRD pattern of NiAl-CO$_3$ LDHs

![XRD pattern of NiAl-CO$_3$ LDHs](image)

**Fig. S2** Powder XRD pattern of NiAl-CO$_3$ LDHs which were synthesized according to the published recipe (M. Wei, X. Y. Xu, X. R. Wang, F. Li, H. Zhang, Y. L. Lu, M. Pu, D. G. Evans and X. Duan, *Eur. J. Inorg. Chem.*, 2006, 2831).
SI-3 EDXS of the top side of the randomly oriented NiAl-CO$_3$ LDH membrane

Fig. S3 Surface EDXS of the randomly oriented NiAl-CO$_3$ LDH membrane.
SI-4 Calculation of the concentration of CO₂ in different precursor solutions

According to Henry's Law: At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

Henry's Law is well-known and can be expressed as follow:

\[ c_{aq} = k_H \cdot p \]

Where:
- \( c_{aq} \): concentration of gas component in solution (molL\(^{-1}\));
- \( k_H \): Henry’s Constant (molL\(^{-1}\)Pa\(^{-1}\));
- \( p \): Partial pressure of gas above the solution (Pa).

The \( k_H \) value for CO₂ in water is available. For instance, when the temperature is between 273 K 303 K, the \( k_H \) value is \( 3.4 \times 10^{-7} \) molL\(^{-1}\)Pa\(^{-1}\) (J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, Inc., 1992).

CO₂ exists in Earth's atmosphere as a trace gas at a concentration of 0.039 % by volume. Data were obtained from the Earth System Research Laboratory, Global Monitoring Division (website: [www.ersl.nogg.gov/gmd/ccgg/trends/#mlo](http://www.ersl.nogg.gov/gmd/ccgg/trends/#mlo)). Data were collected on Oct. 2013.

For the aged DI water, the concentration of dissolved CO₂ in water is calculated as follow:

(aged DI water) \( c_{aq} = 3.4 \times 10^{-7} \times 1.01 \times 10^5 \times 3.9 \times 10^{-4} \) mol/L = 1.3 \times 10^{-5} \) mol/L.

For the CO₂-saturated water, the concentration of dissolved CO₂ in water is calculated as follow:

(CO₂-saturated water) \( c_{aq} = 3.4 \times 10^{-7} \times 1.01 \times 10^5 \) mol/L = 3.4 \times 10^{-2} \) mol/L.

These data are used in the main text to evaluate the influence of concentration of dissolved CO₂ on the microstructure and gas separation performance of prepared LDH membranes.
SI-5 Magnified cross-sectional images of the NiAl-CO$_3$ LDH layer with CO$_2$-saturated water as solvent

Fig. S4 (a) and (b) SEM image of cross-sectional images of LDH layer in-situ grown on γ-Al$_2$O$_3$ modified asymmetric α-Al$_2$O$_3$ substrate with CO$_2$-saturated water as solvent. Hydrothermal growth was kept at 85 °C for 40 h.

Fig. S4 showed the magnified images of the cross-sectional images of NiAl-CO$_3$ LDH membranes prepared with CO$_2$-saturated water as solvent. Unlike the LDH membrane prepared with aged DI water as the solvent, no plate-like morphology characteristic of LDH crystallites was observed, implying that a well-intergrown LDH membrane was formed before LDH crystallites had a chance to evolve with specific crystal faces.
SI-6 Demonstration of the gas separation equipment

Fig. S5 Measurement equipment for both single and mixed gas permeation. MFC: mass flow controller; PC: permeation cell with mounted membrane; GC: gas chromatograph; f: volumetric flow rate; p: pressure.
SI-7 Detailed information on the composition and flux of feed, retentate and permeate during the gas permeability tests

For \textit{ab}-oriented NiAl-CO$_3$ LDH membrane

H$_2$/CO$_2$ mixture:
Feed side: H$_2$: 50.00 ml/min; CO$_2$: 50.00 ml/min; H$_2$/CO$_2$=1.00.
Permeate side: H$_2$: 0.89 ml/min; CO$_2$: 0.15 ml/min; H$_2$/CO$_2$=5.80.
Retentate side: H$_2$: 49.11 ml/min; CO$_2$: 49.85 ml/min. H$_2$/CO$_2$=0.99.

H$_2$/N$_2$ mixture:
Feed side: H$_2$: 50.00 ml/min; N$_2$: 50.00 ml/min; H$_2$/N$_2$=1.00.
Permeate side: H$_2$: 0.96 ml/min; N$_2$: 0.12 ml/min; H$_2$/N$_2$=8.20.
Retentate side: H$_2$: 49.04 ml/min; N$_2$: 49.88 ml/min. H$_2$/N$_2$=0.98.

H$_2$/CH$_4$ mixture:
Feed side: H$_2$: 50.00 ml/min; CH$_4$: 50.00 ml/min; H$_2$/CH$_4$=1.00.
Permeate side: H$_2$: 1.02 ml/min; CH$_4$: 0.12 ml/min; H$_2$/CH$_4$=8.80.
Retentate side: H$_2$: 48.98 ml/min; CH$_4$: 49.88 ml/min. H$_2$/CH$_4$=0.98.

For randomly oriented NiAl-CO$_3$ LDH membrane

H$_2$/CO$_2$ mixture:
Feed side: H$_2$: 50.00 ml/min; CO$_2$: 50.00 ml/min; H$_2$/CO$_2$=1.00.
Permeate side: H$_2$: 0.30 ml/min; CO$_2$: 0.03 ml/min; H$_2$/CO$_2$=10.70.
Retentate side: H$_2$: 49.70 ml/min; CO$_2$: 49.97 ml/min. H$_2$/CO$_2$=0.99.

H$_2$/N$_2$ mixture:
Feed side: H$_2$: 50.00 ml/min; N$_2$: 50.00 ml/min; H$_2$/N$_2$=1.00.
Permeate side: H$_2$: 0.78 ml/min; N$_2$: 0.04 ml/min; H$_2$/N$_2$=18.10.
Retentate side: H$_2$: 49.22 ml/min; N$_2$: 49.96 ml/min. H$_2$/N$_2$=0.99.

H$_2$/CH$_4$ mixture:
Feed side: H$_2$: 50.00 ml/min; CH$_4$: 50.00 ml/min; H$_2$/CH$_4$=1.00.
Permeate side: H$_2$: 0.82 ml/min; CH$_4$: 0.01 ml/min; H$_2$/CH$_4$=78.70.
Retentate side: H$_2$: 49.18 ml/min; CH$_4$: 49.99 ml/min. H$_2$/CH$_4$=0.98.
For randomly oriented ZnAl-NO₃ LDH membrane

H₂/CO₂ mixture:
Feed side:  H₂: 50.00 ml/min; CO₂: 50.00 ml/min; H₂/CO₂=1.00.
Permeate side:  H₂: 0.64 ml/min; CO₂: 0.11 ml/min; H₂/CO₂=5.80.
Retentate side:  H₂: 49.36 ml/min; CO₂: 49.89 ml/min. H₂/CO₂=0.99.

H₂/N₂ mixture:
Feed side:  H₂: 50.00 ml/min; N₂: 50.00 ml/min; H₂/N₂=1.00.
Permeate side:  H₂: 0.71 ml/min; N₂: 0.08 ml/min; H₂/N₂=9.00.
Retentate side:  H₂: 49.29 ml/min; N₂: 49.92 ml/min. H₂/N₂=0.99.

H₂/CH₄ mixture:
Feed side:  H₂: 50.00 ml/min; CH₄: 50.00 ml/min; H₂/CH₄=1.00.
Permeate side:  H₂: 0.66 ml/min; CH₄: 0.05 ml/min; H₂/CH₄=8.80.
Retentate side:  H₂: 49.34 ml/min; CH₄: 49.95 ml/min. H₂/CH₄=0.99.
The relationship between operation temperature and gas permeation behavior of the H$_2$/CH$_4$ mixture

**Fig. S6** H$_2$ Permeance and the separation factor of equimolecular H$_2$/CH$_4$ mixture on ZnAl-NO$_3$ LDH membrane as a function of temperature. $\Delta P = 1$ bar.
SI-9 Thermal stability of prepared ZnAl-NO$_3$ LDH membrane

**Fig. S7** Thermal stability test on prepared ZnAl-NO$_3$ LDH membrane. Equimolecular H$_2$/CH$_4$ mixture was used as feed gas. Test conditions: $\Delta P = 1$ bar, $T = 180 \, ^\circ C$. 