

Supplementary Information

Selective, high-temperature permeation of nitrogen oxides using a supported molten salt membrane

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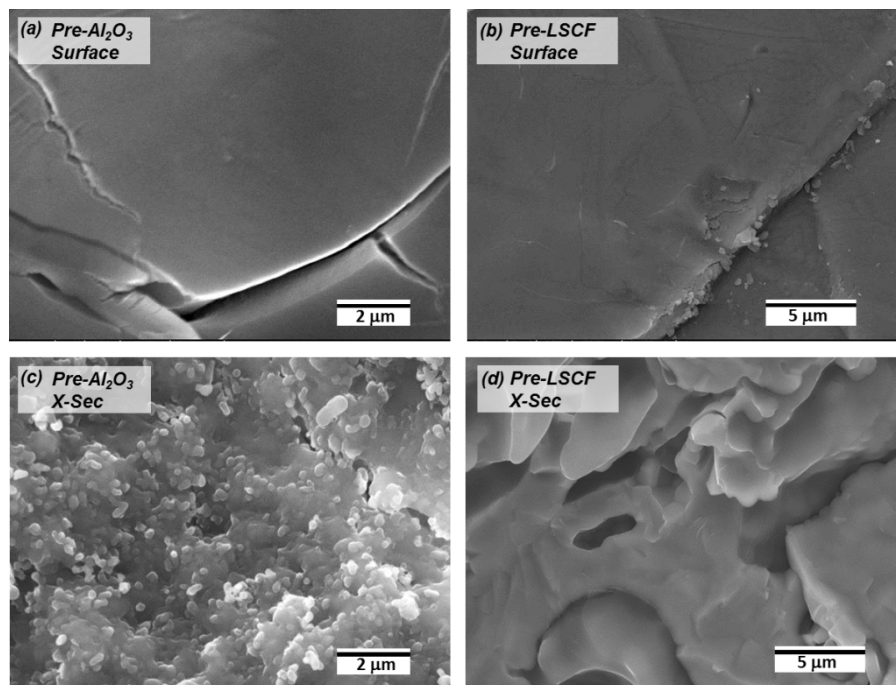
1. Support membrane preparation

LSCF powder (provided by PRAXAIR, $D_{50}=0.8\ \mu\text{m}$) or $\alpha\text{-Al}_2\text{O}_3$ powder (99.95%, Alfa Aesar) was used to prepare porous support membranes. The powder was mixed with approximately 30 wt.% corn starch (Sigma-Aldrich) and then uniaxially pressed at 3 tonnes (ATLAS T25). The green membranes ($3.14\ \text{cm}^2$) were sintered at 1200°C for 5 hours in stagnant air with a heating and cooling rate of $2^\circ\text{C}\ \text{min}^{-1}$. The porosity of the LSCF and Al_2O_3 pellets were 32 % and 54% (Archimedes method), respectively. The sintered porous membranes were polished to a thickness of 1.0 mm for LSCF and 0.75 mm for Al_2O_3 .

2. Dual-phase membrane preparation

The porous LSCF and Al_2O_3 membranes were infiltrated with potassium nitrate (99.95%, Alfa Aesar) to obtain dual-phase membranes. Membranes with nitrate powder (99.95%, Alfa Aesar) placed on top were heated in a furnace to 350°C and held for 1 hour. Potassium nitrate melts above 334°C and subsequently soaks into the membrane via capillary action. The infiltration process was repeated until residual nitrate was seen to be present on the upper surface of the membrane. KNO_3/LSCF and $\text{KNO}_3/\text{Al}_2\text{O}_3$ were prepared for permeation experiments.

3. Microstructure of the dual phase membranes



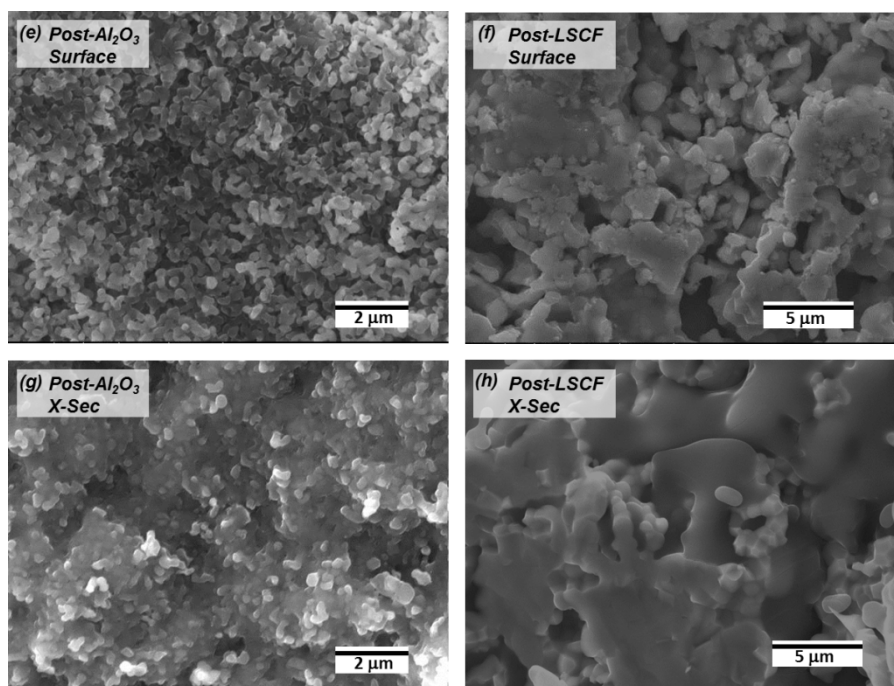


Fig. S1 SEM images of KNO₃/Al₂O₃ and KNO₃/LSCF membranes before (pre-) and after (post-) experiment

Before the experiments, a top layer of solid nitrate on the fresh KNO₃/Al₂O₃ and KNO₃/LSCF membranes (**Fig. S1a and b**) was visible (excess nitrate was observed during the infiltration as a molten layer covering the membrane). Cracks can be observed in the nitrate overlayer possible as a result of the solidification of the molten salt. Such cracks were not visible in the bulk cross-sections of the fresh KNO₃/Al₂O₃ and KNO₃/LSCF membranes (**Fig. S1c and d**). The top solid nitrate overlayer disappeared after experiment (**Fig. S1e and f**) possibly due to further infiltration. As can be seen, there are defects and voids apparent in the fresh KNO₃/Al₂O₃ and KNO₃/LSCF membranes (**Fig. S1c and d**). After the experiments these features seem to have disappeared (**Fig. S1g and h**). This class of dual-phase membrane may have benefited from a self-healing functionality because of the presence of a wetting molten salt. Complete infiltration of the post-experiment KNO₃/Al₂O₃ and KNO₃/LSCF membranes was confirmed by observing SEM images at five or more locations in the membrane cross-section.

4. Experimental setup and procedure

A Schematic diagram of the experimental setup is shown in **Fig. S2**. The pellet membranes were mounted on the top of an alumina tube using a high temperature commercial gold sealant (FuelCellMaterials, AU-I). Cylinders of (C1) 1% NO₂, 1% CO₂ and 1% N₂; (C2) 1% NO₂, 1% CO₂ and 20% O₂; (C3) argon; (C4) 1% CO₂, 1% N₂, 20% O₂; (C5) 5% NO₂, 1%CO₂, 20% O₂; (C6) 200 ppm SO₂ were used. In all cases the balance gas used was argon. Compositions in the feed side inlet were obtained by mixing these gases through mass flow controllers (Brooks, SLA5850). The flows on both the feed and permeate sides were maintained at 30 cm³ (STP)

min^{-1} . N_2 served as a trace gas for periodic leak detection. The permeate side outlet was connected to a NO_x analyser (X-stream, X2GP) and a mass spectrometer (GeneSys) ($\text{CO}_2/\text{N}_2/\text{O}_2$ analysis) in series.

Cylinders C1, C2, C4 and C5 were from StG with a relative accuracy of mole fractions of $\pm 2\%$; Cylinders C3 and C6 were from BOC; C6 had a relative accuracy of mole fractions better than $\pm 5\%$.

The feed side of the membrane was exposed to 200 ppm SO_2 for 2, 4 and 8 hours. After each exposure (2, 4 or 8 hours), the feed side inlet was switched to argon for two hours followed by a NO_2 -containing stream (1% NO_2 , 1% CO_2 and 20% O_2). A similar procedure was also applied for H_2O introduction, where the feed side of the membrane was exposed to around 2.8 % H_2O .

The reactor was placed in a temperature programmable furnace (Vecstar, 2416CG-1100) and held at 100°C prior to heating to 450°C to perform permeation experiments (heating rate was 2°C min^{-1}). Experiments were performed by changing the feed gas inlet composition and monitoring the response of the permeate side outlet composition.

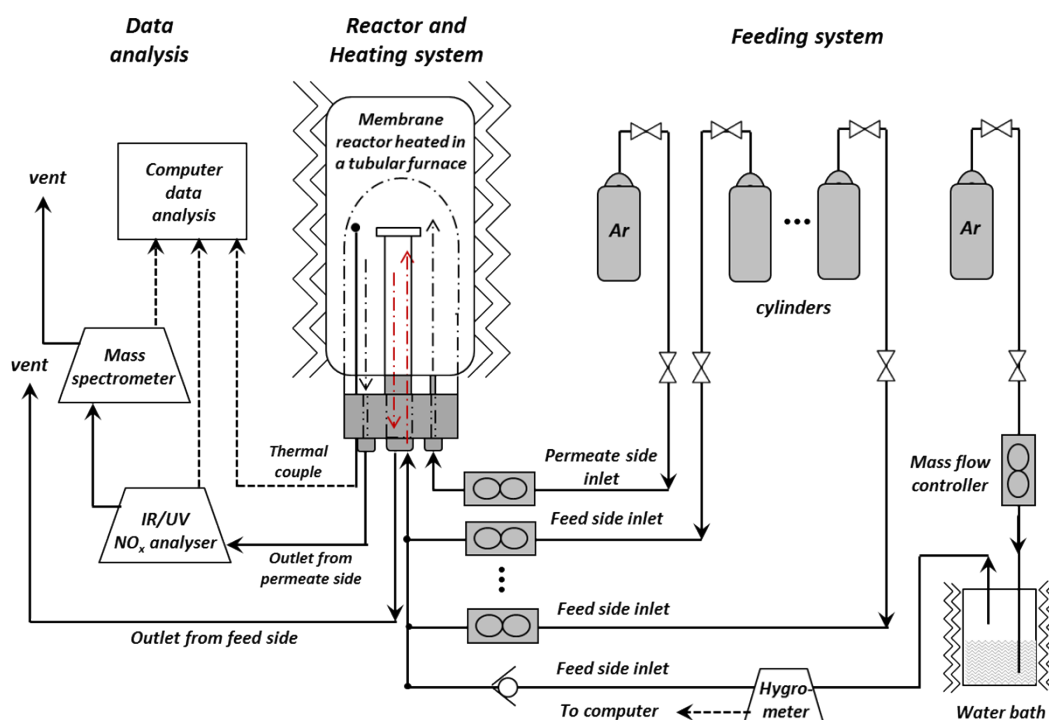
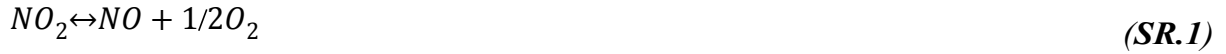


Fig. S2 Schematic diagram of experiment set-up

5. Equilibrium constant

We must also recall that at temperatures of 450°C there is a dynamic equilibrium between NO_2 , NO and O_2 (Reaction *SR.1*),



$$K_{450^\circ C} = \frac{[NO][O_2]^{1/2}}{[NO_2]} = 2.55 \times 10^{-3} \text{ atm}^{1/2} \quad (SE.1)$$

This means that NO₂ and NO in the gas phase are interchangeable, that is, NO₂ may permeate across the membrane but may be observed as NO and O₂ on the permeate side. If on the permeate side we use typical an O₂ mole fraction of 100 ppm and a NO₂ mole fraction of 100 ppm then the equilibrium NO mole fraction will be 26 ppm. This indicates that NO present on the permeate side could be the result of NO₂ decomposition. On the feed side the presence of a significant oxygen mole fraction means that NO₂ decomposition is not a problem and there is little NO present.

6. Calculation of permeance

Here we evaluate the total permeance for NO_x and not individual permeances for NO₂ and NO. The reason for this is the reversible reaction, Reaction **SR.1** as well as the possibility that the LSCF itself may be undergoing a slow oxidation (or reduction) over time that could favour NO appearance on the permeate side over NO₂.

$$\text{Permeance} = (x_{NO_2,perm} + x_{NO,perm}) \times F_{outlet,perm}/V/S/\Delta P \quad (SE.2)$$

$$\Delta P = (x_{NO_2,feed} - x_{NO_x,perm}) \times P \approx x_{NO_2,feed} \times P \quad (SE.3)$$

Where, $F_{outlet,perm}$ is the outlet flow rate in the permeate side, approximately 30 cm³ (STP) min⁻¹ or 0.5 cm³ (STP) s⁻¹; V is the molar volume of an ideal gas at STP; S is the membrane working area (0.5 cm² for both KNO₃/LSCF and KNO₃/Al₂O₃ membranes in **Fig. S3** and 0.32 cm² for KNO₃/LSCF and 0.40 cm² for KNO₃/Al₂O₃ in **Fig. S4**); $x_{NO_2,feed}$ is the inlet NO₂ mole fraction to the feed side and $x_{NO_x,perm}$, $x_{NO_2,perm}$ and $x_{NO,perm}$ are the outlet NO_x (NO and NO₂), NO₂ and NO mole fractions in the permeate side outlet respectively.

7. Experiments with different nitrogen dioxide mole fractions in the feed side inlet

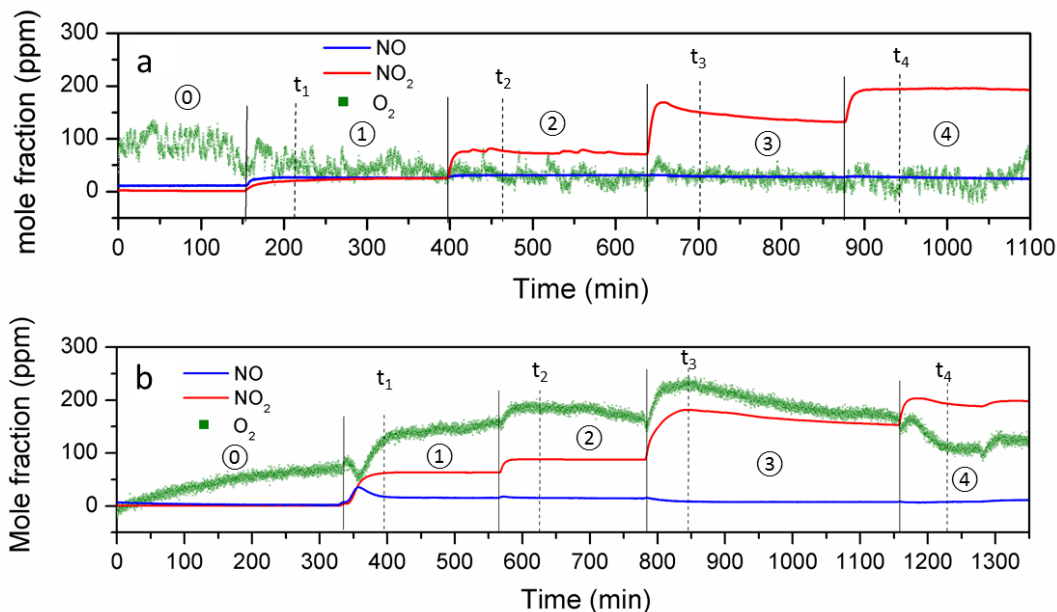


Fig. S3 Mole fraction of NO_2 , NO and O_2 in the permeate side outlet for (a) $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane and (b) KNO_3/LSCF membrane. Step 0 to 4 with different mole fractions of NO_2 at 0%, 0.5%, 1%, 3% and 5% in the feed side inlet, where the mole fraction of O_2 and CO_2 were kept constant at 20% and 1%, respectively. Argon used as the sweep gas and the flow rate in both sides was $30 \text{ ml (STP) min}^{-1}$.

8. Experiments with different oxygen mole fractions in the feed side inlet

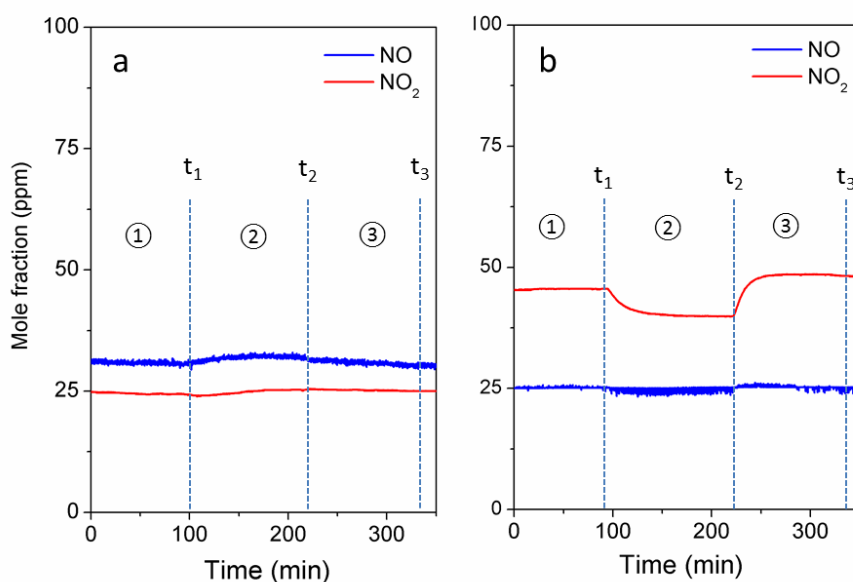


Fig. S4 Mole fraction of NO_2 and NO in the permeate side outlet for (a) $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane and (b) KNO_3/LSCF membrane. Stage 1 to 3 with different mole fractions of O_2 of 10%, 0% and 20% in the feed side inlet, where the mole fractions of NO_2 and CO_2 were kept constant at 1%, respectively. Argon used as the sweep gas and the flow rate in both sides was $30 \text{ ml (STP) min}^{-1}$.

9. Water exposure

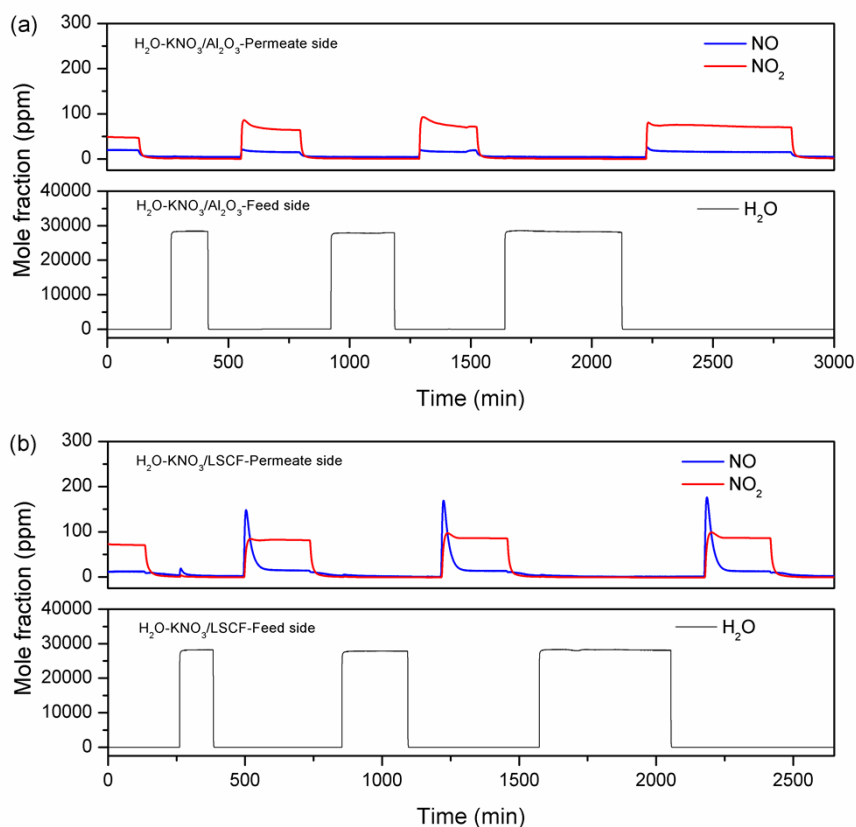
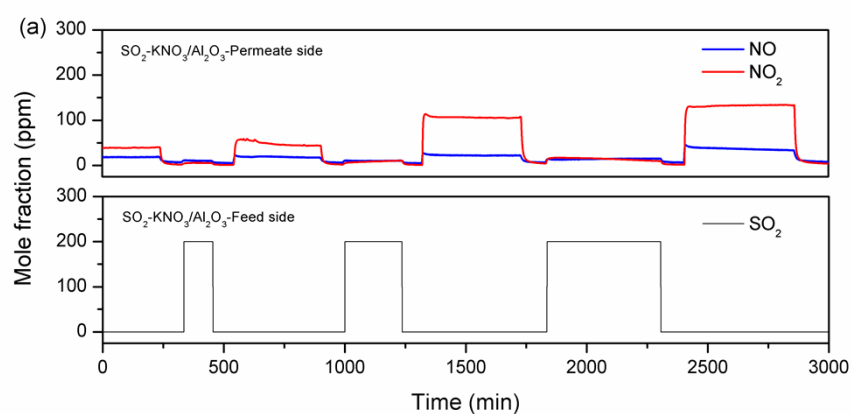


Fig. S5 Effect of H₂O exposure to the permeate side on NO_x permeation of (a) KNO₃/Al₂O₃ and (b) KNO₃/LSCF membranes. The feed side of each membrane was exposed to H₂O (2.8% in argon) for 2, 4 and 8 hours, subsequently, after each step (2, 4 or 8 hours), the feed side inlet was switched back to the NO₂-containing stream (1% NO₂, 1% CO₂ and 20% O₂). Between the H₂O and NO₂ stream switching, there was a 2 hours purge with Ar.

10. Sulphur dioxide exposure



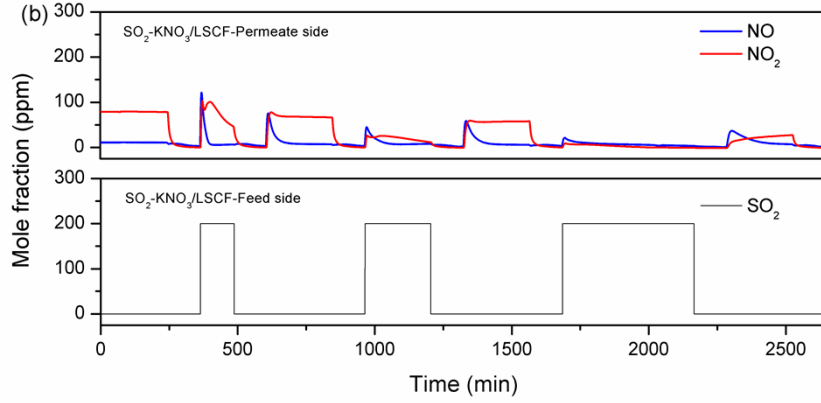


Fig. S6 Effect of SO₂ exposure to the permeate side on NO_x permeation of (a) KNO₃/Al₂O₃ and (b) KNO₃/LSCF membranes. The feed side of each membrane was exposed on SO₂ (200 ppm in argon) for 2, 4 and 8 hours, subsequently, after each step (2, 4 or 8 hours), the feed side inlet was switched back to the NO₂-containing stream (1% NO₂, 1% CO₂ and 20% O₂). Between the SO₂ and NO₂ stream switching, there was a 2 hours purge with Ar.

11. Separation factor

The separation factor (α) for a binary mixture is defined as

$$\alpha_{ij} = \frac{\left(\frac{x_{i,perm}}{x_{j,perm}} \right)}{\left(\frac{x_{i,feed}}{x_{j,feed}} \right)} \quad (SE.4)$$

Where $x_{i,perm}$ and $x_{i,feed}$ are the mole fraction of component i in the permeate side outlet and feed side inlet; the subscripts i, j refer to the component in the mixture.

12. Measurement uncertainty

12.1 NO_x analyser

The non-dispersive infrared and ultraviolet NO_x analyser detects NO (full scale (FS): 0-3000 ppm) and NO₂ (FS: 0-500 ppm), respectively. The NO baseline drift was smaller than 9 ppm over a 3000-minute experiment with an NO₂ drift that was much smaller than this. The mass spectrometer was not suitable for NO and NO₂ analysis because of the dynamic equilibrium between these species which would be of concern particularly at lower pressures.

12.2 Mass spectrometer

The drift of the mass to charge ratio of 32 signal is significant and averages up to 100-120 ppm over 12 hours. Oxygen permeation rates were thus estimated from dynamic changes in the 32 signal in response to changes in the feed side inlet composition using data taken at the time of the change in composition and a time one hour later. Consequently the drift in the signal is

expected to be on average less than 10 ppm. Therefore, for oxygen-related calculations, such as separation factor, an uncertainty can be estimated on this basis and has been presented in oxygen-related data.