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

NO_x treatment is an important environmental technology. We demonstrate a dual-phase (molten salt–solid phase) membrane that is selective for NO_x permeation. Such a membrane could be used to improve NO_x sensing devices or even develop new approaches to NO_x treatment.

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Molten nitrate/ceramic membranes of $\text{KNO}_3/\text{Al}_2\text{O}_3$ and $\text{KNO}_3/\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) were designed and successfully operated for the selective permeation of nitrogen oxides. With the presence of oxygen on the feed side of the membrane, the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane showed no measurable oxygen permeation while the KNO_3/LSCF membrane exhibited nitrogen dioxide and oxygen co-permeation. For the KNO_3/LSCF membrane, a permeance of up to $6.9 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was achieved while the nitrogen dioxide to oxygen permeate ratio appeared to be approximately constant with a value of around unity.

Nitrogen oxides (NO_x), which include nitrogen monoxide (NO) and nitrogen dioxide (NO_2), are responsible for acid rain, ground-level ozone and smog and harmful effects to human health. Efficient treatment systems, such as selective catalytic reduction (SCR) or non-selective catalytic reduction (NSCR) exist for stationary and large vehicular systems.^{1,2} However, nitrogen oxide sensors are critical to the effective performance of such treatment systems. Sensors tend to be amperometric in nature; they reduce nitrogen oxides at an electrode resulting in a sensor signal. However, the selectivity of this reduction process is poor and any oxygen present interferes with the measurement.³ One way to improve the sensor design would be to use a NO_x -selective membrane to prevent oxygen from contacting the electrode in the first place. A successful sensor membrane or barrier should exhibit a high selectivity for NO_x permeation over, in particular, oxygen and should also withstand the harsh (acid gases, particulates), high temperature environment associated with combustion exhausts. In the absence of a high selectivity of nitrogen oxides over oxygen, permeation of nitrogen oxides and oxygen within a range of known ratios would also be beneficial.

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

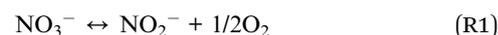
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Broader context

NO_x treatment is an important environmental technology. Such treatment relies upon robust NO_x sensors. However, most sensors suffer from a lack of selectivity when operating in oxygen-containing atmospheres. Here we demonstrate a membrane that is selective for NO_x permeation. Such a membrane could be used to improve NO_x sensing devices or even develop new approaches to NO_x treatment.

To the best of our knowledge, no suitable membrane has ever met these critical requirements.

Here we design a dual phase membrane for the selective permeation of nitrogen oxides (note that some of the potential permeation mechanisms also result in oxygen co-permeation). This membrane employs a molten alkali metal nitrate held within the pores of an electronically conducting ceramic support. Here we use potassium nitrate as the alkali metal nitrate. Potassium nitrate has a melting point of around 334 °C. It is stable in air to 530 °C, undergoing conversion to nitrite with the release of oxygen (reaction (R1)) at higher temperatures,⁴



Here we use $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) as the electronically conducting host phase. We use a ceramic to avoid problems with corrosion due to the high temperatures and molten salt environment. LSCF also exhibits appreciable oxygen-ion conductivity above about 700 °C. However, here we operate at 450 °C and do not expect oxygen-ion transport to be important. Membranes of KNO_3/LSCF or $\text{KNO}_3/\text{Al}_2\text{O}_3$ were fully infiltrated with potassium nitrate (ESI, Fig. S1†).

As shown in Fig. 1a, nitrate ions would be expected to be mobile in the nitrate melt. It may be possible for gas phase nitrogen dioxide to react with gas phase oxygen and electrons from the support to form such nitrate ions. This combination of processes would be expected to result in co-transport of nitrogen dioxide and oxygen across the membrane (reaction (R2)),

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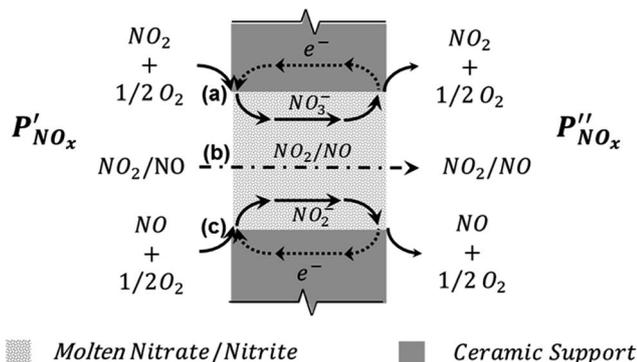


Fig. 1 Membrane transport mechanisms ($P'_{NO_x} > P''_{NO_x}$).



It may also be possible for nitrogen dioxide to dissolve as a molecular species (as opposed to an ionic species but including species where *e.g.* the molecular nitrogen dioxide might associate with a pre-existing species in the melt such as a nitrate ion) in the molten salt, thus resulting in nitrogen dioxide transport through a solution-diffusion process (see Fig. 1b). Additionally if nitrite ions are present in the melt it may be possible for nitrogen monoxide to react with oxygen and support electrons to form a mobile nitrite species which is transported across the membrane (Fig. 1c and reaction (R3)),



In addition nitrogen monoxide may also undergo a solution-diffusion process (see Fig. 1b). The transport mechanisms discussed above indicate that this type of membrane may have selectivity towards nitrogen oxides with oxygen co-permeation while having no fundamental trade-off between selectivity and permeability as is the case of polymeric membranes.⁵

In this study, we also employ an alumina-supported membrane. Alumina is an insulator under the conditions employed here so we do not expect reactions (R2) or (R3) to occur. We suggest that nitrogen dioxide and nitrogen monoxide transport would more likely occur *via* solution-diffusion. (Note that the mechanisms described here are not an exhaustive list as the nature of the melt is likely to be complex, however, the use of an electronically conducting support and an insulating support may nevertheless be expected in general to influence the permeation mechanism.)

A typical exhaust stream from a motor vehicle consists of 100–4000 ppm nitrogen oxides, 7–13% carbon dioxide and 0.2–15% oxygen and also contains carbon monoxide and hydrocarbons and may have a temperature of 400–600 °C.⁶ Here, the mole fractions of both carbon dioxide and nitrogen dioxide in the feed side inlet to the membrane were selected to be 1%, with an oxygen mole fraction varied from 0% to 20%. (The nitrogen dioxide mole fraction was selected to be higher than that in a typical exhaust in order to reduce relative errors in measurement; no carbon monoxide or hydrocarbon was used as these

are present at lower mole fractions than carbon dioxide.) The experiments were conducted at a temperature within the typical range of exhaust gas outlet temperatures, which is 450 °C, by sealing a pellet membrane of KNO_3/LSCF or $\text{KNO}_3/\text{Al}_2\text{O}_3$ onto an alumina tube using a high temperature commercial gold sealant (ESI, Fig. S2†).

Fig. 2 shows the total permeance of nitrogen oxides obtained when different mole fractions of nitrogen dioxide were supplied in the feed side inlet; the mole fraction of oxygen in the feed side inlet was kept constant at 20%. Note that although there was always 1% carbon dioxide present in the feed side inlet no carbon dioxide permeation was ever observed for any of the membranes.

For the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane, the permeance of nitrogen oxides appeared to be approximately constant when the mole fraction of nitrogen dioxide was modified in the feed side inlet. This constant permeance would be consistent with a driving force as a result of a difference in nitrogen dioxide mole fraction alone and may be the result of a process that does not require the involvement of oxygen (*e.g.*, Fig. 1b). We also found that, within experimental error, there was no oxygen permeation for the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane (ESI, Fig. S3†) consistent with this suggestion.

For the KNO_3/LSCF membrane, the permeance of nitrogen oxides increased as the mole fraction of nitrogen dioxide decreased in the feed side inlet. If nitrate is the species responsible for permeation (Fig. 1a) then we would expect the oxygen mole fraction difference across the membrane to contribute to the overall driving force (note the necessity of oxygen in the reaction (R2) of this oxygen-facilitated process). This would mean that on decreasing the nitrogen dioxide mole fraction in the inlet the driving force for permeation will decrease by a smaller factor resulting in an increase in permeance. The other possibility is that the permeation rate is surface controlled and the involvement of oxygen in the reaction (R2) again leads to an increase in permeance with a decrease in nitrogen dioxide mole fraction in the inlet to the

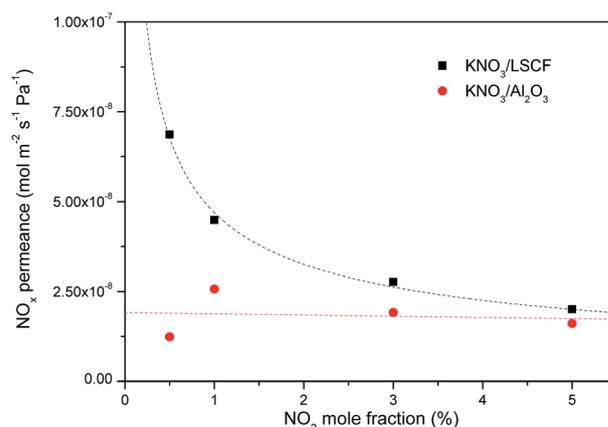


Fig. 2 Permeance of nitrogen oxides with different mole fractions of nitrogen dioxide in the feed side inlet, where the mole fraction of oxygen in the feed side was kept constant at 20%. Argon was used as the sweep gas inlet.



feed side. The fact that we also see evidence for oxygen permeation linked to the nitrogen oxide permeation supports these mechanisms (ESI, Fig. S3†). We must note that in the case of the KNO_3/LSCF membrane we would also expect to see the impact of any process that does not require the involvement of oxygen (*e.g.*, Fig. 1b) superimposed upon the effect of the oxygen-facilitated process (*e.g.*, Fig. 1a). And indeed if oxygen is removed from the feed side inlet to the KNO_3/LSCF membrane we see a decrease in the permeation of nitrogen oxides but this permeation does not go to zero consistent with a permeation mechanism being in place that does not require gas phase oxygen (ESI, Fig. S4†). If oxygen is removed from the feed side inlet to the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane we see no change in the permeation rate of nitrogen oxides (ESI, Fig. S4†). We must note that there is evidence that the composition of molten salts is complex and there may be other species that exist in the melt, such as oxygen ions, which can facilitate the gas transport. The occurrence of such species would of course impact the transport processes that are possible.

For both the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane and the KNO_3/LSCF membrane no carbon dioxide was ever detected in the permeate side outlet. The nitrogen oxide permeance in the KNO_3/LSCF membrane was $4.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ in the case of the 1% nitrogen dioxide/20% oxygen mixture. The permeance of the KNO_3/LSCF membrane reached a maximum of $6.9 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ with a lower nitrogen dioxide mole fraction of 0.5% in the feed side inlet. For the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane, the nitrogen oxide permeance is $2.6 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ in the case of 1% nitrogen dioxide/20% oxygen mixture in the feed side inlet, which is lower than the nitrogen oxide permeance obtained from the KNO_3/LSCF membrane under the same conditions (Fig. 2) (note that in addition the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane is slightly thinner than the KNO_3/LSCF membrane, 0.75 *versus* 1 mm thickness). Although we do not know of any similar membrane work a comparison to a related class of carbonate/ceramic membrane is useful. Lin and co-workers studied carbon dioxide permeation in carbonate/ceramic membranes.^{7,8} They found that at 700 °C, the carbon dioxide permeance was around $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. Teplyakov and co-workers predicted values of nitrogen dioxide permeance in polymer membranes by a mathematic method using a solution-diffusion model.⁹ They found that a theoretical nitrogen dioxide permeance could reach $1.3 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ (assuming a membrane thickness of 1 mm).

Oxygen was observed in the permeate side outlet of the KNO_3/LSCF membrane (there was no measureable oxygen permeation for the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane). Fig. 3 shows the separation factor of nitrogen oxides to oxygen for the KNO_3/LSCF membrane. The separation factor for 0.5% nitrogen dioxide/20% oxygen in the feed side inlet was 57 ± 8 . The separation factor decreased with an increase in the mole fraction of nitrogen dioxide in the feed side inlet (oxygen mole fraction was constant at 20%). The mole fraction of oxygen detected in the permeate side outlet appears, within experimental error, to be proportional to the mole fraction of nitrogen dioxide in the permeate side outlet (ESI, Fig. S3†). A ratio of approximately 1 : 1 nitrogen dioxide to oxygen in the permeate

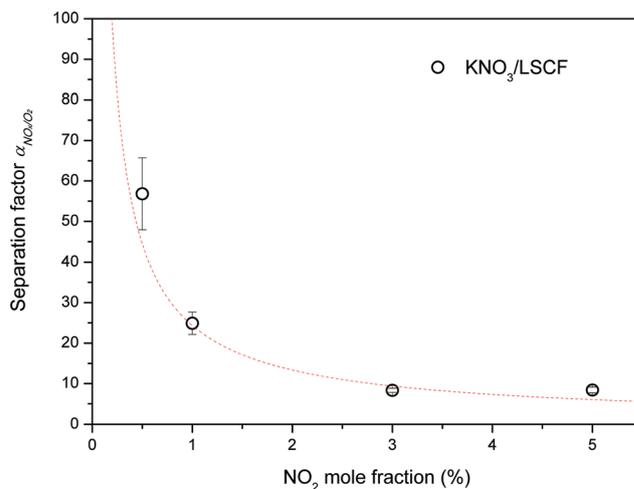


Fig. 3 Separation factors of nitrogen oxides to oxygen with 20% oxygen and different mole fractions of nitrogen dioxide (0.5%, 1%, 3% and 5%) in the feed side inlet for the KNO_3/LSCF membrane.

side outlet was observed. This ratio is lower than the ratio of 2 : 1 expected from the reaction (R2). However, there is a significant degree of uncertainty in this measured ratio due to drift in the mass to charge ratio of 32 signals from the mass spectrometer making a conclusive statement somewhat difficult. Differences in this ratio could also arise from differences in the mechanisms suggested and the nature of the species present in the melt.

The effects of sulphur dioxide and water on permeation were also studied. These gases coexist with nitrogen oxides in a typical exhaust stream. The feed side of the membrane was exposed to sulphur dioxide (200 ppm in argon) or water (2.8% in argon) for 2, 4 and 8 hours. In between these exposures permeation experiments were performed using a feed side inlet composition of 1% nitrogen dioxide, 1% carbon dioxide and 20% oxygen in argon. Water exposure had a promotional effect on nitrogen oxide permeation for both the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane and the KNO_3/LSCF membrane (ESI, Fig. S5†). Sulphur dioxide exposure had a very different effect on permeation. For the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane, a significant increase in the nitrogen oxide mole fraction in the permeate side outlet can be observed after each subsequent sulphur dioxide exposure (ESI, Fig. S6†). For the KNO_3/LSCF membrane, a significant decrease in the nitrogen oxide mole fraction in the permeate side outlet can be observed. This was accompanied by a loss of nitrogen oxides from the membrane during the actual sulphur dioxide exposure steps themselves. This suggests that sulphur dioxide may displace, *e.g.*, nitrate ions, this process being particularly pronounced in the case of the LSCF support perhaps because of its surface chemistry.

Conclusions

This work successfully demonstrates a new concept for the selective permeation of nitrogen oxides using a molten nitrate/ceramic membrane. Both the $\text{KNO}_3/\text{Al}_2\text{O}_3$ membrane and a



KNO₃/LSCF membrane exhibited selective permeation of nitrogen oxides. For the KNO₃/Al₂O₃ membrane no oxygen was detected in the permeate side outlet indicating that nitrogen oxide transport through the membrane may depend upon the dissolution of molecular nitrogen oxides in the molten nitrate salt. For the KNO₃/LSCF membrane, permeance of up to $6.9 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ was achieved while the nitrogen dioxide to oxygen permeate ratio appeared to be approximately constant with a value of around unity. The co-permeation of oxygen with nitrogen dioxide suggests the presence of an oxygen-facilitated transport process. Nitrate/ceramic membranes are suggested as promising candidates for use in nitrogen oxides sensing and gas separation applications.

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