MOLTEN SALT ELECTROCATALYTICAL MEMBRANE CELLS FOR FLUE GAS CLEANING

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ABSTRACT

Initial investigations have been performed regarding the possible use of a molten salt membrane cell for removal of nitrogen oxides from flue gases. At a fixed potential of 1.0 V the performance of a two chamber electrochemical test cell shows that NO indeed can be transported through the cell. The most probable electrode processes involve one electron forming NO₂⁻ at the cathode which is oxidized to O₂ and NO at the anode. Small amounts of nitrite - below around 6 mol% - and temperatures around 300 °C seem to be most appropriate for cell performance. Thus it seems that the presence of NO₂⁻ in the electrolyte enhances the electrode process leading to uptake of NO in the melt. The results seem promising for further research regarding development of a prototype membrane cell where NO in flue gases from e.g. electrical powerplants may be separated and further processed to HNO₃ of commercial grade.

INTRODUCTION

Emission of the gases SO₂ and NO from powerplants and other industrial sources is of great concern due to their harmfulness to the environment e.g. through formation of "acid rain" in the atmosphere. Usually SO₂ is removed from the flue gas by the wet scrubber process where mainly CaSO₄ is formed by treating the gas with lime. Thus a new waste is formed if not all of the produced gypsum can be used for commercial materials. NO is almost always removed catalytically by so-called SCR (Selective Catalytic Reduction) of NO by NH₃ forming N₂ and H₂O. Here the most common catalyst is vanadium oxides supported on anatase (V₂O₅/TiO₂) operating around 380 °C. This catalyst deactivates however gradually due to e.g. alkali salts in the flue gas. There is therefore a need for alternative processes for flue gas cleaning. We are trying to develop feasible membrane processes where the pollutants are removed selectively and obtained in a concentrated form for further processing to useful products e.g. oleum and nitric acid.

These membrane processes have several advantages compared to the conventional methods e.g. the only reactant is electricity, no chemicals are used, a useful product is obtained, no need for cooling or reheating of the flue gas, continuous processes without use
of e.g. pumps for liquids, regeneration of solvents or large pressure drops. Previously (1, 2) we have been dealing with an electrocatalytic membrane cell for removal of \( \text{SO}_2 \) by combined catalytic oxidation and electrolytical transport leading to formation of \( \text{SO}_3 \) and the possible processing to commercial grade sulfuric acid or oleum on the product side of the cell. Here we present our initial attempts to develop a similar cell for removal of NO from flue gas.

![Figure 1. Membrane cell for NO removal](image1)

![Figure 2. Electrochemical test cell for NO removal processes. Gold electrodes are immersed in the nitrate melt where gas in and outlet to the chambers are indicated](image2)

**EXPERIMENTAL**

Previously it has been observed that the \( \text{K}_2\text{S}_2\text{O}_7/\text{V}_2\text{O}_5 \) electrolyte used for \( \text{SO}_2 \) membrane cells is not useful for transporting NO, probably due to a very small solubility in the molten electrolyte. However, possibly nitrate melts are more appropriate for this purpose and this type of electrolytes have therefore been investigated in the present work.

A principal sketch of the cell is shown in Figure 1, based on the well known
technology for molten carbonate fuel cells (MCFC). The flue gas enters the cathode chamber with a porous cathode of lithiated nickel oxide. NO passes under the influence of the electric field through the membrane melt which is supported by a yttria stabilized zirconia matrix and leaves the cell through the porous anode for finally being collected in the sweep gas (e.g. air) for further processing to HNO₃. Initial tests of the nitrate/nitrite electrolytes were performed in a glass cell as shown in Figure 2.

RESULTS AND DISCUSSION

The results of the electrolysis performed on a low melting 48.9% NaNO₂, 6.9% NaNO₃ and 44.2% KNO₃ electrolyte (m.p. ~140 °C) is displayed in Figure 3 where the evolved NO gas is plotted vs. the applied current. Further calculations show that the electrode process leading to the formation of NO is a one electron process. Based on this the most probable electrode reactions taking place in the cell are:

Cathode:  \[ \text{NO} + \text{NO}_3^- + e^- \rightarrow 2\text{NO}_2^- \]  \[1\]

Anode:  \[ 2\text{NO}_2^- \rightarrow \text{NO} + \text{NO}_3^- + e^- \]  \[2\]

Cell reaction:  \[ \text{NO}(\text{dilute}) \rightarrow \text{NO}(\text{conc.}) \]  \[3\]

Figure 3. Observed concentration of NO from anode chamber vs. current, \( T = 250 \) °C, melt composition: NaNO₂(48.9 %) – NaNO₃ (6.9 %) – KNO₃ (44.2 %)

Initial investigations using the glass cell has revealed that uptake and transport of NO indeed takes place. Thus as shown in Figure 4 the measured current increases when NO containing N₂ is bubbled through the melt at a constant potential, indicating the onset of an active electrochemical transport process when NO is administrated to the cathode chamber.
The measured currents are of course small due to the experimental setup using small electrode areas with poor contact to the incoming gas. Increasing the temperature also increases the current and thereby the transport of NO through the melt. When NO is not added, an orange gas is evolved in the anode chamber indicating formation of NO$_2$ by anodic oxidation of the nitrate solvent ($2$NO$_3^-$ = 2NO$_2$ + O$_2$ + 2e$^-$) instead of oxidation of NO$_2^-$ forming the colorless NO gas.

**Figure 4.** Current at 1.0 V vs. temperature for different flow rates of 1,000 ppm NO in N$_2$

Melt composition: KNO$_3$(40 %) – NaN$_3$ (60 %)

Addition of KNO$_2$ to the nitrate electrolyte increases the current and thereby the transport of NO markedly as seen in Figures 5-7. However, as shown in Figure 8, the promotion is only in favor of NO transport up to around 6 mol% KNO$_2$, since increasing addition beyond that amount seems to lead to increased decomposition of the solvent melt.
Figure 5. Current at 1.0 V vs. temperature for different flow rates of 1,000 ppm NO in N₂
Melt composition: KNO₃(37.8 %) – NaNO₃ (56.6 %) – KNO₂ (5.6 %)

Figure 6. Current at 1.0 V vs. temperature for different flow rates of 1,000 ppm NO in N₂
Melt composition: KNO₃(41.9 %) – NaNO₃ (48.0 %) – KNO₂ (10.1 %)
**Figure 7.** Current at 1.0 V vs. temperature for different flow rates of 1,000 ppm NO in N₂
Melt composition: KNO₃ (35.5 %) – NaNO₃ (53.3 %) – KNO₂ (11.2 %)

**Figure 8.** Current at 1.0 V as function nitrite content at 300 °C
Finally we can conclude that the initial investigation seems promising for a membrane cell to work. Further investigations including the construction of a virtual membrane cell for NO transport in analogy with the SO$_2$ cell will hopefully be carried out in a future project.

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